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Non-destructive and Microanalytical Techniques in Art and Cultural Heritage

Book of Abstracts

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Universidad del País Vasco
Euskal Herriko Unibertsitatea

University of The Basque Country

Programme and Abstracts

TECHNART 2017

Non-destructive and Microanalytical Techniques in Art and Cultural Heritage

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Editors

IBeA Research Group, University of The Basque Country
Organizing Committee of TECHNART 2017

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Foreword

Technart2017 is the international biannual congress on the application of Analytical Techniques in Art and Cultural Heritage. This is a European Conference and the aim of TECHNART is to provide a scientific forum to present and promote the use of Analytical Spectroscopic Techniques in Cultural Heritage on a worldwide scale to stimulate contacts and exchange of experience, making the bridge between Science and Art. The conference builds on the momentum of the previous TECHNART editions of Lisbon, Athens, Berlin, Amsterdam and Catania, offering an outstanding and unique opportunity for exchanging knowledge on leading edge developments.

Cultural heritage studies are interpreted in a broad sense, including pigments, stones, metals, glass, ceramics, chemometrics on artwork studies, resins, fibers, forensic applications in art, history, archaeology and conservation science. The meeting is focused on different aspects:

- X-ray analysis (XRF, PIXE, XRD, SEM-EDX)
- Confocal X-ray microscopy (3D Micro-XRF, 3D Micro-PIXE)
- Synchrotron, ion beam and neutron based techniques/instrumentation
- FT-IR and Raman spectroscopy
- UV-Vis and NIR absorption/reflectance and fluorescence
- Laser-based analytical techniques (LIBS, etc)
- Magnetic resonance techniques
- Chromatography (GC, HPLC) and mass spectrometry
- Optical imaging and coherence techniques
- Mobile spectrometry and remote sensing

The Conference includes 7 invited presentations:

- Silvia A. Centeno, The Metropolitan Museum of Art, USA
- Caroline Tokarski, Miniaturisation pour la Synthèse, l'Analyse et la Protéomique (MSAP), Université de Lille 1, France.
- Maria Perla Colombini, Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Italy
- Jennifer L. Mass, Scientific Analysis of Fine Art LLC, USA
- **María José Ayora**, Universidad de Jaén, Spain
- George Filippidis, FORTH-IESL, Greece
- Claudia Conti, Istituto per la Conservazione e la Valorizzazione dei Beni Culturali, Italy

together with more than 120 oral communications, distributed in three parallel sessions every day, and more than 90 poster communications. The total number of attendees in this Technart 2017 was about 350 researchers and professionals from all around the world.

All those contributions are collected in this Book of Abstracts. Moreover, the works showing a clear analytical advance (not just "novelty") will be published in a Virtual Special Issue of *Microchemical Journal* after the standard peer review process.

Juan Manuel Madariaga, May 2017

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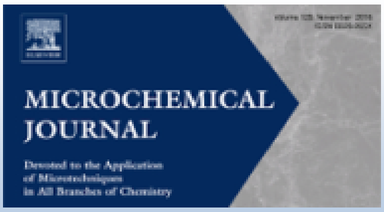
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3. CONFERENCE PROGRAM

TUESDAY (I/III)

8:00-9:00	Registration		
9:00-9:20	Opening		
9:20-10:10	Plenary Lecture 1: Potential of Micro-SORS for Cultural Heritage. C. Conti, A. Botteon, C. Colombo, M. Realini, P. Matousek		
	Parallel session A	Parallel session B	Parallel session C
10:10-10:30	MA-XRF scanning as tool in authentication studies of paintings. *S. Saverwyns, E. Lamas-Delgado, C. Currie and M. Van Bos*	A novel methodological approach for the assessment of surface cleaning of acrylic emulsion paints. *T. Fardi, V. Pintus, E. Kampasakali, E. Pavlidou, K. G. Papaspyropoulos, M. Schreiner, G. Kyriakou*	Advanced extraction and analytical methods applied to discrimination of different lichen species used for orcein dyed yarns. *I. Serafini, L. Lombardi, M. Aceto, E. Calà, A. Idone, F. Sciubba, M. Guiso, A. Bianco*
10:30-10:50	Moisture transport and sorption in oil-painted linen canvas documented by X-ray and neutron imaging. *D. Derome, R. Hendrickx, S. Carl, G. Desmarais, D. Mannes, A. Kaestner, E. S.B. Ferreira*	Insight on colour change and chemical alteration of green copper-based organometallic painting pigments. *M. Alter, A.-S. Le Hô, C. Doublet, D. Gourier, L. Binet, N. Touati, F. Mirambet, N. Lubin-Germain*	Identification and classification of textile fibres using ATR-FT-IR spectroscopy with chemometric methods. *P. Peets, S. Vahur, I. Leito*
10:50-11:10	A novel mobile X-ray scanner integrating MA-XRF, µXRF and confocal-XRF for a real-time elemental imaging of painted artworks- *F.P. Romano, C. Caliri, P. Nicotra, S. Di Martino, L. Pappalardo, F. Rizzo, H.C. Santos*	Elucidating Daguerreotype Degradation By Surface Species Formation Using Surface Plasmon Resonance Scattering Spectroscopy. *A. E. Schlather, S. A. Centeno*	Surface Enhanced Raman Spectroscopy of Antraquinone-aluminum complexes on Dyed Fibers. *T. Aguayo*
11:10-11:50	Coffee Break		

TUESDAY (II/III)

	Parallel session A	Parallel session B	Parallel session C
11:50-12:10	Removal of absorption artefacts in the macro-XRF imaging of paintings. *P. M. Wrobel, P. Fraczek, M. Lankosz*	Analytical challenges in studying degradation processes in paintings: ultramarine disease. *A. A. Gambardella, K. Schnetz, R. van Elsas, P. Iedema, K. Keune*	An Innovative Method for the Non-invasive Proteomic Analysis of Cultural Heritage Objects. *M. Manfredi, E. Barberis, E. Conte, F. Gosetti, S. Baiocco, P.G. Righetti, E. Marengo*
12:10-12:30	Macro XRF scanning: New opportunities for non-destructive analysis of two episcopal mitres, attributed to bishop Jacques de Vitry (12-13th c. AD). *I. Vanden Berghe, M. Van Bos*	Combining synchrotron photoluminescence imaging and microspectroscopy to study zinc white degradation in oil paint. *S. Hageraats, K. Keune, A. van Loon, B. Berrie, M. Thoury*	A non-invasive methodology for stratigraphy investigation of historical violins using reflection IR spectroscopy and UV induced fluorescence technique. *C. Invernizzi, T. Rovetta, M. Licchelli, M. Malagodi*
12:30-12:50	Scanning X-ray fluorescence imaging for evaluation of platinum prints and other 19th-20th century photographs. *L. Smieska, A. Lundgren, N. Kennedy, S. A. Centeno*	Influence of lead white and cobalt blue on the degradation of Eosin lakes. *A. Álvarez-Martín, K. Janssens*	Complementary use of Optical Coherence Tomography (OCT) and Reflection mid-FTIR spectroscopy for in situ monitoring of varnish removal from easel paintings. *M. Iwanicka, P. Moretti, S. van Oudheusden, M. Sylwestrzak, L. Cartechini, K. J. van den Berg, P. Targowski, C. Miliani*
12:50-13:10	Use of Macro-scale Tri-Modal Imaging Spectroscopy To Map and Identify Faded Organic Red Lakes in Van Gogh Paintings *J. K. Delaney, K. Dooley, C. Miliani, K. Janssens*	Blanching of paint and varnish layers: from the characterization to the development of conservation treatments. *A. Genty-Vincent, M. Eveno, W. Nowik, G. Bastian, E. Ravaud, J. Uziel, R. Giorgi, P. Baglioni, N. Lubin-Germain, M. Menu*	A non-Invasive Study of Surface Coatings of Electric Guitars. *A. Michelin, S. Vaiedelich, C. Andraud, A. Tournié, P. Bruguière*
13:10-13:30	Spatially resolved X-ray fluorescence: State of the ART. *R. Tagle, M. Bügler, F. Reinhardt, U. Waldschläger*	Role of defects in the reactivity of Cd-yellow. *L. Giacopetti, A. Satta, A. Nevin, D. Comelli, G. Valentini*	Fluorination technique to identify the type of resin in aged vanishes and lacquers using infrared spectroscopy *S. Zumbühl, A. Hochuli, N. C. Scherrer, B. Soulier*
13:30-15:00	Lunch		

TUESDAY (III/III)

15:00-15:50	Plenary Lecture 2: Multimodal analytical approach for characterization of decorative revetments in the Alhambra monument. **María José Ayora-Cañada, Paz Arjonilla, Ana Domínguez-Vidal, María José de la Torre López, Ramón Rubio Domene, Elena Correa**		
	Parallel session A	Parallel session B	Parallel session C
15:50-16:10	An integrate use of Raman and Time Resolved Laser Induced Fluorescence spectroscopy to identify ancient and contemporary painted materials. *M. Romani, S. Almaviva, F. Colao, R. Fantoni, M. Marinelli, A. Pasqualucci, G. Verona-Rinati*	Design of Experiments – Investigating the effect of paint formulation on degradation rates of TiO_2-based oil paints. *B.A. van Driel, K.J. van den Berg, M. Smout, N. Dekker, J.Dik*	Readability recovery in damaged ancient parchment artefacts: a comparative study among multispectral imaging techniques. *A. Pasqualucci, C. Cicero, M Marinelli, F. Mercuri, N. Orazi, S. Paoloni, M. Romani, A. Terrei, G. Verona-Rinati, U. Zammit*
16:10-16:30	Portable Raman Spectroscopy for Cultural Heritage Objects. *K. Frano, D. Yang, J. Mass*	Portable non-destructive handheld Mid-infrared FT-IR analysis of three diverse antiquities for spectral analysis combined with multivariate chemometric analysis and assessment of potential benefits in art cultural heritage studies. *P. Leung Tang*	Usability of spectroscopic, diffraction and microscopic analytical tools to recognize old Moroccan Jewish parchments *L. Hajji, J. Assouik, A. Lhassani, A. Ainane, M. El Kouali, Y. Samia, M. Talbi, M. Manso, M. L. Carvalho*
16:30-16:50	A Technological Investigation of Grounds in Paintings by a Group of Italian 17th Century Artists with links to Roman and Neapolitan Practice. *D. Buti, T. Filtenborg, L. Ludvigsen, A. Vila*		Mappa Mundi of Albi – Scientific study of the oldest map. *L. Robinet, J. Deschaux, A. Tournié, S. Vaiedelich, G. Latour, A. Michelin, S. Thao, C. Andraud, M.-C. Schanne-Klein, B. Lavédrine*
16:50-17:10	In-situ and laboratory spectroscopic study of the mural painting of Ribera de Valderejo (Álava, Basque Country). *I. Costantini, M. Veneranda, M. Irazola, J. Aramendia, K. Castro, J. M. Madariaga*	Characterization and provenance study of Pompeian red and yellow ochre pigments. *I. Marcaida, M. Maguregui, S. Fdez-Ortiz de Vallejuelo, H. Morillas, K. Castro, N. Prieto-Taboada, M. Veneranda, J. M. Madariaga*	A multi-analytical study of the 'Hay Cookbook' Coptic magical manuscripts on leather reveal their mysteries. *L.-A. Skinner, R. Stacey, B. Wills, L. Spindler, E. O'Connell*
17:10-17:30	Identification of organic dyes and pigments in ukiyo-e Japanese woodblock prints by non-invasive and mobile techniques. *C. Biron, G. Le Bourdon, A. Mounier, J. Pérez-Arantegui, L. Servant, R. Chapoulie, F. Daniel*	Real-time diagnosis of collagen-based artworks by thermal shrinkage imaging. *E. Badea, C. Carote, O. A. Miu, I. Bornoiu, D. Ichim*	Non-invasive in-situ and SR-based imaging techniques for recovering the text from a recycled parchment. *E. Pouyet, L. Smieska , A. Woll, A. Katsaggelos, O. Cossairt, J. Salvant , M. Walton*
17:30-19:00	Coffee Break, Poster session 1		

WEDNESDAY (I/III)

8:30-10:30	Round Table E-RIHS: Cultural Heritage's new Alliance. L. Pezzatti, M. Castillejo, S. Hermon		
	Parallel session A	Parallel session B	Parallel session C
10:30-10:50	Identification of inorganic mordants from liquid extracts of madder lakes by laser induced breakdown spectroscopy. *B. Campanella, I. Degano, E. Grifoni, S. Legnaioli, G. Lorenzetti, S. Pagnotta, F. Poggialini, V. Palleschi*	Micro-spectroscopy of rock art paintings from the Cueva Mayor of the Atapuerca site (Burgos, Spain). *A. Hernanz, D. Paredes-Roibás, J.M. Gavira-Vallejo, J.J. Fernández, B. García, M. Iriarte*	3D Imaging of artefacts by EDXRF- SCANNING. *R. Cesareo, S. Ridolfi, A. Brunetti,G. E. Gigante*
10:50-11:10	Differentiating natural and amorphous arsenic sulfide in painted artifacts by means of Raman spectroscopy. *M. Vermeulen, J. Sanyova, K. Janssens*	Non-destructive analysis of Still Bay (>70 ka) pointed artefacts from Sibudu Cave, South Africa. *M. Wojcieszak, L. Wadley*	The processional cross of Santa Maria Maggiore at Guardiagrele: materials and techniques of Nicola da Guardiagrele investigated by X-ray fluorescence. *A. Esposito, M. Ferretti, A. Gorghinian*
11:10-11:50	Coffee Break		

WEDNESDAY (II/III)

	Parallel session A	Parallel session B	Parallel session C
11:50-12:10	Colours and pigments in late ukiyo-e paintings: a non-invasive study of a series of woodblock prints by Shuntei. *J. Pérez-Arantegui, D. Rupérez, D. Almazán, N. Díez de Pinos*	Advanced characterization of new nanostructured stone treatments for the conservation of European Architectural Heritage. *F. Gherardi, T. Poli, M. Roveri, O. Chiantore, L. Toniolo*	Study of applicability of non-invasive analyses methods in archaeology. *A. M. Gójska, E. A. Mita*
12:10-12:30	Non destructive study of the pigments and the watermarks of engravings in North European Chiaroscuro. *K. Laclavetine, C. Boust, L. Clivet, A. de La Chapelle, A. S. Le Hô, E. Laval, R. Mathis, M. Menu, E. Pagliano, R. Pillay, X. Salmon, V. Selbach, S. Lepape*	The first use of portable Raman instrumentation for the analysis of Patagonian prehistoric rock art paintings: pigments, accretions and substrata. *A. Rousaki, C. Vázquez, V. Aldazábal, C. Bellelli, M. Carballido Calatayud, A. Hajduk, E. Vargas, O. Palacios, A. Culka, J. Jehlika, L. Moens, P. Vandenabeele*	Non-invasive studies on technological provenance of medieval silver jewelry form Baltic Sea region. *E. A. Mita, W. Duczko, R. Czech-Boska, A. M. Gójska, A. Turos, P. Ciepielewski*
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12:50-13:10	'Do you see what I see?' A non-invasive multi-analytical study of the limits of detection of smalt in ultramarine mixtures. *P. Ricciardi, D. MacLennan, G. Bertolotti, S. Bucklow, N. Turner, J. K. Delaney, K. Dooley, C. Patterson*	New in situ non invasive analytical methodology to determinate the state of preservation of prehistoric rock art sites. *J. F. Ruiz, S. Fdez-Ortiz de Vallejuelo, J. Aramendia, M. Maguregui, J. M. Madariaga*	A spectroscopic study of metal foils and its layering in Norwegian Medieval objects. *A. Vila, E. Platania, D. Buti, N. Streeton*
13:10-13:30	Synchrotron study of micro-structure and luminescence of lead carbonates: revealing the Old Masters pigments qualities. *V. Gonzalez, T. Calligaro, D. Comelli, M. Cotte, D. Gourier, A. Nevin, M. Réfrégiers, M. Thoury, G. Wallez, M. Menu*	The investigation of calcium carbonate formation using micro-Raman spectroscopy *Radek evík, Petra Mácová, Alberto Viani*	Unveiling ancient gold inlay technique of a bronze belt plaque. *M.-w. Tang, W.-f. Lai*
13:30-15:00	Lunch		

WEDNESDAY (III/III)

	Parallel session A	Parallel session B	Parallel session C
15:00-15:50	Plenary Lecture 3: Art and Cultural Heritage natural polymers by bottom up and top down approaches. Caroline Tokarski.		
15:50-16:10	A Multi-Analytical Approach to Identify Historic Carbonaceous Media on 19th Century French Drawings. *N. Daly, M. Sullivan, L. Lee, K. Trentelman*	X-ray photoelectron spectroscopy of pictorial samples. *E. Carrasco, M. Oujja, M. Sanz, J. F. Marco, M. Castillejo*	What synchrotron radiation based experiments can tell about Poverty Point Objects (PPOs). *J. Hormes, G.-L. Bovenkamp-Langlois, M. W. Schaefer, O. Kiyilkaza, W. Klysubun, D. M. Greenlee*
16:10-16:30	Large volume imaging of cultural heritage with optical coherence tomography. *T. Callewaert, J. Kalkman, J. Dik*	From micro to macro: A multiscale Raman mapping approach for the analysis of inks and pigments on paper, panels and walls. *S. Mosca, A. Artesani, D. Gulotta, A. Nevin, G. Valentini, D.Comelli*	Towards non-destructive analysis of archaeological ceramics by micro X-ray fluorescence spectrometry. *E. Calparsoro, M. Maguregui, J. G. Iñañez, J. M. Madariaga*
16:30-16:50	Macroscopic X-ray powder diffraction imaging: highly specific pigment mapping using mobile equipment. *F. Vanmeert, S. De Meyer, S. Legrand, G. Van der Snickt, K. Janssens, L. Klaasen, N. De Keyser, P. Noble, A. Van Loon, J. Dik*	A system for scientific microscope color calibration at the Rijksmuseum for the Paint Sample Database. *S. Smelt, R. Erdmann*	Portable XRF setup with monochromatic radiation for the analysis of Cultural Heritage. *S. Pessanha, M. Guerra, J. M. Sampaio, M. L. Carvalho, I. Queralt*
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17:10-17:30	Capabilities of in-situ Spectroscopic Imaging for Visualizing Traces of Antique Polychromy. *M. Alfeld, M. Mulliez, J. Devogelaere, P. Martinez, L. de Viguerie(1), P. Jockey, P. Walter*	MA-XRF imaging spectroscopy on the Archaic painted panels from Pitsa (6th c. BC, Corinthia, Greece): New evidence on their original polychromy and their iconography. *H. Brekoulaki, F.P. Romano, A.G. Karydas, G. Kavvadias*	In situ characterization of the materials and techniques of Roman Egyptian mummy portraits using combined forensic photography and spectroscopy. *R. Radpour, Y. Lin, M. Svoboda, G. Chiari, C. Fischer, I. Kakoulli*
17:30-19:00	Coffee Break, Poster session 2		

THURSDAY (I/III)

8:40-9:30	Plenary Lecture 4: Macromolecules in Archaeology. M. P. Colombini		
	Parallel session A	Parallel session B	Parallel session C
9:30-9:50	p-XRF analysis of lapis lazuli for provenance studies. *A. Lo Giudice, A. Re, D. Angelici, M. Zangirolami, A. Agostino, M. Gulmini, A. Borghi, A. Mazzinghi, C. Ruberto, L. Castelli, A. Impallaria, F. Taccetti, G. Pratesi, M. C. Guidotti*	The Glass beads as markers of the trade to Southern Africa from the 8th to the 19th century A.D. *Ph. Colomban, F. Koleini, L. C. Prinsloo, W. Biemond, J. C.A. Boeyens, M. M. van der Ryst, I. Pikirayi*	Rubrication in historic manuscripts. ***B. Frühmann, F. Cappa, W. Vetter, M. Schreiner***
9:50-10:10	Multidisciplinary non-invasive image diagnostics based on mobile techniques of 15th century paintings from Sicily. *M. Barucci, C. Caliri, L. Castelli, E. Grifoni, A. Impallaria, S. Legnaioli, A. Orlando, F.C. Petrucci, M. Raffaelli, F.P. Romano, C.H. Santos, F. Taccetti, F. Tisato*	A novel tool for Cultural Heritage material analysis: Transmission Electron Microscope (TEM) 3D Electron Diffraction Tomography and Orientation/Phase Mapping applied to ancient Roman glass tesserae. *N. Zacharias, F. Karavasili, P. Das, A. Galanis, E. Rauch, S. Nicolopoulos, A. Oikonomou, I. Margiolaki*	The presence of iron in the inks of the Valencian manuscripts from the 13th to the 17th centuries. *G. M. Contreras Zamorano*
10:10-10:30	Non-invasive analysis of mural paintings from a Republican house (1st century B.C.) in Ostia. *D. Strivay, E. Herens, T. Morard, C. Defeyt*	**Study of a modern Chinese cloisonné vase by means of EDXRF and Raman spectroscopy**. *I. Queralt, S. Pessanha, M. Manso, M. L. Carvalho*	Applicability of micro-reflection-FTIR-mapping for the investigation of medieval manuscripts – a case study. *W. Vetter, B. Fruehmann, M. Schreiner*
10:30-10:50	Characterization of Arsenic Sulfide Pigments in Japanese Prints of the late Edo Period. *S. Zaleski, M. Leona*	Investigation of 18th-century Chinese double-walled vases in yangcai painted enamel. *T.-H. Chen, C.-C. Huang*	A multi-analytical characterization of French paper negatives: how to see through many processes?. *C. Daher, M.-**A. Languille, A. de Mondenard, A. Tournié, S. Aubenas, B. Lavédrine***
10:50-11:10	Time-resolved ATR-FTIR as a tool to monitor chemical reactivity in oil paint model systems. *L. Baij, J. Hermans, K. Keune, P. Iedema*	The magic of colour of medieval stained glass windows. Insights into composition of red and violet flashed glasses. *M. Walczak, D. Wilk, **M. Kamiska, E. Bernady, E. Bulska***	In situ spectrofluorimetric analysis of red & blue colours on 19th century Japanese engravings (Torralba collection, Zaragoza Museum). *A. Mounier, G. Le Bourdon, C. Aupetit, S. Lazare, J. Perez-Arantegui, F. Daniel*
11:10-11:50	Coffee Break		

THURSDAY (II/III)

	Parallel session A	Parallel session B	Parallel session C
11:50-12:10	Iba and Fors mapping applied to the analysis of cultural heritage artefacts: Last improvements on the aglae facility. *Q. Lemasson, B. Moignard, C. Pacheco, L. Pichon, T. Calligaro, J. Rumolo, C. Boust, M. Guiavarc'h, G. Querré*	Mycenaean Glass from the Argolid, Peloponnese, Greece: A Technological and Provenance Study. *N. Zacharias, M. Kaparou, A. Oikonomou, Z. Kasztovszky*	Printing materials and technologies in the 15th-17th century book production: an underestimated research field. *F. Albertin, E. Balliana, G. Pizzol, G. Colavizza, E. Zendri, D. Raines*
12:10-12:30	Advanced techniques of photo-luminescence microscopy for the analysis of precious semiconductor-based painting layers. *D. Comelli, A. Artesani, A. Nevin, V. Gonzalez, M. Réfrégiers, M. Thoury*	Historic conservation materials on stained glass windows in the Naumburg cathedral *E. Kanaki, J. Brandt*	The use of polyamidoamines for the deacidification of iron-gall inked papers. *C. Isca, L. Bergamonti, C. Graiff, G. Predieri, P. P. Lottici*
12:30-12:50	The new "CRONO" macro-XRF scanner applied to Cimabue's masterpiece. *T. Frizzi, G. Sciutto, N. Aresi, E. Catelli, S. Prati, R. Alberti, R. Mazzeo*	Characterization of glaze ceramics from the archaeological site of La Alcazaba, Almería (Spain). *I. Ortega-Feliu, B. Gómez-Tubío, Y. Cáceres, M. A. Respaldiza*	Interdisciplinary approach for cleaning graphic artworks: the case study of Diana Scultori engraving. *L. Micheli, C. Mazzuca, M. Missori, L. Teodonio, A. Mosca Conte, O. Pulci, L. Arcadipane, S. Dominijanni, S. Iannuccelli, S. Sotgiu*
12:50-13:10	A multi-analytical approach to the painting technique and the green and blue pigments used in Andean colonial wall paintings *E. Tomasini, V. Careaga, C. Rúa Landa, F. Guzmán, G. Siracusano, M. Maier*	Assessing the firing temperature of Uruk pottery in the Middle Euphrates Valley (Syria): bevelled rim bowls. *J. Sanjurjo-Sánchez, J. L. Montero Fenollós, V. Barrientos, G. S. Polymeris*	Combined macroscopic XRF and FTIR mapping of a 14th century illuminated manuscript fragment. *S. Legrand, P. Ricciardi, L. Nodari, K. Janssens*
13:10-13:30	The Giotto's workshop in the XXI century: looking inside the "God the Father with Angels" Cusp. *A. Galli, R. Alberti, N. Aresi, L. Bonizzoni, M. Caccia, I. Castiglioni, M. Gargano, M. Interlenghi, N. Ludwig, C. Salvatore, M. Martini*	Use of small angle neutron scattering and X-ray powder diffraction with the Rietveld method in the assessment of firing conditions in historical fired-clay bricks. *A. Viani, K. Sotiriadis, R. evík*	Highly retentive hydrogels for paper cleaning. *C. Mazzuca, L. Micheli, G. Poggi, N. Bonelli, R. Giorgi, P. Baglioni, A. Palleschi*
13:30-15:00	Lunch		

THURSDAY (III/III)

15:00-15:50 Plenary Lecture 5: Applications of non-linear imaging microscopy techniques for Cultural Heritage studies. M. Mari, S. Psilodimitrakopoulos, K. Melessanaki, G. Filippidis

	Parallel session A	Parallel session B	Parallel session C
15:50-16:10	Pigment identification in historical samples of Matisse Cut-Outs. *A. Martins, A. Ondate, A. Cesaratto, K. Buchberg, C. McGlinchey, M. Leona*	XRF analyses of the Serra d'Alto pottery (Matera, Italy). *S. Legnaioli, L. Angeli, E. Grifoni, V. Palleschi, C. Fabbri, G. Radi*	Direct fluorimetric characterization of dyes in ancient purple codices. *A. Idone, I. Miletto, P. Davit, M. Aceto, M. Gulmini*
16:10-16:30	A tale of two pigments: the characterization and synthesis of Indian yellow, and zinc orange from Toulouse-Lautrec's early palette. *A. Shugar, R. Ploeger, K. Harada, K. Spendel, S. Goodman*	Not too white': an investigation into the influence of the use of calcium carbonate-rich imported marls on 17 - 18th century Dutch tin-glaze tile production. *K. van Lookeren Campagne, S. Pereira, L. Megens, O. **Çopurolu**, E. Goemaere, N. H. Tennent, M. van Bommel*	Shades of blue: non-invasive spectroscopic investigations of blue paints on Mesoamerican Pre-Hispanic codices. *C. Grazia, D. Buti, A. Romani,A. Sgamellotti, C. Miliani*
16:30-16:50	Comparative technical analysis of the medieval altarpieces by Hermen Rode in Tallinn and in Lübeck. A. Uueni, S. Vahur, H. Hiiop, H. Pagi, R. Rebane	Jun Ware – A Technical Study. *L. Cooper, K. Eremin, M. Walton, E. Pouyet, A. Shortland, L. Dussubieux*	Quantitative diagnostics of ancient paper using THz time-domain spectroscopy. *M. Missori, R. Fastampa, M. Peccianti, M. S. Maggio, C. Violante, A. Mosca Conte, O. Pulci, J. Lojewska*
16:50-17:10	Nicolas Poussin's painting technique in the scope of a mobile laboratory: X-ray fluorescence, X-ray diffraction and reflectance hyperspectral imaging. *L. de Viguerie, M. Radepont, H. Glanville, M. Alfeld, S. Pedetti, Ph. Walter*	LA-ICP-MS multi-element analyses of blue & white tin-glazed earthenware tiles: 2D surface and depth mapping of glazes. *N. H. Tennent, J. T. van Elteren, V. S. elih*	What Vis-NIR reflectance spectroscopy can reveal about 15th century illuminated manuscripts: the Corale 43 by Beato Angelico at the Biblioteca Medicea Laurenziana in Florence (Italy). *C. Cucci, S. Innocenti, M. Picollo, I. G. Rao, M. Scudieri*
17:10-17:30	New insights into Indian yellow and its use in Rajasthani wall paintings – a multi-analytical study. *D. Tamburini, C. Martin de Fonjaudran, G. Verri, G. Accorsi, A. Rava, S. Whittaker, D. Saunders*	Computed radiography, pixe and XRF analysis of pre-colonial pottery from Maranhão, Brazil. *R. A. Ikeoka, C. R. Appoloni, M. A. Rizzutto, A. M. Bandeira*	Quantitative monitoring of works of art on paper with spectral imaging. *R. Padoan, M. E. Klein, R. Erdmann, M. Strli*

17:30-19:00 Coffee Break, Poster session 3

FRIDAY (I/III)

	Parallel session A	Parallel session B	Parallel session C
8:40-9:30	Plenary Lecture 6: Capturing Artists' Intent in the Works of the Impressionists through the Expressionists: Pigment Manufacture and Alteration. J. L. Mass, B. Levin, D. Muller, L. Monico, F. Vanmeert, K. Janssens, C. Miliani, A. Hull, A. C. Finnefrock, E. Uffelman, E. Storevik Teit, B. Buckley, R. Opila		
9:30-9:50	Portable instrumentation for the study of wall pantings: the case of S. Maria ad Undas in Idro (BS-Italy). *L. de Ferri, F. Mazzini, D. Manzini, G. Pojana*	Self-cleaning coatings by N-doped TiO_2 on limestones. *L. Fornasini, L. Bergamonti, G. Predieri, Y. Paz, D. Bersani, P.P. Lottici, F. Bondioli*	Spectroscopic methods for mapping and dating restoration phases on two Egyptian sarcophagi (XXI dynasty). *L. Bonizzoni, S. Bruni, M. Gargano, V. Guglielmi, C. Zaffino, A. Pezzotta, N. Ludwig*
9:50-10:10	"Precious powder": Designing a methodology for the technical and analytical study of pastel paintings from the Rijksmuseum collection. *L. Sauvage, S. Settimi, I. van Leeuwen, J. Schultz, K. Abdulah*	Limestone chromatic changes: a microbial-mediated inorganic process. *L. Dias, T. Rosado, A. Coelho, L. Lopes, J. Mirão, A. T. Caldeira, A. Candeias*	An insight into the complexity of agar gels. M. Bertasa, T.Poli, C. Riedo, V. Di Tullio, D. *Capitani, N. Proietti, C. Canevali, A. Sansonetti, D. Scalarone*
10:10-10:30	Paul Gauguin's graphic works: multi-analytical characterization of the artist's techniques and materials. *C. Daher, K. Sutherland, H. Stratis, F. Casadio*	Novel materials for the restoration of marble and limestone substrates based on oxalate derivatives: an experimental and DFT-theoretical approach. *L. Giacopetti, M. C. Aragoni, G. Carcangiu, O. Cocco, V. Lippolis, L. Maiore, P. Meloni, A. Murru, M. Arca*	Evaluating the exploitability of several Essential Oils constituents as a new biological treatment against Cultural Heritage biodeterioration. *I. Costantini, M. Veneranda, L. Blanco, P. Cinaglia, G. Di Girolami, K. Castro, J.M. Madariaga*
10:30-10:50	300-400 nm UV fluorescence multispectral imaging for organic pictorial materials identification. *Tiziana Cavaleri, Marco Gargano, Marco Pisani, Massimo Zucco, Paola Buscaglia*	Analysis of typomorphic minerals applied in the investigation of origin of archeological objects and painting materials. *B. ydba-Kopczyska, B. Kosmowska-Ceranowicz, M. Sachanbinski*	Testing of new mortars for the conservation of frescoes in the wooden church in Amrti, Romania. *I. Mohanu, D. Mohanu, I. Gomoiu, O.-H. Barbu, I. Petre, N. Vlad, G. Voicu, R. Truc*
10:50-11:10	A comparison of non-invasive imaging and portable techniques for the study of Old Master paintings: Rembrandt's The Jewish Bride c. 1665 *P. Noble, A. van Loon, K. Janssens, J. Delaney, Y. Abe, I. Nakai, J. Dik*		A multidisciplinary investigation on a pair of leonardesque canal gates. *M. Gargano, A. Galli, C. Giorgione, N. Ludwig, F. Maspero, M. Orlandi, L. Zoia, M. Martini*
11:10-11:50	Coffee Break		

FRIDAY (II/III)

	Parallel session A	Parallel session B	Parallel session C
11:50-12:10	Two in one: Unraveling a hidden Jan Steen painting. *W.-Y.Lee, R. Tagle*	New insights into the characterization of lipids in pre-Hispanic ceramics by mass spectrometry techniques. *I. J. Lantos, V. P. Careaga, E. L. Bonifazi, D. M. Castellanos* ***Rodríguez, M. S. Maier***	In-situ micro XRF investigation of four Mycenaean gold signet rings from the grave of the Griffin Warrior at the Palace of Nestor in Pylos *V. Kantarelou, A. G. Karydas, J. L. Davis, S. R. Stocker*
12:10-12:30	Micro and Macro Scale Chemical Imaging on Van Eyck's Ghent Altarpiece (1432). *G. Van der Snickt, H. Dubois, J. Sanyova, S. Legrand, K. Janssens*	Nuclear Magnetic Resonance Analysis for Treatment Decisions: The case of a White Sculptural Environment by Louise Nevelson. *C. Kehlet, S. Nunberg, C. Tomkiewicz, S. Alcala, J. Dittmer*	Combined μ-XRF and μ-PIXE/μ-EBS analysis of ancient copper coins. *J. Cruz, V. Corregidor, M. Manso, L.C. Alves, L. Carvalho*
12:30-12:50	Concealed features in Botticelli's fresco unveiled by multispectral visible-near infrared and X-ray Fluorescence imaging. *J. Striova, A. Mazzinghi, C. Ruberto, M. Barucci, C. Czelusniak,* ***L. Giuntini, P. A. Mandò, L. Palla, E.*** *Pampaloni, F. Taccetti, R. Fontana*	Discrimination of Acacia gums by MALDI-MS: developments and applications to samples from Ancient Egypt. *C. Granzotto, J. Arslanoglu, K. Sutherland*	Chemical analysis of the Pharaonic Period bronze mirrors stored in the Museo Egizio and study of the degradation phenomena. A completely non-invasive approach. *S. Robotti, P. Rizzi, C. Soffritti, G. L. Garagnani, C. Greco, M. Borla, L. Operti, A. Agostino*
12:50-13:10	Analytical and Technological Investigation of the Paintings and other Decorative Elements of the Holy Aedicule of the Holy Selpuchre in Jerusalem. *A. Moropoulou, E. T. Delegou, I. Ntoutsi, M. Apostolopoulou*	Development of a new methodology for the analysis of sterols and bile acids in archaeological soils for the characterization of species. ***J. Gea, M. C. Sampedro, A. Vallejo, A. Polo, J. Fernández-*** *Eraso, R. J. Barrio*	Metallurgy of the earliest lost-wax cast. ***M. Thoury, B. Mille, T. Séverin*** *-Fabiani, L. Robbiola, M.* ***Réfrégiers, A. Didier, L. Bertrand***
13:10-13:30	On-site analysis of paintings by means of portable XRD. *I. Nakai, A. Hirayama, S. Akagi, Y. Abe, K. Tantrakarn, K. Taniguchi, A. van Loon, P. Noble, G.D. Vivo, K. Janssens*		
13:30-15:00	Lunch		

FRIDAY (III/III)

15:00-15:50 Plenary Lecture 7: Structure, Coordination Environment and Dynamics of Lead Carboxylates implicated in Soap Deterioration in Oil Paintings. J. Catalano, A. Murphy, Y. Yao, N. Zumbulyadis, S. A. Centeno, C. Dybowski

	Parallel session A	Parallel session B	Parallel session C
15:50-16:10	The use of smalt in Rembrandt's Homer – new research combining MA-XRF, quantitative microanalysis, paint reconstructions and OCT. *A. van Loon, P. Noble, D. de Man, G. Van der Snickt, K. Janssens, M. Alfeld, T. Callewaert, J. Dik*	GC-MS and HPLC-APCI-MS for the research, valorization and dissemination of the Iberian Culture. *D. J. Parras, A. Sánchez, J. A. Tuñón, C. Rueda, J. F. García-Reyes*	Effectiveness of optical micro-profilometry for monitoring the surface morphology in metals and pictorial layers under aging process. *C. Daffara, N. Gaburro, G. Marchioro, I. Ciortan, A. Giachetti, G. Karagiannis and M. Galeotti*
16:10-16:30	Jan Davidsz. de Heem: a technical examination of fruit and flower still lifes combining MA-XRF scanning, cross-section analysis and technical historical sources. *N. De Keyser, G. Van der Snickt, A. Van Loon, S. Legrand, A. Wallert, K. Janssens*	Identification of organic residues in archaeological ceramic vessels of Basque whalers from 16th to 17th century. *L. Blanco-Zubiaguirre, E. Ribechini, I. Degano, J. La Nasa, J. García-Iñañez, M. Olivares, K. Castro*	None invasive Synchrotron based X-ray Diffraction investigations of Archaeological Bronze and Gold. *M. Freudenberg, A. Rothkirch, L. Glaser*
16:30-16:50	A New Innovative Sampling Technique for Analysis of Microorganisms on Angkor Temples in Cambodia. *J.-D. Gu, Y. Katayama*	DMFDMA: a new/old GC-MS derivatization agent for the analysis of binders in cultural heritage objects. *F. Caruso, B. Ebert, E. Platania, C. C. Steindal, N. L.W. Streeton*	Armourers' marks and their detection A. Williams, N. Kardjilov, F. Grazzi, D. Edge
16:50-17:10	A comprehensive study of the effects induced by brown rot fungi on archaeological waterlogged wood. *J. J. Lucejko, M. Mattonai, M. Zborowska, C. Cartwright, D. Tamburini, G. Cofta, F. Modugno, M. P. Colombini, E. Ribechini*	Development of a qualitative and quantitative analytical method for the characterisation of mixtures of free fatty acids and metal soaps in paint samples. *J. La Nasa, A. Lluveras Tenorio, F. Modugno, I. Bonaduce*	
17:10-17:30	Closing		

4. LIST OF COMMUNICATIONS

4.1 PLENARY LECTURES

POTENTIAL OF MICRO-SORS FOR CULTURAL HERITAGE

C. CONTI , A. BOTTEON , C. COLOMBO , M. REALINI , P. MATOUSEK

MULTIMODAL ANALYTICAL APPROACH FOR CHARACTERIZATION OF DECORATIVE REVETMENTS IN THE ALHAMBRA MONUMENT

MARÍA JOSÉ AYORA-CAÑADA , PAZ ARJONILLA , ANA DOMÍNGUEZ-VIDAL , MARÍA JOSÉ DE LA TORRE LÓPEZ , RAMÓN RUBIO DOMENE , ELENA CORREA

ART AND CULTURAL HERITAGE NATURAL POLYMERS BY BOTTOM UP AND TOP DOWN APPROACHES

CAROLINE TOKARSKI

MACROMOLECULES IN ARCHAEOLOGY

MARIA PERLA COLOMBINI

APPLICATIONS OF NON-LINEAR IMAGING MICROSCOPY TECHNIQUES FOR CULTURAL HERITAGE STUDIES

MEROPI MARI , SOTIRIS PSILODIMITRAKOPOULOS , KRISTALLIA MELESSANAKI , GEORGE FILIPPIDIS *

CAPTURING ARTISTS' INTENT IN THE WORKS OF THE IMPRESSIONISTS THROUGH THE EXPRESSIONISTS: PIGMENT MANUFACTURE AND ALTERATION

JENNIFER L. MASS, BARNABY LEVIN , DAVID MULLER , LETIZIA MONICO , FREDERIK VANMEERT , KOEN JANSSENS , COSTANZA MILIANI , ALYSSA HULL , ADAM C. FINNEFROCK , ERICH UFFELMAN , EVA STOREVIK TEIT , BARBARA BUCKLEY , ROBERT OPILA

STRUCTURE, COORDINATION ENVIRONMENT AND DYNAMICS OF LEAD CARBOXYLATES IMPLICATED IN SOAP DETERIORATION IN OIL PAINTINGS

JACLYN CATALANO , ANNA MURPHY , YAO YAO , NICHOLAS ZUMBULYADIS , SILVIA A. CENTENO , CECIL DYBOWSKI

4.2 ORAL COMMUNICATIONS: PARALLEL SESSION A

MA-XRF SCANNING AS TOOL IN AUTHENTICATION STUDIES OF PAINTINGS

STEVEN SAVERWYNS, EDUARDO LAMAS-DELGADO, CHRISTINA CURRIE, MARINA VAN BOS

MOISTURE TRANSPORT AND SORPTION IN OIL-PAINTED LINEN CANVAS DOCUMENTED BY X-RAY AND NEUTRON IMAGING

DOMINIQUE DEROME, ROEL HENDRICKX, STEFAN CARL, GUYLAINE DESMARAIS, DAVID MANNES, ANDERS KAESTNER, ESTER S.B. FERREIRA

A NOVEL MOBILE X-RAY SCANNER INTEGRATING MA-**XRF, µXRF AND CONFOC**AL-XRF FOR A REAL-TIME ELEMENTAL IMAGING OF PAINTED ARTWORKS

F.P. ROMANO, C. CALIRI, P. NICOTRA, S. DI MARTINO, L. PAPPALARDO, F. RIZZO, H.C. SANTOS

REMOVAL OF ABSORPTION ARTEFACTS IN THE MACRO-XRF IMAGING OF PAINTINGS

PAWEL M. WROBEL*, PIOTR FRACZEK, MAREK LANKOSZ

MACRO XRF SCANNING: NEW OPPORTUNITIES FOR NON-DESTRUCTIVE ANALYSIS OF TWO EPISCOPAL MITRES, ATTRIBUTED TO BISHOP JACQUES DE VITRY (12-13TH C. AD)

INA VANDEN BERGHE, MARINA VAN BOS

SCANNING X-RAY FLUORESCENCE IMAGING FOR EVALUATION OF PLATINUM PRINTS AND OTHER 19TH-20TH CENTURY PHOTOGRAPHS

LOUISA SMIESKA, ADRIENNE LUNDGREN, NORA KENNEDY, SILVIA A. CENTENO

USE OF MACRO-SCALE TRI-MODAL IMAGING SPECTROSCOPY TO MAP AND IDENTIFY FADED ORGANIC RED LAKES IN VAN GOGH PAINTINGS

JOHN K. DELANEY, KATHRYN DOOLEY, COSTANZA MILIANI, KOEN JANSSENS

SPATIALLY RESOLVED X-RAY FLUORESCENCE: STATE OF THE ART

ROALD TAGLE, MAX BÜGLER, FALK REINHARDT, ULRICH WALDSCHLÄGER

AN INTEGRATE USE OF RAMAN AND TIME RESOLVED LASER INDUCED FLUORESCENCE SPECTROSCOPY TO IDENTIFY ANCIENT AND CONTEMPORARY PAINTED MATERIALS

M. ROMANI, S. ALMAVIVA, F. COLAO, R. FANTONI, M. MARINELLI, A. PASQUALUCCI, G. VERONA-RINATI

PORTABLE RAMAN SPECTROSCOPY FOR CULTURAL HERITAGE OBJECTS

KRISTEN FRANO, DAWN YANG, JENNIFER MASS

A TECHNOLOGICAL INVESTIGATION OF GROUNDS IN PAINTINGS BY A GROUP OF ITALIAN 17TH CENTURY ARTISTS WITH LINKS TO ROMAN AND NEAPOLITAN PRACTICE

DAVID BUTI, TROELS FILTENBORG, LOA LUDVIGSEN, ANNA VILA

IN-SITU AND LABORATORY SPECTROSCOPIC STUDY OF THE MURAL PAINTING OF RIBERA DE VALDEREJO **(ÁLAVA, BASQUE COUNT**RY)

ILARIA COSTANTINI, MARCO VENERANDA, MIREIA IRAZOLA, JULENE ARAMENDIA, KEPA CASTRO*, JUAN MANUEL MADARIAGA

IDENTIFICATION OF ORGANIC DYES AND PIGMENTS IN UKIYO-E JAPANESE WOODBLOCK PRINTS BY NON-INVASIVE AND MOBILE TECHNIQUES

CAROLE BIRON, GWÉNAËLLE LE BOURDON, AURÉLIE MOUNIER, JOSEFINA PÉREZ-ARANTEGUI, LAURENT SERVANT, RÉMY CHAPOULIE, FLORÉAL DANIEL

IDENTIFICATION OF INORGANIC MORDANTS FROM LIQUID EXTRACTS OF MADDER LAKES BY LASER INDUCED BREAKDOWN SPECTROSCOPY

B. Campanella, I. Degano, E. Grifoni, S. Legnaioli, G. Lorenzetti, S. Pagnotta, F. Poggialini, V. Palleschi

DIFFERENTIATING NATURAL AND AMORPHOUS ARSENIC SULFIDE IN PAINTED ARTIFACTS BY MEANS OF RAMAN SPECTROSCOPY

Marc Vermeulen, Jana Sanyova, Koen Janssens

COLOURS AND PIGMENTS IN LATE *UKIYO-E* PAINTINGS: A NON-INVASIVE STUDY OF A SERIES OF WOODBLOCK PRINTS BY SHUNTEI

Josefina Pérez-Arantegui, David Rupérez, David Almazán, Nerea Díez de Pinos

NON DESTRUCTIVE STUDY OF THE PIGMENTS AND THE WATERMARKS OF ENGRAVINGS IN NORTH EUROPEAN CHIAROSCURO

K. Laclavetine*, C. Boust, L. Clivet, A. de La Chapelle, A. S. Le Ho, E. Laval, R. Mathis, M. Menu, E. Pagliano, R. Pillay, X. Salmon, V. Selbach, S. Lepape

CHARACTERIZATION AND PHOTOSTABILITY OF RED SYNTHETIC ORGANIC PIGMENTS IN ALKYD AND ACRYLIC PAINTS

Marta Anghelone, Dubravka Jembrih-Simbürger, Zdravko Siketić, Manfred Schreiner, Iva Bogdanović Radović

‘DO YOU SEE WHAT I SEE?’A NON-INVASIVE MULTI-ANALYTICAL STUDY OF THE LIMITS OF DETECTION OF SMALT IN ULTRAMARINE MIXTURES

Paola Ricciardi, Douglas MacLennan, Giulia Bertolotti, Spike Bucklow, Nancy Turner, John K. Delaney, Kathryn Dooley, Catherine Patterson

SYNCHROTRON STUDY OF MICRO-STRUCTURE AND LUMINESCENCE OF LEAD CARBONATES: REVEALING THE OLD MASTERS PIGMENTS QUALITIES

Victor Gonzalez, Thomas Calligaro, Daniela Comelli, Marine Cotte, Didier Gourier, Austin Nevin, Matthieu Réfrégiers, Mathieu Thoury, Gilles Wallez, Michel Menu

A MULTI-ANALYTICAL APPROACH TO IDENTIFY HISTORIC CARBONACEOUS MEDIA ON 19TH CENTURY FRENCH DRAWINGS

Nathan Daly, Michelle Sullivan, Lynn Lee, Karen Trentelman

LARGE VOLUME IMAGING OF CULTURAL HERITAGE WITH OPTICAL COHERENCE TOMOGRAPHY

Tom Callewaert, Jeroen Kalkman, Joris Dik

MACROSCOPIC X-RAY POWDER DIFFRACTION IMAGING: HIGHLY SPECIFIC PIGMENT MAPPING USING MOBILE EQUIPMENT

F. Vanmeert, S. De Meyer, S. Legrand, G. Van der Snickt, K. Janssens, L. Klaasen, N. De Keyser, P. Noble, A. van Loon, J. Dik

FT-IR INVESTIGATION OF PAINTING CROSS-SECTIONS

Ewa Pięta, Justyna Olszewska-Świetlik, Jolanta Adamczyk, Aleksandra Zając, Czesława Paluszkiewicz

CAPABILITIES OF *IN-SITU* SPECTROSCOPIC IMAGING FOR VISUALIZING TRACES OF ANTIQUE POLYCHROMY

Matthias Alfeld, Maud Mulliez, Jonathan Devogelaere, Philippe Martinez, Laurence de Viguerie, Philippe Jockey, Philippe Walter

P-XRF ANALYSIS OF LAPIS LAZULI FOR PROVENANCE STUDIES

Alessandro Lo Giudice, Alessandro Re, Debora Angelici, Marco Zangirolami, Angelo Agostino, Monica Gulmini, Alessandro Borghi, Anna Mazzinghi, Chiara Ruberto, Lisa Castelli, Anna Impallaria, Francesco Taccetti, Giovanni Pratesi, Maria Cristina Guidotti

MULTIDISCIPLINARY NON-INVASIVE IMAGE DIAGNOSTICS BASED ON MOBILE TECHNIQUES OF 15TH CENTURY PAINTINGS FROM SICILY

M. Barucci, C. Caliri, L. Castelli, E. Grifoni, A. Impallaria, S. Legnaioli, A. Orlando, F.C. Petrucci, M. Raffaelli, F.P. Romano, C.H. Santos, F. Taccetti, F. Tisato

NON-INVASIVE ANALYSIS OF MURAL PAINTINGS FROM A REPUBLICAN HOUSE (1ST CENTURY B.C.) IN OSTIA

D. Strivay, E. Herens, T. Morard, C. Defeyt

CHARACTERIZATION OF ARSENIC SULFIDE PIGMENTS IN JAPANESE PRINTS OF THE LATE EDO PERIOD

Stephanie Zaleski, Marco Leona

TIME-RESOLVED ATR-FTIR AS A TOOL TO MONITOR CHEMICAL REACTIVITY IN OIL PAINT MODEL SYSTEMS

L. Baij*, J. Hermans, K. Keune, P. Iedema

IBA AND FORS MAPPINGS APPLIED TO THE ANALYSIS OF CULTURAL HERITAGE ARTEFACTS: LAST IMPROVEMENTS ON THE AGLAE FACILITY

Q. Lemasson, B. Moignard, C. Pacheco, L. Pichon, T. Calligaro, J. Rumolo, C. Boust, M. Guiavarc'h, G. Querré

ADVANCED TECHNIQUES OF PHOTO-LUMINESCENCE MICROSCOPY FOR THE ANALYSIS OF PRECIOUS SEMICONDUCTOR-BASED PAINTING LAYERS

Daniela Comelli, Alessia Artesani , Austin Nevin, Victor Gonzalez, Matthieu Réfrégiers, Mathieu Thoury

THE NEW “CRONO” MACRO-XRF SCANNER APP**LIED TO CIMABUE’S MA**STERPIECE

T. Frizzi, G. Sciutto, N. Aresi, E. Catelli, S. Prati, R. Alberti, R. Mazzeo

A MULTI-ANALYTICAL APPROACH TO THE PAINTING TECHNIQUE AND THE GREEN AND BLUE PIGMENTS USED IN ANDEAN COLONIAL WALL PAINTINGS

Eugenia Tomasini, Valeria Careaga, Carlos Rúa Landa, Fernando Guzmán, Gabriela Siracusano, Marta Maier

THE GIOTTO’S WORKSHOP IN THE XXI CENTURY: LOOKING INS**IDE THE “GOD THE FATHER WITH ANGELS”** CUSP

Anna Galli, Roberto Alberti, Nicola Aresi, Letizia Bonizzoni, Michele Caccia, Isabella Castiglioni, Marco Gargano, Matteo Interlenghi, Nicola Ludwig, Christian Salvatore, Marco Martini

PIGMENT IDENTIFICATION IN HISTORICAL SAMPLES OF MATISSE CUT-OUTS

Ana Martins , Asami Ondate, Anna Cesaratto, Karl Buchberg, Chris McGlinchey, Marco Leona

A TALE OF TWO PIGMENTS: THE CHARACTERIZATION AND SYNTHESIS OF INDIAN YELLOW, AND ZINC ORANGE FROM TOULOUSE-**LAUTREC’S EARLY PALE**TTE

Aaron Shugar, Rebecca Ploeger, Kathryn Harada, Katherine Spendel, Scott Goodman

COMPARATIVE TECHNICAL ANALYSIS OF THE MEDIEVAL ALTARPIECES BY HERMEN RODE IN TALLINN AND **IN LÜBECK**

Andres Uueni, Signe Vahur, Hilkka Hiiop, Hembo Pagi, Riin Rebane

NICOLAS POUSSIN’S PAINTING TECHNIQUE IN THE SCOPE OF A MOBILE LABORATORY: X-RAY FLUORESCENCE, X-RAY DIFFRACTION AND REFLECTANCE HYPERSPECTRAL IMAGING

L. de Viguerie, M. Radepont, H. Glanville, M. Alfeld, S. Pedetti, Ph. Walter

NEW INSIGHTS INTO INDIAN YELLOW AND ITS USE IN RAJASTHANI WALL PAINTINGS – A MULTI-ANALYTICAL STUDY

Diego Tamburini, Charlotte Martin de Fonjaudran, Giovanni Verri, Gianluca Accorsi, Amarilli Rava, Samuel Whittaker, David Saunders

PORTABLE INSTRUMENTATION FOR THE STUDY OF WALL PAINTINGS: THE CASE OF S. MARIA AD UNDAS IN IDRO (BS-ITALY)

Lavinia de Ferri , Francesca Mazzini , Davide Manzini , Giulio Pojana

"PRECIOUS POWDER": DESIGNING A METHODOLOGY FOR THE TECHNICAL AND ANALYTICAL STUDY OF PASTEL PAINTINGS FROM THE RIJKSMUSEUM COLLECTION

Leila Sauvage , Silvia Settimi , Idelette van Leeuwen , Julia Schultz , Kanaan Abdulah

PAUL GAUGUIN'S GRAPHIC WORKS: MULTI-ANALYTICALCHARACTERIZATION OF THE ARTIST**'S** TECHNIQUES AND MATERIALS

Celine Daher*, Ken Sutherland , Harriet Stratis , Francesca Casadio

300-400 NM UV FLUORESCENCE MULTISPECTRAL IMAGING FOR ORGANIC PICTORIAL MATERIALS IDENTIFICATION

Tiziana Cavaleri , Marco Gargano , Marco Pisani , Massimo Zucco , Paola Buscaglia

A COMPARISON OF NON-INVASIVE IMAGING AND PORTABLE TECHNIQUES FOR THE STUDY OF OLD MASTER PAINTINGS: REMBRANDT**'S** *THE JEWISH BRIDE* C. 1665

P. Noble*, A. van Loon, K. Janssens , J. Delaney , Y. Abe , I. Nakai , J. Dik

TWO IN ONE: UNRAVELING A HIDDEN JAN STEEN PAINTING

Wen-Yuan Lee , Roald Tagle ,

MICRO AND MACRO SCALE CHEMICAL IMAGING O**N VAN EYCK'S GHENT A**LTARPIECE (1432)

Geert Van der Snickt , Hélène Dubois , Jana Sanyova , Stijn Legrand , Koen Janssens

CONCEALED FEATURES I**N BOTTICELLI'S FRESC**O UNVEILED BY MULTISPECTRAL VISIBLE-NEAR INFRARED AND X-RAY FLUORESCENCE IMAGING

Jana Striova , Anna Mazzinghi , Chiara Ruberto , Marco Barucci , Caroline Czelusniak , Lorenzo Giuntini , Pier Andrea Mandò , Lara Palla , Enrico Pampaloni , Francesco Taccetti , Raffaella Fontana

ANALYTICAL AND TECHNOLOGICAL INVESTIGATION OF THE PAINTINGS AND OTHER DECORATIVE ELEMENTS OF THE HOLY AEDICULE OF THE HOLY SELPUCHRE IN JERUSALEM

A. Moropoulou , E. T. Delegou , I. Ntoutsi , M. Apostolopoulou

ON-SITE ANALYSIS OF PAINTINGS BY MEANS OF PORTABLE XRD

I. Nakai , A.Hirayama , S. Akagi , Y. Abe , K. Tantrakarn , K. Taniguchi , A. van Loon , P. Noble , G.D. Vivo , K. Janssens

THE USE OF SMALT IN **REMBRANDT'S** *HOMER* **–** NEW RESEARCH COMBINING MA-XRF, QUANTITATIVE MICROANALYSIS, PAINT RECONSTRUCTIONS AND OCT

A. van Loon, P. Noble , D. de Man, G. Van der Snickt , K. Janssens , M. Alfeld, T. Callewaert , J. Dik

JAN DAVIDSZ. DE HEEM: A TECHNICAL EXAMINATION OF FRUIT AND FLOWER STILL LIFES COMBINING MA-XRF SCANNING, CROSS-SECTION ANALYSIS AND TECHNICAL HISTORICAL SOURCES

Nouchka De Keyser , Geert Van der Snickt , Annelies van Loon , Stijn Legrand , Arie Wallert , Koen Janssens

A NEW INNOVATIVE SAMPLING TECHNIQUE FOR ANALYSIS OF MICROORGANISMS ON ANGKOR TEMPLES IN CAMBODIA

Ji-Dong Gu*, Yoko Katayama

A COMPREHENSIVE STUDY OF THE EFFECTS INDUCED BY BROWN ROT FUNGI ON ARCHAEOLOGICAL WATERLOGGED WOOD

Jeannette Jacqueline Lucejko , Marco Mattonai , Magdalena Zborowska , Caroline Cartwright , Diego Tamburini , Grzegorz Cofta , Francesca Modugno , Maria Perla Colombini , Erika Ribechini

4.3 ORAL COMMUNICATIONS: PARALLEL SESSION B

A NOVEL METHODOLOGICAL APPROACH FOR THE ASSESSMENT OF SURFACE CLEANING OF ACRYLIC EMULSION PAINTS

Theodora Fardi

INSIGHT ON COLOUR CHANGE AND CHEMICAL ALTERATION OF GREEN COPPER-BASED ORGANOMETALLIC PAINTING PIGMENTS

Marion Alter, Anne-Solenn Le Hô, Christel Doublet, Didier Gourier, Laurent Binet, Nadia Touati, François Mirambet, Nadège Lubin-Germain

ELUCIDATING DAGUERREOTYPE DEGRADATION BY SURFACE SPECIES FORMATION USING SURFACE PLASMON RESONANCE SCATTERING SPECTROSCOPY

Andrea E. Schlather, Silvia A. Centeno

ANALYTICAL CHALLENGES IN STUDYING DEGRADATION PROCESSES IN PAINTINGS: ULTRAMARINE DISEASE

Alessa A. Gambardella, Kokkie Schnetz, Roel van Elsas, Pieter Iedema, Katrien Keune

COMBINING SYNCHROTRON PHOTOLUMINESCENCE IMAGING AND MICROSPECTROSCOPY TO STUDY ZINC WHITE DEGRADATION IN OIL PAINT

S. Hageraats, K. Keune, A. van Loon, B. Berrie, M. Thoury

INFLUENCE OF LEAD WHITE AND COBALT BLUE ON THE DEGRADATION OF EOSIN LAKES

Alba Álvarez-Martín, Koen Janssens

BLANCHING OF PAINT AND VARNISH LAYERS: FROM THE CHARACTERIZATION TO THE DEVELOPMENT OF CONSERVATION TREATMENTS

Genty-Vincent, M. Eveno, W. Nowik, G. Bastian, E. Ravaud, J. Uziel, R. Giorgi, P. Baglioni, N. Lubin-Germain, M. Menu

ROLE OF DEFECTS IN THE REACTIVITY OF CD-YELLOW

Laura Giacopetti, Alessandra Satta, Austin Nevin, Daniela Comelli, Gianluca Valentini

DESIGN OF EXPERIMENTS – INVESTIGATING THE EFFECT OF PAINT FORMULATION ON DEGRADATION RATES OF TIO$_2$-BASED OIL PAINTS

B.A. van Driel, K.J. van den Berg, M. Smout, N. Dekker, J.Dik

PORTABLE NON-DESTRUCTIVE HANDHELD MID-INFRARED FT-IR ANALYSIS OF THREE DIVERSE ANTIQUITIES FOR SPECTRAL ANALYSIS COMBINED WITH MULTIVARIATE CHEMOMETRIC ANALYSIS AND ASSESSMENT OF POTENTIAL BENEFITS IN ART CULTURAL HERITAGE STUDIES

Pik Leung Tang

CHARACTERIZATION AND PROVENANCE STUDY OF POMPEIAN RED AND YELLOW OCHRE PIGMENTS

Iker Marcaida, Maite Maguregui, S. Fdez-Ortiz de Vallejuelo, Héctor Morillas, K. Castro, N. Prieto-Taboada, Marco Veneranda, Juan Manuel Madariaga

REAL-TIME DIAGNOSIS OF COLLAGEN-BASED ARTWORKS BY THERMAL SHRINKAGE IMAGING

Elena Badea, Cristina Carote, Oana Andreea Miu, Ionu Bornoiu, Daniela Ichim

MICRO-SPECTROSCOPY OF ROCK ART PAINTINGS FROM THE CUEVA MAYOR OF THE ATAPUERCA SITE (BURGOS, SPAIN)

A. Hernanz, D. Paredes-Roibás, J.M. Gavira-Vallejo, J.J. Fernández, B. García, M. Iriarte

NON-DESTRUCTIVE ANALYSIS OF STILL BAY (>70 KA) POINTED ARTEFACTS FROM SIBUDU CAVE, SOUTH AFRICA

Marine Wojcieszak, Lyn Wadley

ADVANCED CHARACTERIZATION OF NEW NANOSTRUCTURED STONE TREATMENTS FOR THE CONSERVATION OF EUROPEAN ARCHITECTURAL HERITAGE

F. Gherardi , T. Poli , M. Roveri , O. Chiantore , L. Toniolo

THE FIRST USE OF PORTABLE RAMAN INSTRUMENTATION FOR THE ANALYSIS OF PATAGONIAN PREHISTORIC ROCK ART PAINTINGS: PIGMENTS, ACCRETIONS AND SUBSTRATA

Anastasia Rousaki , Cristina Vázquez , Verónica Aldazábal , Cristina Bellelli , Mariana Carballido Calatayud , Adam Hajduk , Emmanuel Vargas , Oscar Palacios , Adam Culka , Jan Jehlička , Luc Moens , Peter Vandenabeele

INVESTIGATION ON CONSTRUCTION MATERIALS AND THEIR ENVIRONMENTAL INTERACTION AT THE PANAMANIAN UNESCO SITES

Chiara Ciantelli*, Alessandro Sardella ,Carmela Vaccaro , Alessandra Bonazza

NEW *IN SITU* NON INVASIVE ANALYTICAL METHODOLOGY TO DETERMINATE THE STATE OF PRESERVATION OF PREHISTORIC ROCK ART SITES

Juan Francisco Ruiz*, Silvia Fdez-Ortiz de Vallejuelo , Julene Aramendia , Maite Maguregui , Juan Manuel Madariaga

THE INVESTIGATION OF CALCIUM CARBONATE FORMATION USING MICRO-RAMAN SPECTROSCOPY

Radek Ševčík , Petra Mácová , Alberto Viani

X-RAY PHOTOELECTRON SPECTROSCOPY OF PICTORIAL SAMPLES

E. Carrasco, M. Oujja, M. Sanz*, J. F. Marco, M. Castillejo

FROM MICRO TO MACRO: A MULTISCALE RAMAN MAPPING APPROACH FOR THE ANALYSIS OF INKS AND PIGMENTS ON PAPER, PANELS AND WALLS

S.Mosca , A.Artesani , D.Gulotta , A.Nevin , G.Valentini , D.Comelli

A SYSTEM FOR SCIENTIFIC MICROSCOPE COLOR CALIBRATION AT THE RIJKSMUSEUM FOR THE PAINT SAMPLE DATABASE

Susan Smelt , Robert Erdmann

THE AGGREGATION OF LEAD AND CALCIUM CARBOXYLATES ON EXPERIMENTAL MODELS. A COMBINED ANALYTICAL APPROACH FOR THEIR SAMPLING, IDENTIFICATION AND CHARACTERIZATION

Elena Aguado-Guardiola[*], Laura Fuster-López , Oscar Chiantore , Anna Piccirillo , Tommaso Poli , Paola Croveri, Marco Nervo

MA-XRF IMAGING SPECTROSCOPY ON THE ARCHAIC PAINTED PANELS FROM PITSA (6TH C. BC, CORINTHIA, GREECE): NEW EVIDENCE ON THEIR ORIGINAL POLYCHROMY AND THEIR ICONOGRAPHY

H. Brekoulaki , F.P. Romano , A.G. Karydas , G. Kavvadias

THE GLASS BEADS AS MARKERS OF THE TRADE TO SOUTHERN AFRICA FROM THE 8TH TO THE 19TH CENTURY AD

Ph. Colomban , F. Koleini , L.C. Prinsloo, W. Biemond , J. C.A. Boeyens , M. M. van der Ryst , I. Pikirayi

A NOVEL TOOL FOR CULTURAL HERITAGE MATERIAL ANALYSIS: TRANSMISSION ELECTRON MICROSCOPE (TEM) 3D ELECTRON DIFFRACTION TOMOGRAPHY AND ORIENTATION/PHASE MAPPING APPLIED TO ANCIENT ROMAN GLASS TESSERAE

Nikolaos Zacharias , Fotini Karavasili , Partha Das , Athanasios Galanis , Edgar Rauch , Stavros Nicolopoulos , Artemios Oikonomou, Irene Margiolaki

STUDY OF A MODERN CHINESE CLOIS**ONNÉ VASE BY MEANS O**F EDXRF AND RAMAN SPECTROSCOPY

I.Queralt*, S.Pessanha , M.Manso , M. L.Carvalho

INVESTIGATION OF 18^{TH}-CENTURY CHINESE DOUBLE-WALLED VASES IN *YANGCAI* PAINTED ENAMEL

Tung-Ho Chen, Chien-Chi Huang

THE MAGIC OF COLOUR OF MEDIEVAL STAINED GLASS WINDOWS. INSIGHTS INTO COMPOSITION OF RED AND VIOLET FLASHED GLASSES

Małgorzata Walczak , Dariusz Wilk , Marta Kamiska , Edyta Bernady , Ewa Bulska

Nikolaos Zacharias , Maria Kaparou , Artemios Oikonomou , Zsolt Kasztovszky

HISTORIC CONSERVATION MATERIALS ON STAINED GLASS WINDOWS IN THE NAUMBURG CATHEDRAL

Elisavet Kanaki , Josef Brandt

CHARACTERIZATION OF GLAZE CERAMICS FROM THE ARCHAEOLOGICAL SITE OF LA ALCAZABA, **ALMERÍA** (SPAIN)

Inés Ortega-Feliu , Blanca Gómez-Tubío , Yasmina Cáceres , Miguel Ángel Respaldiza

ASSESSING THE FIRING TEMPERATURE OF URUK POTTERY IN THE MIDDLE EUPHRATES VALLEY (SYRIA): BEVELLED RIM BOWLS

Jorge Sanjurjo-Sánchez , Juan Luis Montero Fenollós , Victor Barrientos , George S. Polymeris

USE OF SMALL ANGLE NEUTRON SCATTERING AND X-RAY POWDER DIFFRACTION WITH THE RIETVELD METHOD IN THE ASSESSMENT OF FIRING CONDITIONS IN HISTORICAL FIRED-CLAY BRICKS

Alberto Viani , Konstantinos Sotiriadis , Radek Ševčík

XRF ANALYSES OF THE SERRA D'ALTO POTTERY (MATERA, ITALY)

S. Legnaioli , L. Angeli , E. Grifoni , V. Palleschi , C. Fabbri , G. Radi

'NOT TOO WHITE': AN INVESTIGATION INTO THE INFLUENCE OF THE USE OF CALCIUM CARBONATE-RICH IMPORTED MARLS ON 17 - 18^{TH} CENTURY DUTCH TIN-GLAZE TILE PRODUCTION

Kate van Lookeren Campagne , Silvia Pereira , Luc Megens , Ouzhan Çopurolu Eric Goemaere Norman H. Tennent Maarten van Bommel

JUN WARE – A TECHNICAL STUDY

Lucy Cooper , Katherine Eremin , Marc Walton , Emeline Pouyet , Andrew Shortland , Laure Dussubieux

LA-ICP-MS MULTI-ELEMENT ANALYSES OF BLUE & WHITE TIN-GLAZED EARTHENWARE TILES: 2D SURFACE AND DEPTH MAPPING OF GLAZES

Norman H. Tennent , Johannes T. van Elteren , Vid S. elih

COMPUTED RADIOGRAPHY, PIXE AND XRF ANALYSIS OF PRE-COLONIAL POTTERY FRO**M MARANHÃO,** BRAZIL

Renato A. Ikeoka , Carlos R. Appoloni , Marcia A. Rizzutto , Arkley M. Bandeira

SELF-CLEANING COATINGS BY N-DOPED TIO_2 ON LIMESTONES

L. Fornasini , L. Bergamonti , G. Predieri, Y. Paz , D. Bersani , P.P. Lottici, F. Bondioli

LIMESTONE CHROMATIC CHANGES: A MICROBIAL-MEDIATED INORGANIC PROCESS

L. Dias , T. Rosado , A. Coelho , L. Lopes , J. Mirão , A. T. Caldeira, A. Candeias

NOVEL MATERIALS FOR THE RESTORATION OF MARBLE AND LIMESTONE SUBSTRATES BASED ON OXALATE DERIVATIVES: AN EXPERIMENTAL AND DFT-THEORETICAL APPROACH

Laura Giacopetti*, M. Carla Aragoni , Gianfranco Carcangiu , Ombretta Cocco , Vito Lippolis , Laura Maiore , Paola Meloni , Arianna Murru , Massimiliano Arca

ANALYSIS OF TYPOMORPHIC MINERALS APPLIED IN THE INVESTIGATION OF ORIGIN OF ARCHEOLOGICAL OBJECTS AND PAINTING MATERIALS

Barbara Łydżba-Kopczyńska*, Barbara Kosmowska Ceranowicz, Micha Sachanbinski

NEW INSIGHTS INTO THE CHARACTERIZATION OF LIPIDS IN PRE-HISPANIC CERAMICS BY MASS SPECTROMETRY TECHNIQUES

Irene J. Lantos, Valeria P. Careaga, Evelyn L. Bonifazi Diana M. Castellanos Rodríguez, Marta S. Maier

NUCLEAR MAGNETIC RESONANCE ANALYSIS FOR TREATMENT DECISIONS: THE CASE OF A WHITE SCULPTURAL ENVIRONMENT BY LOUISE NEVELSON

Cindie Kehlet, Sarah Nunberg, Carolyn Tomkiewicz, Soraya Alcala, Jens Dittmer

DISCRIMINATION OF ACACIA GUMS BY MALDI-MS: DEVELOPMENTS AND APPLICATIONS TO SAMPLES FROM ANCIENT EGYPT

Clara Granzotto, Julie Arslanoglu, Ken Sutherland

DEVELOPMENT OF A NEW METHODOLOGY FOR THE ANALYSIS OF STEROLS AND BILE ACIDS IN ARCHAEOLOGICAL SOILS FOR THE CHARACTERIZATION OF SPECIES

Jaime Gea, María Carmen Sampedro, Asier Vallejo, Ana Polo, Javier Fernández-Eraso, Ramón J. Barrio

GC-MS AND HPLC-APCI-MS FOR THE RESEARCH, VALORIZATION AND DISSEMINATION OF THE IBERIAN CULTURE

David J. Parras , Alberto Sánchez , José A. Tuñón, Carmen Rueda, Juan F. García-Reyes

IDENTIFICATION OF ORGANIC RESIDUES IN ARCHAEOLOGICAL CERAMIC VESSELS OF BASQUE WHALERS FROM 16TH TO 17TH CENTURY

Laura Blanco-Zubiaguirre, Erika Ribechini, Ilaria Degano, Jacopo La Nasa, Javier García-Iñañez, Maitane Olivares, Kepa Castro

DMFDMA: A NEW/OLD GC-MS DERIVATIZATION AGENT FOR THE ANALYSIS OF BINDERS IN CULTURAL HERITAGE OBJECTS

Francesco Caruso, Bettina Ebert, Elena Platania, Calin Constantin Steindal, Noelle L.W. Streeton

DEVELOPMENT OF A QUALITATIVE AND QUANTITATIVE ANALYTICAL METHOD FOR THE CHARACTERISATION OF MIXTURES OF FREE FATTY ACIDS AND METAL SOAPS IN PAINT SAMPLES

Jacopo La Nasa, Anna Lluveras Tenorio, Francesca Modugno, Ilaria Bonaduce

4.4 ORAL COMMUNICATIONS: PARALLEL SESSION C

ADVANCED EXTRACTION AND ANALYTICAL METHODS APPLIED TO DISCRIMINATION OF DIFFERENT LICHEN SPECIES USED FOR ORCEIN DYED YARNS

ILARIA SERAFINI , LIVIA LOMBARDI , MAURIZIO ACETO , ELISA CALÀ , AMBRA IDONE , FABIO SCIUBBA , MARCELLA GUISO , ARMANDODORIANO BIANCO

IDENTIFICATION AND CLASSIFICATION OF TEXTILE FIBRES USING ATR-FT-IR SPECTROSCOPY WITH CHEMOMETRIC METHODS

PILLERIIN PEETS, SIGNE VAHUR, IVO LEITO

SURFACE ENHANCED RAMAN SPECTROSCOPY OF ANTRAQUINONE-ALUMINUM COMPLEXES ON DYED FIBERS

TOMÁS AGUAYO

AN INNOVATIVE METHOD FOR THE NON-INVASIVE PROTEOMIC ANALYSIS OF CULTURAL HERITAGE OBJECTS

MARCELLO MANFREDI , ELETTRA BARBERIS , ELEONORA CONTE , FABIO GOSETTI , SIMONE BAIOCCO , PIER GIORGIO RIGHETTI , EMILIO MARENGO

A NON-INVASIVE METHODOLOGY FOR STRATIGRAPHY INVESTIGATION OF HISTORICAL VIOLINS USING REFLECTION IR SPECTROSCOPY AND UV INDUCED FLUORESCENCE TECHNIQUE

C. INVERNIZZI , T. ROVETTA , M. LICCHELLI , M. MALAGODI

COMPLEMENTARY USE OF OPTICAL COHERENCE TOMOGRAPHY (OCT) AND REFLECTION MID-FTIR SPECTROSCOPY FOR IN SITU MONITORING OF VARNISH REMOVAL FROM EASEL PAINTINGS

MAGDALENA IWANICKA , PATRIZIA MORETTI , SASKIA VAN OUDHEUSDEN , MARCIN SYLWESTRZAK , LAURA CARTECHINI , KLAAS JAN VAN DEN BERG , PIOTR TARGOWSKI , COSTANZA MILIANI

A NON-INVASIVE STUDY OF SURFACE COATINGS OF ELECTRIC GUITARS

ANNE MICHELIN , STEPHANE VAIEDELICH , CHRISTINE ANDRAUD , AURELIE TOURNIE , PHILIPPE BRUGUIERE

FLUORINATION TECHNIQUE TO IDENTIFY THE TYPE OF RESIN IN AGED VANISHES AND LACQUERS USING INFRARED SPECTROSCOPY

STEFAN ZUMBÜHL , ANDREAS HOCHULI , NADIM C. SCHERRER , BALTHAZAR SOULIER

READABILITY RECOVERY IN DAMAGED ANCIENT PARCHMENT ARTEFACTS: A COMPARATIVE STUDY AMONG MULTISPECTRAL IMAGING TECHNIQUES.

A. PASQUALUCCI , C. CICERO , M MARINELLI , F. MERCURI , N. ORAZI ,

S. PAOLONI , M. ROMANI , A. TERREI , G. VERONA-RINATI , U. ZAMMIT

USABILITY OF SPECTROSCOPIC, DIFFRACTION AND MICROSCOPIC ANALYTICAL TOOLS TO RECOGNIZE OLD MOROCCAN JEWISH PARCHMENTS

LATIFA. HAJJI*,JAMAL ASSOUIK , ABDELHADI LHASSANI , AYOUB AINANE , M'HAMMED EL KOUALI , YOUSFI SAMIA , MOHAMMED TALBI , MARTA MANSO , MARIA LUISA CARVALHO

MAPPA MUNDI OF ALBI – SCIENTIFIC STUDY OF THE OLDEST MAP

LAURIANNE ROBINET , JOCELYNE DESCHAUX , AURÉLIE TOURNIÉ , STÉPHANE VAIEDELICH(1,4), GAËL LATOUR , ANNE MICHELIN , SYLVIE THAO , CHRISTINE ANDRAUD , MARIE-CLAIRE SCHANNE-KLEIN , BERTRAND LAVÉDRINE

A MULTI-ANALYTICAL STUDY OF **THE 'HAY COOKBOOK' C**OPTIC MAGICAL MANUSCRIPTS ON LEATHER REVEAL THEIR MYSTERIES

LUCY-ANNE SKINNER , REBECCA STACEY , BARBARA WILLS , LUKE SPINDLER , ELISABETH O'CONNELL

NON-INVASIVE *IN-SITU* AND SR-BASED IMAGING TECHNIQUES FOR RECOVERING THE TEXT FROM A RECYCLED PARCHMENT

E. Pouyet, L. Smieska, A. Woll, A. Katsaggelos, O. Cossairt, J. Salvant, M. Walton

3D IMAGING OF ARTEFACTS BY EDXRF- SCANNING

Roberto Cesareo, Stefano Ridolfi, Antonio Brunetti, Giovanni E. Gigante

THE PROCESSIONAL CROSS OF SANTA MARIA MAGGIORE AT GUARDIAGRELE: MATERIALS AND TECHNIQUES OF NICOLA DA GUARDIAGRELE INVESTIGATED BY X-RAY FLUORESCENCE

A. Esposito, M. Ferretti, A. Gorghinian

STUDY OF APPLICABILITY OF NON-INVASIVE ANALYSES METHODS IN ARCHAEOLOGY

Aneta Maria Gójska, Ewelina Agnieszka Miśta

NON-INVASIVE STUDIES ON TECHNOLOGICAL PROVENANCE OF MEDIEVAL SILVER JEWELRY FORM BALTIC SEA REGION

Ewelina A. Miśta, Wadysaw Duczko, Renata Czech-Boska, Aneta M. Gójska, Andrzej Turos, Pawe Ciepielewski

ELECTROCHEMICAL DISCRIMINATION OF MONETARY EMISSIONS: CHARACTERIZING TEN-CASH DRAGON COPPER COINS

Antonio Doménech-Carbó, María Teresa Doménech-Carbó, Elena Montagna, Yu Lee

A SPECTROSCOPIC STUDY OF METAL FOILS AND ITS LAYERING IN NORWEGIAN MEDIEVAL OBJECTS

Anna Vila, Elena Platania, David Buti, Noelle Streeton

UNVEILING ANCIENT GOLD INLAY TECHNIQUE OF A BRONZE BELT PLAQUE

Man-wai Tang, Wing-fai Lai

WHAT SYNCHROTRON RADIATION BASED EXPERIMENTS CAN TELL ABOUT POVERTY POINT OBJECTS (PPOS)

Josef Hormes, Gudrun-Lisa Bovenkamp-Langlois, Martha W. Schaefer, Orhan Kiyilkaza, Wantana Klysubun, Diana M. Greenlee

TOWARDS NON-DESTRUCTIVE ANALYSIS OF ARCHAEOLOGICAL CERAMICS BY MICRO X-RAY FLUORESCENCE SPECTROMETRY

Estefania Calparsoro, Maite Maguregui, Javier G. Iñañez Juan Manuel Madariaga

PORTABLE XRF SETUP WITH MONOCHROMATIC RADIATION FOR THE ANALYSIS OF CULTURAL HERITAGE

Sofia Pessanha, Mauro Guerra, Jorge Miguel Sampaio, Maria Luisa Carvalho, Ignasi Queralt

THE MATERIAL CHARACTERISATION OF INDUSTRIAL AND TECHNICAL HERITAGE: THE POWER PLANT IN LEVADA DE TOMAR – PORTUGAL

M. Manso, M.L. Carvalho, J.F. Fonseca, I. Queralt, M. Lemos, M. Tissot

IN SITU CHARACTERIZATION OF THE MATERIALS AND TECHNIQUES OF ROMAN EGYPTIAN MUMMY PORTRAITS USING COMBINED FORENSIC PHOTOGRAPHY AND SPECTROSCOPY

Roxanne Radpour, Yuan Lin, Marie Svoboda, Giacomo Chiari, Christian Fischer, Ioanna Kakoulli

RUBRICATION IN HISTORIC MANUSCRIPTS

Bernadette Frühmann, Federica Cappa, Wilfried Vetter, Manfred Schreiner

THE PRESENCE OF IRON IN THE INKS OF THE VALENCIAN MANUSCRIPTS FROM THE 13TH TO THE 17TH CENTURIES

Gemma María Contreras Zamorano

APPLICABILITY OF MICRO-REFLECTION-FTIR-MAPPING FOR THE INVESTIGATION OF MEDIEVAL MANUSCRIPTS – A CASE STUDY

Wilfried Vetter, Bernadette Fruehmann, Manfred Schreiner

A MULTI-ANALYTICAL CHARACTERIZATION OF FRENCH PAPER NEGATIVES: HOW TO SEE THROUGH MANY PROCESSES?

Celine Daher , Marie-Angelique Languille , Anne de Mondenard , Aurelie Tournie , Sylvie Aubenas , Bertrand Lavedrine

IN SITU SPECTROFLUORIMETRIC ANALYSIS OF RED & BLUE COLOURS ON 19TH CENTURY JAPANESE ENGRAVINGS (TORRALBA COLLECTION, ZARAGOZA MUSEUM)

A. Mounier*, G. Le Bourdon , C. Aupetit , S. Lazare , J. Pérez-Arantegui , F. Daniel

PRINTING MATERIALS AND TECHNOLOGIES IN THE 15TH-17TH CENTURY BOOK PRODUCTION: AN UNDERESTIMATED RESEARCH FIELD

F. Albertin , E. Balliana , G. Pizzol , G. Colavizza , E. Zendri, D. Raines

THE USE OF POLYAMIDOAMINES FOR THE DEACIDIFICATION OF IRON-GALL INKED PAPERS

Clelia Isca , Laura Bergamonti , Claudia Graiff , Giovanni Predieri , Pier Paolo Lottici

INTERDISCIPLINARY APPROACH FOR CLEANING GRAPHIC ARTWORKS: THE CASE STUDY OF DIANA SCULTORI ENGRAVING

L. Micheli , C. Mazzuca , M. Missori , L. Teodonio , A. Mosca Conte , O. Pulci , L. Arcadipane , S. Dominijanni , S. Iannuccelli , S. Sotgiu

COMBINED MACROSCOPIC XRF AND FTIR MAPPING OF A 14TH CENTURY ILLUMINATED MANUSCRIPT FRAGMENT

S. Legrand , P. Ricciardi , L. Nodari , K. Janssens

HIGHLY RETENTIVE HYDROGELS FOR PAPER CLEANING

C. Mazzuca , L. Micheli , G. Poggi , N. Bonelli , R. Giorgi , P. Baglioni , A. Palleschi

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Rui Silva, Elin Figueiredo

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Susana Sousa Gomes, Maria Fátima Araújo, António Monge Soares, João Pimenta, Henrique Mendes

STUDYING THE THERMAL TRANSFORMATION OF LEAD CARBONATES INVOLVED IN ANTIQUE ROMAN EYE CARE MEDICINE

Marlène Aubin, Murielle Labonnelie, Philippe Walter, Ludovic Bellot-Gurlet

ANALYSES OF 6 CANVASES FROM OSMAN HAMDI **BEY'S PAINTINGS USIN**G PCA ON FTIR-ATR DATA

Cüneyt H. Ünlü, Filiz Kuvvetli

5. ABSTRACTS: PLENARY LECTURES

Potential of Micro-SORS for Cultural Heritage

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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 [1]. The technique combines conventional Spatially Offset Raman Spectroscopy [2] with microscopy concepts and represents a new imaging modality in Raman microscopy.

Two principal variants of the method were developed: i) 'Defocusing micro-SORS', exceptionally simple and usable with existing Raman microscopes without any modifications. The technique involves measurements performed at several defocusing distances from the 'imaged' position inducing the enlargement of both the collection and illumination points; ii) 'Full micro-SORS', a more effective variant mimicking classical macro-scale SORS effect on micro-scale using fully separated Raman collection and laser illumination zones. This variant requires adaptations to the configuration of existing Raman microscopes in order to be practised in its unrestricted form [3].

By examining the relative rate of the decay of signals from individual layers, micro-SORS techniques, in general, are capable of determining the order in which layers are laid. Moreover, it is also possible to determine whether two chemical components detected by micro-SORS belong to two separate layers or if they are deposited within a single-layer mixed up [4].

The practical applicability of micro-SORS has been demonstrated conceptually in several application areas, such as stratified polymer and glossy paper systems. Satisfactory results have been achieved also analysing non-invasively the structure of wheat seed, consisting of external envelope and more internal kernel: the Raman spectrum in the 'imaged' position is dominated by the contribution from a ferulic acid layer (top layer), and micro-SORS measurements show the increasing of starch signal (internal layer) [1].

The potential of the method in Cultural Heritage field has been demonstrated analysing painted sculptures and plasters. Measurements carried out on terracotta sculptures originating from 'Sacred Mounts', devotional places constructed during the late fifteenth and seventeenth century in Northern Italy (UNESCO World Heritage sites), permitted the elucidation of the molecular composition of their complex stratigraphy. The 'imaged' position spectrum exhibits signal related to the more external layer, and micro-SORS analysis allowed to discern the contribution from internal layers. In this way, the resorting to cross sectional analysis to retrieve chemical information from such sub-layers could be avoided.

In general, the limitations of the micro-SORS technique include its inapplicability to highly absorbing top layers, extremely thin sublayers, layers buried too deep (beyond the reach of micro-SORS) and compounds with low Raman cross sections or highly fluorescent at the subsurface position. Samples possessing very high heterogeneity across their surface or within sublayers are also challenging and may require the use of a more complex data acquisition methodology. It should also be noted that the spatial resolution of micro-SORS is significantly inferior to that of conventional Raman microscopy and as such it should only be used at depths where conventional confocal Raman microscopy is not applicable.

Here we will focus on our latest results of micro-SORS experiments carried out with an aim to explore the applicability of the method in challenging situations including the recovering of sublayer signal in presence of a fluorescent compound: specifically, micrometric layers of fluorescent pigments were spread over marble or different layers of pigments. A comparative study between the fluorescence suppression of the top layer achieved by defocusing and full micro-SORS was carried out, highlighting that the latter modality is significantly more effective, capable of recovering the sublayer signal, even when conventional Raman measurement yields only strong fluorescence [5].

Recently, the ability of micro-SORS for the non-invasive recovery and reconstruction of 2D images within overpainted sublayers has been also demonstrated [6]. The technique was conceptually verified on specimens mimicking real situations encountered in Cultural Heritage. Additionally, using a letter as a hidden image, it was demonstrated that hidden writing could also be retrieved by this method (Figure 1).

Furthermore, recent development of the first portable full micro-SORS prototype will also be illustrated. This advancement unlocks fully the non-invasive and non-destructive potential of micro-SORS. First, a conventional portable Raman equipped with 785 nm excitation wavelength was adapted for a basic defocusing micro-SORS analysis, obtaining significant results on artificial micrometric layer systems consisting of spray paint on stone and painted stratigraphy [7]. In a further step, portable full micro-SORS was developed; due to the presence of real offset between beam and collection areas it is more effective compared with defocusing micro-SORS variant yielding generally higher discrimination levels against top layers and deeper penetration depths.

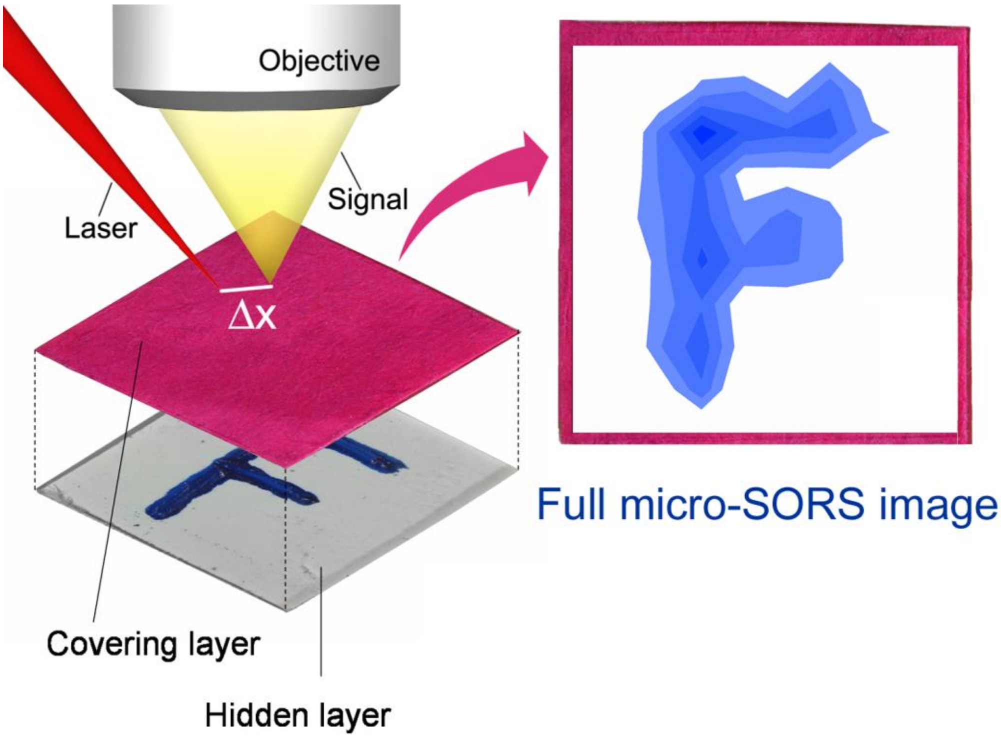

Figure 1. A scheme of ‘full micro-SORS’ variant applied to the reconstruction of hidden 2D painted images.

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Multimodal analytical approach for characterization of decorative revetments in the Alhambra monument

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The Alhambra stands as one of the most well-known and most-visited World Cultural Heritage sites in Spain. This momumental complex is still one of the most spectacular reminders of 800 years of Islamic settlement in Spain and one of the best surviving examples of Moorish art and architecture in the world. In Islamic architecture buildings look extremely minimalistic and simple from outside but are intensely decorated and elaborate inside. In this work a complete analytical study of different types of decorations located in several spaces of the monument is presented.

A combination of analytical techniques involving both non-invasive tecniques able to work in situ, like Raman spectroscopy and X-Ray Fluorescence and microanalytical tecnniques that work on microsamples like SEM-EDS, FTIR microscopy and confocal Raman microespectroscopy, is proposed to characterize the decorative revetments. Polychrome decorations on plasterwork, marble columns, brick walls and wood ceilings have been studied. The obtained results have provided a better knowledge of these decorations, particularly the pigments and techniques employed, and the conservation problems affecting them. Special emphasis has been paid to exploit the complementary nature of the information provided by the different analytical techniques and to overcome the challenges found in the in situ studies.

Art and Cultural Heritage natural polymers by bottom up and top down approaches

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The study of organic matter in Cultural Heritage samples is a real analytical challenge. Organic compounds are included in a complex matrix and submitted to denaturation due to environment and ageing. Their characterization is an invaluable source of information for the understanding of a manufacturing process or an artist's technique, but also for a better conservation conditions and preservation/restoration treatments.

The conference will address analysis of the three main organic compounds, the proteins, the polysaccharides and the (poly)lipids, using high and very high resolution mass spectrometry:

(i) Our most recent optimization of bottom up proteomics workflow will be discussed

Because bottom up proteomics sometimes causes a loss of structural information or suffers from modifications induced by sample handling, our new developments based on native protein analysis and top down proteomics will be presented and discussed [1, 2]

Application to the study of artworks (art paintings, photographs) will show how top down proteomics inform accurately on the degradation mechanisms of the organic media (e.g. protein breakdown) and protein chemical modifications such as oxidation, deamidation etc. (i.e. impact of restoration procedures and conservation conditions at molecular level). On another aspect, applied to the study of archaeological bones, relationship between protein chemical modifications, environment and ageing will be introduced (e.g. study of the 10-years frontier between forensics sciences and archaeology).

(ii) Our new methodology based on oligosaccharide mass fingerprints for identification of historic gums will be described [3]

Application to the study of watercolors and drawings will show how the strategy developed on standard natural polysaccharides using an enzyme cocktail is applicable to more complex and partially unknown structures starting from very low sample amounts. This is the first time that a gum is accurately identified in a cultural heritage sample using structural information.

(iii) (a) Our analytical workflow will show how very high resolution mass spectrometry is deciphering the complexity of triacylglycerols from archaeological samples

(b) Our new develoments related to soft depolymerization experiments and very high resolution mass spectrometry to unravel the 3D networks formed by the insoluble lipid-based film in oil-paintings will be shown

[1] S. Dallongeville, N. Garnier, C. Rolando, C. Tokarski, Chemical Reviews 116, 2016, 2.

[2] C. Tokarski Proteomics in the Study of Archeological Materials. In Technological Innovation Liliane Bettencourt; Chemical Analysis: History and Innovations, Philippe Walter; Haroche, S., Ed.; Collège de France: Paris, 2014.

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Macromolecules in Archaeology

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Since ancient times, natural materials have been used to produce functional objects and works of art which are part of our cultural heritage. Archaeological excavations often bring to light a wide variety of objects and materials. Particularly, archaeological wood findings and ceramic objects, together with the organic residues found in association with them (e.g. cosmetics, medicines, perfumes, food), are an invaluable source of information regarding technological skills, habits and traditions of people from past civilizations. Because of their long period underground or underwater, these materials and objects, especially those of an organic nature undergo biological, chemical, and thermal degradation. Understanding the composition of organic materials means to identify natural substances and their degradation products: though this is a challenge, this permits to shed light on the nature and the origin of the material employed, the artistic techniques used and the state of conservation.

This lecture outlines the latest progresses in advancing chromatographic-mass spectrometric analytical approaches, characterizing archaeological organic materials and organic residues materials and understanding their degradation.

Most organic natural materials encountered in cultural heritage are macromolecular, in some cases, they are natural polymers (such as proteins, plant gums, wood), others undergo oligomerisation or cross-linking reactions as an effect of exposure to light and air (such as natural resins or drying oils). Archaeological organic samples involve a range of critical characteristics, making their study more challenging. Their investigation is complicated by the ageing and degradation of the molecules present in the organic substances. This means that in order to establish the origin of the natural substances in the sample and to understand the alteration processes that have modified the materials it is essential to identify the molecular composition as well as to reveal the presence of molecular markers. Organic materials in archaeology are also polar and have a low volatility. Their analysis by GC/MS thus entails chemical or thermal treatments in order to reduce the original macromolecules into low polarity, low molecular weight components, thus facilitating their volatilisation and subsequent separation onto a gas chromatographic column. This can be achieved by coupling analytical pyrolysis with gas chromatography mass spectrometry (Py-GC/MS) or by a wet-chemical treatment of the samples prior to GC/MS.

In the last 10 years, analytical approaches involving these techniques try to solve some analytical and technical questions, among which: what manufacturing technique has been applied? Which chemical markers or features allow to detect a specific material? Which analytical procedure detects a specific analyte?

The answers clearly depend on the classes of organic materials found in the sample and the nature of the sample itself. Organic materials in archaeological contexts can vary considerably, depending on ageing and chemical environments: thus, case studies requiring different analytical approaches, are presented and examined.

Applications of non-linear imaging microscopy techniques for Cultural Heritage studies

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Non-linear image contrast modalities (multi-photon excitation fluorescence (MPEF), second harmonic generation (SHG) third harmonic generation (THG)) have been proved to be powerful diagnostic tools for Cultural Heritage (CH) studies [1].

MPEF imaging measurements provide information related to the identification of the chemical composition of artefacts. In contrast to MPEF, which relies on non-linear absorption, SHG and THG rely on non-linear scattering and, thus, are regarded as minimally invasive imaging techniques. SHG signal is produced exclusively from non-centrosymmetric molecules. SHG modality provides information related to structures with high degree of orientation and organization but without inversion symmetry such as stacked membranes and arranged proteins [2]. Moreover, the SHG signal is sensitive to the incoming excitation polarization and to the SHG active structures architecture. Polarization sensitive SHG (PSHG) measurements can provide unique structural and molecular information unreachable by common intensity only SHG imaging. On the contrary, THG is sensitive to local differences in third-order nonlinear susceptibility χ (3), refractive index and dispersion. Under tight focusing conditions, the extent of THG signal increases dramatically when the beam focus spans an interface between two optically different materials [3]. The latter THG property allows to resolve otherwise transparent interfaces and inhomogeneities within the resolution of the confocal parameter and without the use of external dyes. For this reason, THG comprises an ideal diagnostic tool providing unique structural and morphological information for various samples.

Non-linear imaging microscopy presents many advantages compared to other microscopy methods; it is capable of intrinsic three dimensional (3D) deep sectioning, eliminating of photobleaching or phototoxicity phenomena on the out-of focus area, diminishing any damage on the object. Optical high harmonic generation methods such as SHG and THG ensure minimal sample disturbance, as they are scattering phenomena relying on energy conservation characteristics, which is beneficial for CH studies. A single tightly focused femtosecond (fs) laser beam is required for the realization of the non-linear measurements. The main advantage of the non-linear imaging is that all the above mentioned signals (MPEF, SHG, THG) are generated simultaneously in the focal volume of the examined object. Thus, they provide unique complementary information related to the chemical composition of the sample, the centrosymmetry of its molecules (through SHG measurements) and the structural delineation of the CH objects.

In the current study, an overview of the implementation of non-linear imaging contrast techniques to various CH objects is presented. The potential of these techniques for compositional identification and depth resolved imaging of materials in CH such as fresh and aged varnishes [4,5], lining glues [6,7], paint [1,8] and corrosion layer in metal-based artefacts [9] has been shown. These non destructive, high resolution modalities can been used as diagnostic tools for CH studies providing new insights and extremely useful results that have the ability to facilitate the accurate control of any cleaning interventions.

Figure 1 presents SHG and THG signals from a fresh starch based glue (flour paste), used for conservation or restoration of painted artworks or papers and books of cultural heritage. The high intensity SHG signals mainly originate from the starch granules. THG imaging provides complementary structural information from the sample since detects optical inhomogeneities.

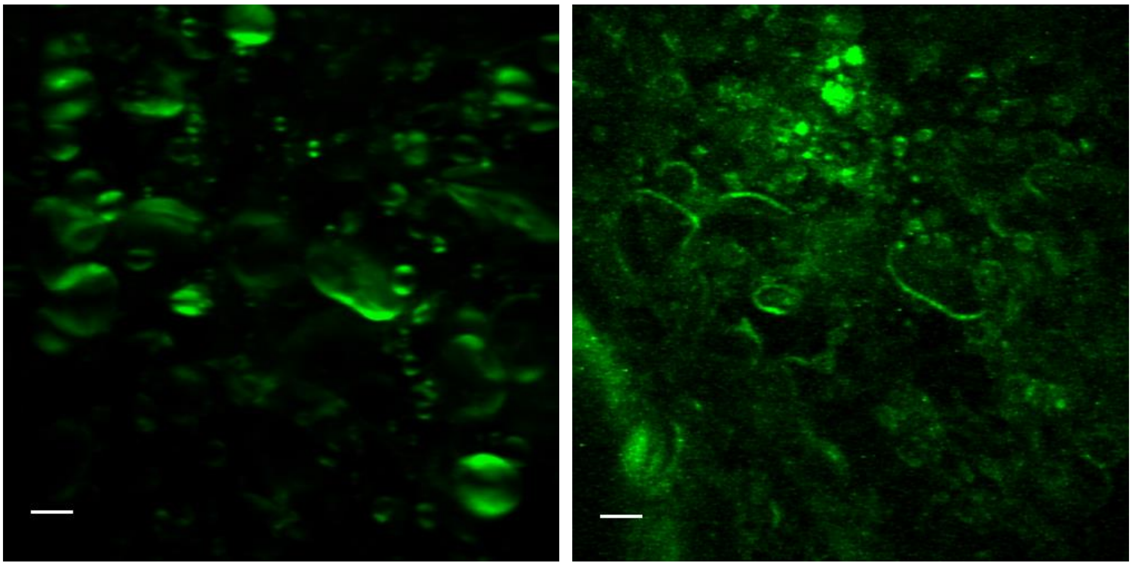

Figure 1. SHG (left) and THG (right) images from a flour paste. Scale bar denotes 10 m.

Multiphoton microscopes are now commercially available and constitute flexible and relatively easy to use, single fs laser beam, systems. We anticipate that, the non-linear optical imaging can be extensively used as new, minimally invasive diagnostic tool for in situ analysis of various CH objects.

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Capturing Artists' Intent in the Works of the Impressionists through the Expressionists: Pigment Manufacture and Alteration

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The painting materials used by the Impressionists, the post-Impressionists, the early modernists, and the Expressionists were critical components of their break with traditional modes of representation. These artists explored synthetic organic and inorganic pigments that were newly available to them due to the chemical revolutions of the 19th century. However, we now know that the bright and novel hues that made their way onto these artists' palettes, and in many cases defined these movements, were not always synthesized properly. As a result, pigments could be highly fugitive or rapidly discoloring. These unstable materials might react with adjacent or admixed pigments, agents of degradation in the environment, and even the binding media surrounding them.

Figures 1 and 2. Munch Museet Scream (c. 1910) and Nasjonalmuseet Scream (1893).

Many artists working in this period of the 1880s to the 1920s were aware of the limitations of the materials that were available to them, and they attempted to make choices based upon the most stable options at hand. Likewise, paint manufacturers were aware that not all of their offerings were equally stable, and would note the stability of the various hues of a pigment offered for sale. Given this context, however, we still have a number of important works from this period that have changed so substantially that they no longer represent the artists' original intent. Pigments from this period that have been found to alter over time include chrome yellow, zinc yellow, cadmium yellow, emerald green, eosin red (germanium lake), purpurin, and cochineal (carmine lake).

There are noninvasive ways to identify these pigments both before and after their alteration, including x-ray fluorescence, hyperspectral imaging, and ultraviolet-induced infrared fluorescence. To understand their mechanisms of degradation, however, requires microscale x-ray diffraction methods (XRD), x-ray absorption near edge spectroscopy (XANES), and scanning transmission electron microscopy (STEM) based methodologies such as electron energy loss spectroscopy (EELS). Edvard Munch's four versions of The Scream, Henri Matisse's four versions of Le Bonheur de vivre (1905-6) and Henri Matisse's Flower Piece (1906-7) were used to examine the efficacy of the different analytical techniques for identifying even highly altered pigments, their technologies of manufacture, and their mechanisms of degradation.

The alteration of the Munch Museet's version of The Scream (c. 1910 see Figure 1) is a result of his use of cadmium yellow in this mixed media work (tempera and oil) on cardboard. Three of the cadmium yellow paints used in this work have faded to an ivory color and flaked over time. These are shown below in Figure 3, with a close-up of a faded brushstroke in the sky and its digital reconstruction shown in Figure 4.

Figures 3 and 4. Munch Museet Scream (c. 1910, highlighting areas of alteration), and macro view of the alteration of a brushstroke in the painting's sky, shown above a digital reconstruction of Edvard Munch's original intent.

Evidence of alteration can be seen not only macroscopically, but also on the microscale where sodium, oxygen, and carbon-rich rod-shaped crystals are protruding from the surface of the paint (see Figure 5).

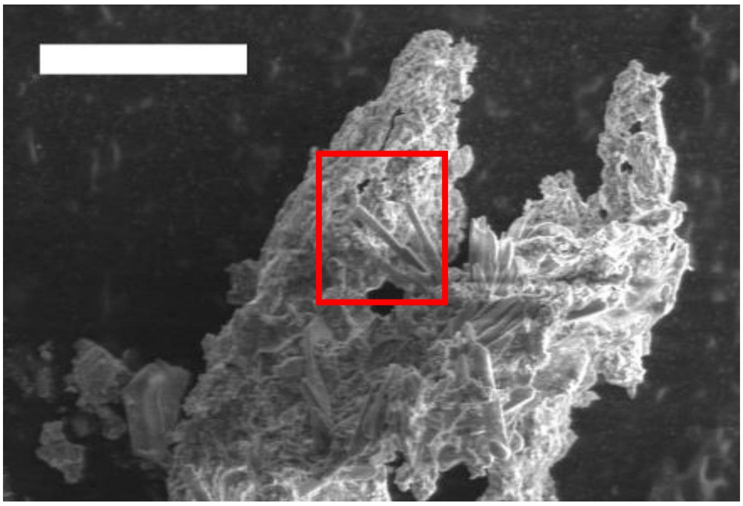

Figure 5. Edvard Munch's The Scream (c. 1910, Munch Museet). Powder sample in the EM before FIB lift-out.

STEM imaging reveals a heterogeneous mixture of particle sizes (Figure 6), and EDS mapping suggests a complex mixture of phases beyond CdS (Figure 7). Diffraction data and HRTEM lattice imaging from CdS regions show that CdS is composed of clusters of nanocrystallites, on the order of 10 nm or less (Figure 8). The isolated nanoparticles are expected to be alteration products.

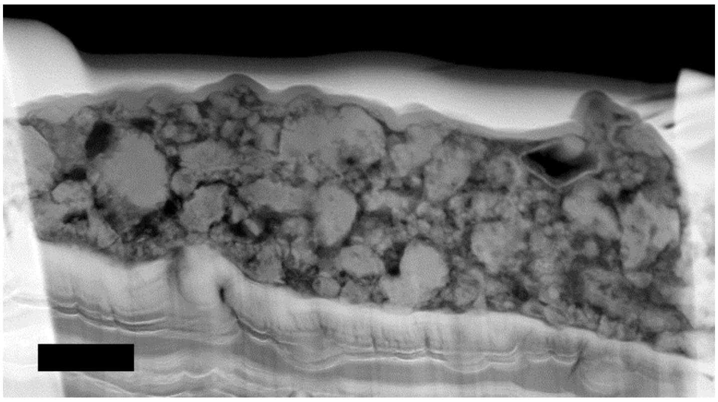

Figure 6. Individual pigment particles, residual starting reagents, and alteration products are made visible using the ADF-STEM.

Red regions of the map below (Figure 7) correspond mainly to cadmium carbonate. Large cadmium carbonate particles, on the order of 1 µm, are most likely residual starting reagent from the indirect wet process synthesis of CdS, whereas smaller particles may be a CdS photodegradation product. The chlorine-containing particles were found by µXANES and µXRD to be predominately Cd(OH)Cl, and EM methods confirm this. This compound is also present in cadmium yellow paint tubes from the period, and so cannot be definitively identified as an alteration product. Some CdSO4, a photodegradation product, may be present in areas of red/green overlap.

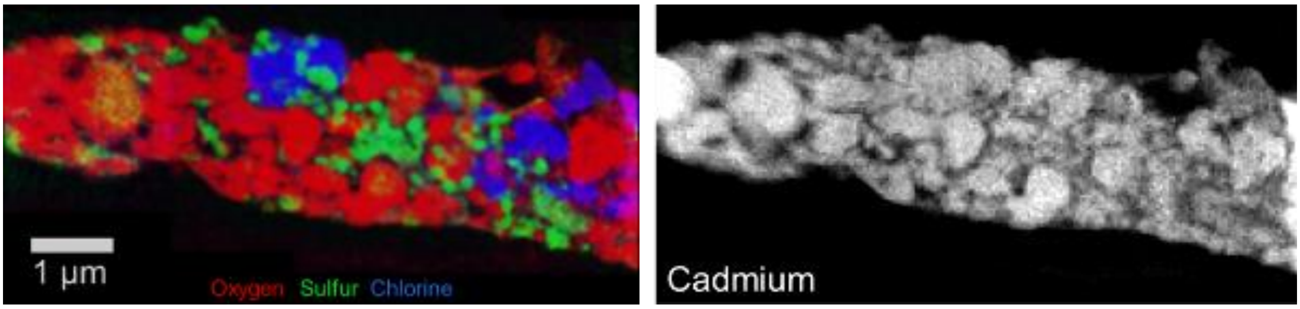

Figure 7. EDS of pigment particles, leftover starting reagents, and alteration products are shown here. CdS is composed of clusters of nanocrystallites, on the order of 10 nm or less.

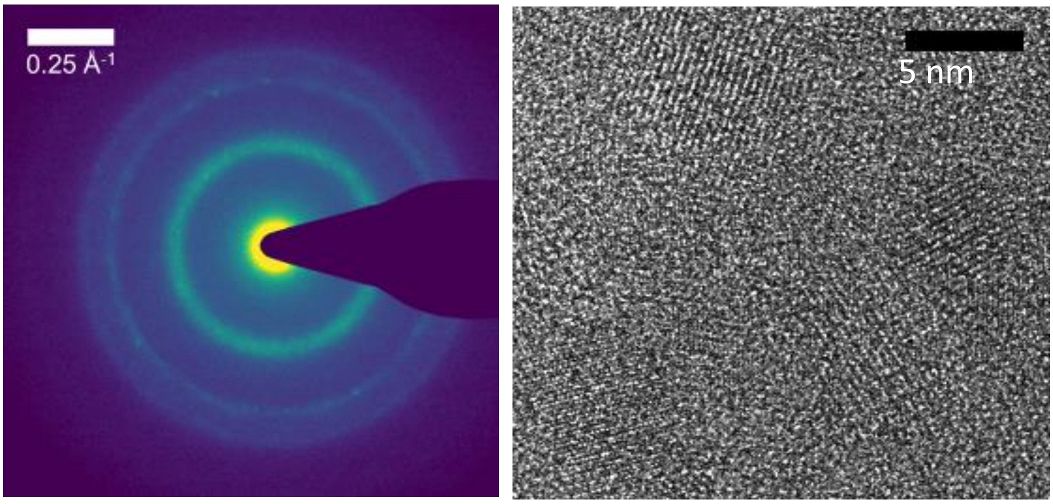

Figure 8. Selected area diffraction pattern from a CdS cluster. The broad inner ring, and large space between the first and second rings is suggestive of a polytype nanocrystalline structure. The crystals are neither cubic nor hexagonal, but occur as a polytype as a result of stacking faults. This lack of long-range order provides one reason for the reactivity of the particles. Lattice images of CdS particles show them to be of the order 10 nm or smaller in size.

The data shown above reveal that turn of the 20th century paints were often highly heterogeneous and incompletely calcined/annealed. This was in part intentional, to control the shade of CdS through the precipitation process by allowing residual starting materials to remain. However, this process led to an inherently unstable form of CdS. Cadmium orange, composed of larger particle sizes, does not show the same photosensitivity for this reason.

Structure, Coordination Environment and Dynamics of Lead Carboxylates implicated in Soap Deterioration in Oil Paintings

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Hundreds of oil paintings, dating from the 15th through the 20th century, in collections around the world are affected by the formation of heavy-metal carboxylates, or soaps, that alter the structural integrity and appearance of the works. Through transport phenomena not yet understood, free fatty acids from the oil in the binding media migrate through the paint film and react with heavy-metal ions that are constituents of pigments and/or driers, forming metal carboxylates. The local molecular dynamics of the fatty acids and of the metal carboxylates are among the properties influencing the material transport in these systems. To understand the mechanisms and factors that trigger soap formation and the dynamics of the reactive compounds in the paints, we used advanced nuclear magnetic resonance (NMR) and X-ray techniques, complemented by Raman and FTIR spectroscopies. We have explored soap formation in model paint films by 13C NMR and we have studied the dynamics and mobility of relevant fatty acids and soaps, namely palmitic acid and lead palmitate, in a linseed oil matrix at different temperatures (T) by 2H NMR. The results show the extent of mobility of palmitic acid and lead palmitate in the paint matrix, how they differ, and how they depend on T. Examination with techniques such as solid-state 207Pb, 119Sn, and 13C NMR, and X-ray diffraction provided the basis for interpreting dynamics in terms of the effects of structure and lead ion coordination environments [1-5]. The results will be discussed in the context of their implications for the conservation and preservation of the works of art affected by lead soap formation.

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[3] J. Catalano et al. J. Phys. Chem. A, 118, 2014, 7952.

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6. ABSTRACTS: ORAL COMMUNICATIONS

6.1 PARALLEL SESSION A

MA-XRF scanning as tool in authentication studies of paintings

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Painting materials, and especially pigments, can provide valuable information on an earliest possible creation date, and hence on the authenticity of paintings. In order to respect the integrity of the artwork, non-invasive analysis techniques, such as X-ray fluorescence (XRF), are preferred for pigment characterisation. Traditional XRF analysis provides valuable information on pigments beneath the surface, but interpretation can be complicated by the presence of many pigments simultaneously producing secondary X-rays. Also, the extent of later retouching is difficult to assess when only specific spots in the painting are analysed. This makes it difficult to discern genuine discrepancies between the pigments identified and the supposed period of execution. The recent introduction of macro-XRF scanning (MA-XRF) deals effectively with these drawbacks [1].

During this presentation the focus will be on the study of three paintings, the first attributed to the Spanish painter Francisco de Zurbarán (1598-1664), the second in the style of Pieter Paul Rubens (of unknown date) and the third a modern painting attributed to Karl Hermann Haupt (signed and dated 1923). Stylistic research casted doubts on the authenticity of the Zurbaran still life. Classic XRF point analyses indicated the presence of both ancient and modern pigments in many spots. The question was raised as to whether the painting was heavily retouched (hyper-restoration) or whether it was a copy on an old, reused canvas. The MA-XRF elemental distribution maps demonstrate that the painting is a copy, made on an old canvas. For the painting in the style of Rubens, a stamp on the reverse of the original canvas, hidden behind the lining canvas, could be visualized through the mercury distribution map. This enabled us to accurately date the support, which proves that the painting was executed at least two centuries later than it would initially appear. In case of the Haupt painting, the presence of certain synthetic organic pigments identified by micro-Raman spectroscopy played a key role in assessing the authenticity, complemented by valuable information obtained by MA-XRF on the material-technical history of the painting.

Figure 1. Central part of the Zurbaran painting under investigation, together with the MA-XRF elemental distribution maps of zinc (Zn), titanium (Ti) and lead (Pb). The presence of Zn and Ti throughout the painting allowed the classification of the painting as a copy, while the lead distribution map shows part of the original, painting, now hidden.

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Moisture transport and sorption in oil-painted linen canvas documented by X-ray and neutron imaging

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Paintings may be exposed to daily or seasonal variations in relative humidity, although most museums try to minimize such loads. The paintings of interest here are made of a canvas (often linen textile), a size layer (often animal glue), a chalk-glue ground layer and an oil paint layer. The canvas and the size used are hygroscopic, as the textile is made of flax fibers, which cell walls are a polymer-based (i.e. cellulose, hemicellulose and pectins) nanoporous material, while the glue is a protein-based material with subsequent loss of stiffness at high relative humidity. Both materials undergo significant swelling and shrinkage under moisture content variation. On the other hand, the oil layer is hydrophobic and comparably stable under varying moisture conditions [1]. The behavior of painted canvas samples undergoing changes in moisture content is documented using neutron and X-ray imaging experiments in order to better understand the coupled hygro-thermo-mechanical response of paintings as complex layered systems.

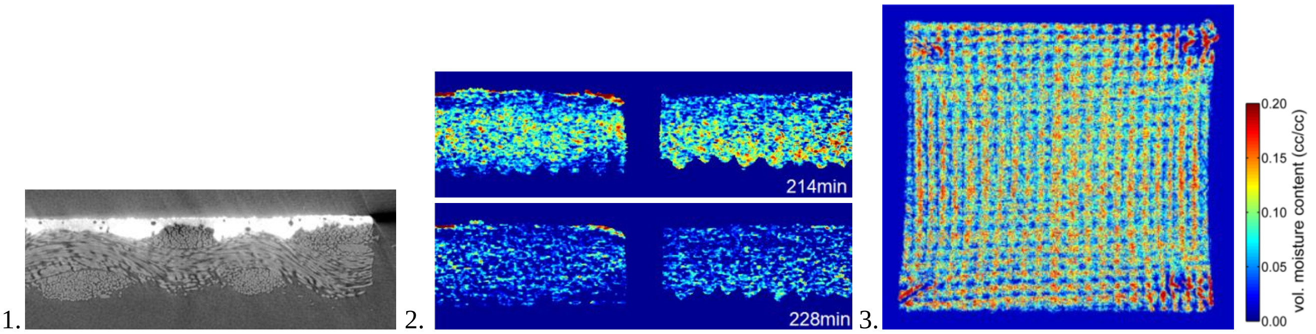

Figure 1. slice from microCT scan, 2. moisture content distribution seen along canvas plane at end of high (above) and low (below) relative humidity, 3. moisture content distribution seen perpendicular to canvas plane.

Neutron radiography, in the ICON cold neutron beamline at SINQ, PSI, Switzerland, was used to observe in-situ the adsorption and desorption behavior, and the accompanied swelling, of the layered painting system in a time and space-resolved manner [2,3]. The high interaction of neutrons with hydrogen allows the quantification of the water present in the samples. In parallel, X-ray computer tomography is used to capture the geometry of the samples at different moisture content. A difference in behavior between canvases impregnated with glue, with more uniform moisture distribution, and those covered by a layer of glue is remarked. Swelling and moisture content distribution are documented concurrently, allowing understanding and modeling of the hygromechanical behavior of the layered systems.

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[2] R. Hendrickx et al. Studies in Conservation, 2016, doi 10.1080/00393630.2016.1181899.

[3] J.J. Boon, R. Hendrickx, G. Eijkel, I. Cerjak, A. Kaestner, E.S.B. Ferreira, Applied Physics A, 121, 2015, 837.

A novel mobile X-ray scanner integrating MA-XRF, µXRF and confocal-XRF for a real-time elemental imaging of painted artworks

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A novel mobile X-ray scanner integrating MA-XRF, XRF and confocal-XRF is presented for performing a real-time elemental imaging of paintings. The instrument (named LANDIS-X) is modular and it is based on an X-ray source focused with a polycapillary and two SDD detectors operated simultaneously in event-mode. An interchangeable Rh or Cr target excitation can be selected for scanning samples allowing an efficient excitation of both low and high Z elements and for investigating the pictorial layer with a different analytical depth. The scanner is based on a three-axis system presenting a 110×70×20 cm3 travel range.

The MA-XRF scanning is performed by positioning samples out of the polycapillary focus with the primary beam presenting a spot size of some hundreds of microns. The full area is covered in 4.3 h with a pixel size of 500 m and 5ms dwell time (i.e., 100 mm/sec scanning speed). A lateral resolution of 25 m can be achieved at the focus positon, allowing the use of the scanner for a high resolution micro-XRF mapping of pigment materials. Finally, a conical polycapillary equips an ancillary SDD detector easily enabling a confocal-XRF set-up. A depth profile of the pictorial layer can be performed with 15-20 µm resolution.

X-ray spectra are processed on the fly with a least square fitting procedure and images are elaborated in a live mode during scanning. Additionally, different processing functions can be applied to the forming images thanks to a robust software programmed in a real-time Labview. Final elemental images are available to users at the end of the scanning and, in most of the cases, they are ready for the interpretation. Analytical capabilities of the instrument have been verified in a number of real applications in Archeology (Egyptian, Greek and Hellenistic Art) and Art History (old master paintings). Some valuable examples are presented and discussed.

Figure 1. "The prophet" by Jusepe de Ribera (ca. 1620). MAXRF scanning allowed identifying original pigments, restorations with modern pigments and the presence of a hidden painting below the visible surface depicting a woman in adoration.

Removal of absorption artefacts in the macro-XRF imaging of paintings

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One of the main disadvantages of macro-XRF technique is the fact that characteristic X-rays from deeper paint layers are absorbed in the covering layers. This effect manifest itself in form of artefacts that may impede proper interpretation of acquired images. Here we introduce a new methodology of correction of those effects that is applicable to the case of polychromatic excitation [1]. In this approach we overcame the problem of empirically chosen correction parameters [2] that introduces a human factor that may distort the result of correction.

The method was tested with use of test and mock-up paintings measured with table-top setup equipped with low-power X-ray tube [3]. For all samples an area of 5x5 cm2 was scanned. An example of result of correction is shown in Fig 3. In case of the mock-up painting the ground layer was made with lead white. In the base of mountains, lead white was also used. The bluish-grey landscape in the background was prepared using azurite.

Figure 1. The investigated area of the mock-up painting.

Figure 2. The original Pb-La image with the absorption artefacts.

Figure 3. The corrected Pb-La image.

The left figure shows the Pb-L intensity map acquired during the macro-XRF experiment. The fluorescence signal from lead-white layer is strongly affected by absorption effects from azurite layers. The right figure shows the Pb-L intensity map after absorption correction – the proper shape of the base of the mountains was revealed. Presented approach gives very promising results and it opens up a possibility for semi-automatic correction of the absorption effects.

[1] P. Wrobel, P. Fraczek, M. Lankosz Anal Chem 88, 2016, 1661.

[2] M. Alfeld et. al. Appl Phys A 111, 2013, 165.

[3] P. Wrobel et. al. Talanta 93, 2012, 186.

Macro XRF scanning: New opportunities for non-destructive analysis of two episcopal mitres, attributed to bishop Jacques de Vitry (12-13th c. AD)

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A multidisciplinary study was done of two episcopal mitres dating from the 13th century, pieces classified from the Treasure of Oignies, Belgium [1]. Together with the bones, they are part of the reliquary content attributed to bishop Jacques de Vitry, born in Champagne in 1165/1170 and died in Rome in 1240, after which the remains were transferred to the St.-Nicolas church in Oignies. Mitre (047) is made of parchment with painted decorations (figure left, top), while the second mitre (075) is constructed of several textiles richly decorated with gold and silver threads (figure left, bottom) [2].

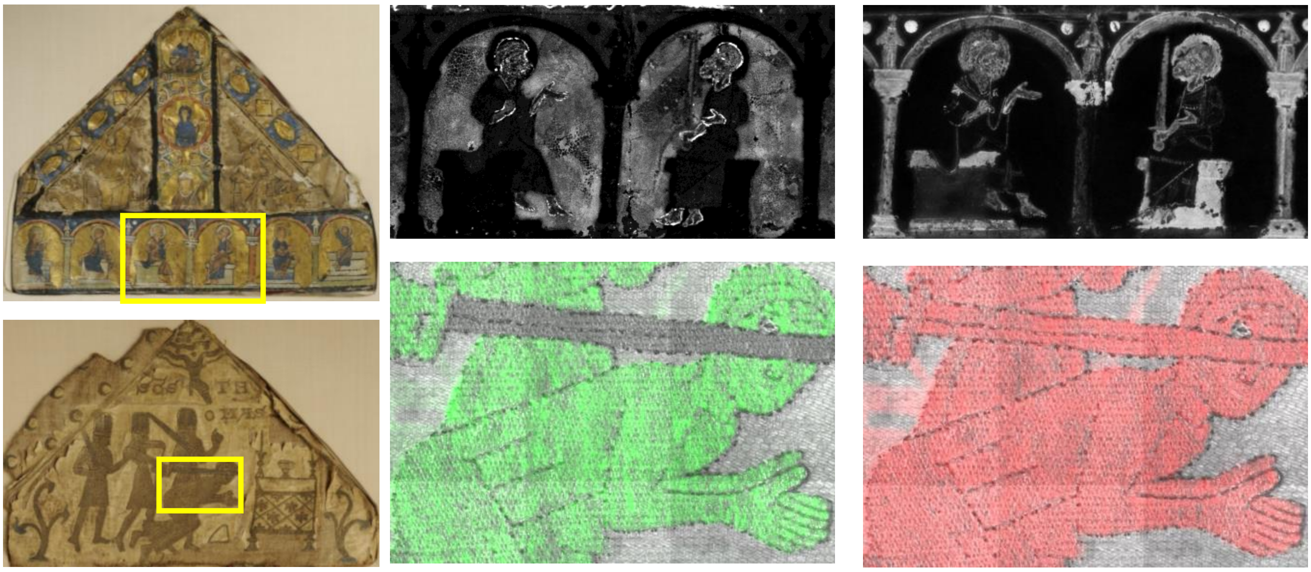

Figure 1. (left) detail of the front side of the parchment (top) and textile (bottom) mitre with indication of areas (in yellow) of the macro XRF analyses; (right) Macro XRF distribution plots of respectively iron and lead (top) in the painted decoration and gold and silver in the embroidery (bottom).

Besides the study of the composition of the pigments, dyes and metal threads with Raman spectroscopy, reversed phase liquid chromatography and scanning electron microscopy, macro X-ray fluorescence scanning allows the identification of the chemical elements on or beneath the surface of the object as well as the visualization of the element distribution.

As such, this technique brings significant added value compared to single-point identifications of pigments, metal threads and metal mordants. Besides, it is a new, interesting non-destructive tool for condition evaluation of cultural objects as it might reveal the presence of restorations based on differences in element distribution over large scaled areas.

[1] The study is part of the project CROMIOSS (Multidisciplinary Studies in History and Science on Mitres and Bones of the Bishop Jacques de Vitry) developed by the Société Archéologique de Namur and funded by the Fondation Roi Baudouin.

[2] The two mitres are on the list of the masterpieces of the Walloon Region.

Scanning X-ray fluorescence imaging for evaluation of platinum prints and other 19th-20th century photographs

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Macroscopic scanning X-ray fluorescence imaging, often referred to as MA-XRF, has demonstrated great utility as a method for examining paintings and other pigmented surfaces [1-3], but very few examples of MA-XRF applications for photographic materials have been published [4,5]. By contrast, point X-ray fluorescence (XRF) is a well-established method for examining photographic prints [6-8]. However, it can be difficult to discern how elemental composition at a single location relates to image density using a few point measurements [9-11]. In addition, the small amount of image material in photographic prints means that the XRF signal, even from important heavy elements, may be relatively weak, adding to the challenge of interpretation [6].

Are the spatial information and large number of measurements inherent to MA-XRF sufficient to improve upon point XRF analysis of photographic prints? In this work, we evaluate laboratory-based macroscopic scanning XRF imaging as a method for noninvasive analysis of materials in 19th- and 20th-century photographic prints. Advantages and limitations of the technique will be discussed in the context of measurements from prints in the collection of The Metropolitan Museum of Art. Objects discussed will include examples of platinum prints, with and without glycerine development; gum bichromate over platinum; and salted paper prints.

In particular, a case study of platinum prints by Joseph T. Keiley, pioneer of the glycerine-development process [12], will be highlighted. Instead of using a developer bath, the Stieglitz-Keiley glycerin process involves saturating the exposed latent print with glycerin and applying developer mixed with glycerin to the print with a brush, offering the photographer greater control. The image color could be shifted to a warmer sepia tonality, either overall or locally, by adding mercuric chloride to the developer. We will explore to what degree MA-XRF can distinguish differences between Keiley’s experimental platinum prints.

[1] A. Martins et al. Heritage Science, 4(33), 2016. DOI: 10.1186/s40494-016-0105-2

[2] D. Thurrowgood et al. Scientific Reports, 6, 2016, 29594.

[3] P. Ricciardi et al. Microchemical Journal, 124, 2016, 785.

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[6] C. McCabe, L. D. Glinsman. Studies in the History of Art, 51, 1995, 70.

[7] A. Gottlieb, Journal of the American Institute for Conservation, 34(1), 1995, 11.

[8] D. C. Stulik, A. Kaplan. “Application of a Handheld XRF Spectrometer in Research and Identification of Photographs.” Handheld XRF for Art and Archaeology, Edited by Aaron N. Shugar and Jennifer L. Mass, vol. 3, Leuven University Press, Leuven, Belgium, 2012, 75–130.

[9] A. Vila and S. Centeno. Microchemical Journal, 106, 2013, 255.

[10] A. Vila et al. Studies in Conservation, 58(3), 2013, 176.

[11] C. Sessa et al. X-Ray Spectrometry, 45(3), 2016, 176-184.

[12] J. T. Keiley. Camera Notes, 3, 1900, 221-226.

Use of Macro-scale Tri-Modal Imaging Spectroscopy To Map and Identify Faded Organic Red Lakes in Van Gogh Paintings

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In this paper we present findings on the use of macro-scale imaging spectroscopy to aid in the identification and mapping of faded red lake pigments used in three paintings by Vincent Van Gogh in the collection of the National Gallery of Art, Washington DC: Roses, 1890, The Olive Orchard, 1889 and La Mousmé, 1888. Using a high sensitivity, visible-to-near-infrared (400 to 1000 nm, 2.5 nm sampling), transmission grating hyperspectral camera, diffuse reflectance and molecular fluorescence image cubes were collected from these paintings. Separately, a novel macro-XRF scanner consisting of a Rh x-ray tube with capillary optics and a silicon drift detector having a 50mm2 area was used to collect the XRF image cubes. All three image cubes for each painting were spatially registered to allow comparison of the spectral information from all three modalities. The diffuse reflectance cube was used to make maps of pixels having similar reflectance spectra. The reflectance image cube was also used to correct the hyperspectral molecular fluorescence image cube for self-absorption, and then the corrected fluorescence image cube was used to create maps of areas having the same spectral emission. The XRF spectra were fit using an empirical model to make elemental maps for comparison with those of the molecular fluorescence and reflectance maps.

Using test panels of red lake pigments, especially Eosin lake, spectral areas of partially and nearly completely faded regions of eosin lake were found in all three paintings. The assignment relied on results from all three imaging modalities in regions where some red reflectance could be seen. In some areas, the molecular fluorescence provided evidence for the presence of un-faded eosin, whereas elemental maps of Br showed areas where no eosin was detected by molecular fluorescence or reflectance. An explanation of these findings will be presented. In the case of The Olive Orchards, two additional red lake pigments were found and mapped. These results show the fusion of all three imaging modalities provide a more complete understanding of the use and distribution of fugitive red lakes in Van Gogh paintings.

Spatially resolved X-ray fluorescence: State of the ART

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Spatially resolved X-ray fluorescence (XRF), also called micro-XRF, has over the last years developed into a powerful tool for analysis of art and conservation in the field. This technique combines the strength of multi-element sensitivity of XRF with the spatial resolution it can provide using a focusing optic. The spatial resolution is a requirement for the study of non-homogenous samples. Therefore a polycapillary lens/optic to focus the X-ray beam not only allows to achieve spot sizes below 100 µm while ensuring a high intensity of X-rays in the irradiated location (brilliance), reducing the required acquisition time per pixel.

The M6 Jetstream was developed by Bruker in cooperation with the Delft University of Technology as a transportable large area micro-XRF scanner. Recently the instrument's capabilities were extended by two main features:

A signal processing unit whose signal shaping time can be switched in order to achieve either 130 kcps or 275 kcps maximum signal throughput (MST). This, in combination with the newly available 60 mm² SD Detector, allows for over 1 million counts per second input count rate on objects with high fluorescence yield. For the presented measurement, this combination resulted in a reduction of dead time by ½ as well as more than 40% higher input count rate due to the increased solid angle.

A freely adjustable He flow that allows to measure light element down to sodium irrespective of the instruments arrangement - vertical for upright objects or horizontal for flat lying pieces of art.

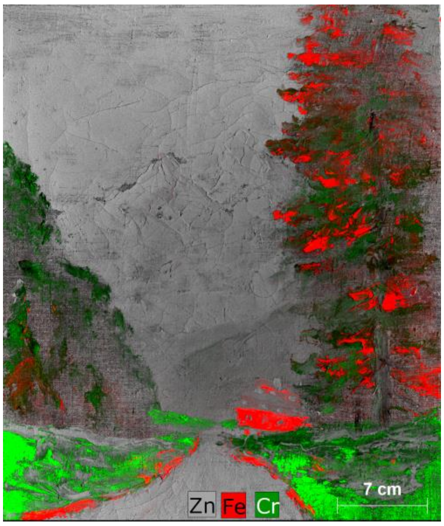

Figure 1. Scan using 60 mm² SDD and 275 kcps MST, 2.2 million pixel 15 ms, 250 µm step size and 11 h total time.

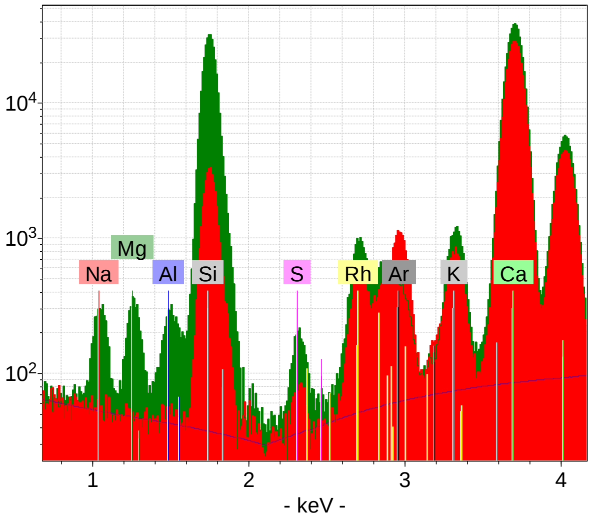

Figure 2.Comparison of glass spectra without(red) and with helium (green), 60 s measurement time with the 100 µm spot.

The introduction of the He flush option improves the M6's capabilities for the light element identification in pigments, as for example lapis lazuli. In which most of the characteristic elements have very low atomic number and, thus, very low-energetic fluorescence lines. The M6 Jetstream is characterized by an extremely low acquisition time, usually below 20 ms per pixel. The larger detector in combination with the new signal processing unit allows for reduction in measurement time, reducing the dosage deposited in the specimen.

An integrate use of Raman and Time Resolved Laser Induced Fluorescence spectroscopy to identify ancient and contemporary painted materials

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An integrate use of Raman and Time Resolved Laser Induced Fluorescence (TR-LIF) spectroscopy to characterized painted materials is proposed in this paper. The main goal of this work is to demonstrate the complementary capability of the above-mentioned techniques in order to identify traditional or contemporary pigments and binders. Indeed, during the Twentieth century many synthetic painting materials have been synthesized and commercialized. In this work, several pigments, binders and consolidates routinely employed in ancient and contemporary artworks were analyzed by Raman and TR-LIF spectroscopy.

The achieved results show how the Raman spectroscopy enable the identification of materials used in ancient times, thanks to their characteristic Raman signatures, as for example pigments based on iron oxide. On the other hand, the characterization of such compounds by TR-LIF spectroscopy results to be difficult due to lack of any characteristic fluorescence features.

Differently, the materials used in contemporary artworks are often characterized by intense fluorescence emissions, as for example acrylic ones, which make it difficult to appreciate weak Raman signals. In addition, when a mixture of different compounds is investigated, it could be hard to isolate the contributions arising from pigments and binders, due to high fluorescence emissions of the last ones.

The results discussed in this works show how this issue, in selected cases, can be overcome using TR-LIF technique, which allows studying characteristic emission wavelengths and decay times. Indeed, through the analysis of the time evolution of their fluorescence spectra, it is possible to discriminate from different compounds when they are mixed together, in order to obtain a complete characterization of contemporary materials employed in painted artworks. Finally, the complementary information obtained from Raman and TR-LIF analysis provide useful information about the characterization of the palettes used by the artist in different historical periods.

Portable Raman Spectroscopy for Cultural Heritage Objects

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Chemical identification of the components in artworks and cultural heritage objects is an extremely crucial task in the world of art conservation, as knowing the chemical makeup of an object can aid museum scientists and appraisers in determining the artist, provenance, and the authenticity of an unknown object, in addition to providing art conservators and historians a richer understanding of artists' materials used. Raman spectroscopy is especially suited for identifying both organic and inorganic pigments used in artworks and cultural heritage objects because of its nondestructive nature and its superior ability to measure lower energy vibrations mainly associated with inorganic mineral pigments. In this study we used portable Raman spectroscopy to investigate both organic and inorganic materials in a wide range of cultural heritage objects, including paintings, painted dishware, and jewelry. Raman microscopy was used to make measurements of specific detailed areas of an object, while a fiber optic probe allowed for measurements of regions of the objects that are difficult to analyze with the portable microscope system. Pigments including Mars red, Naples yellow, and indigo were positively identified in the painted materials analyzed.

A Technological Investigation of Grounds in Paintings by a Group of Italian 17th Century Artists with links to Roman and Neapolitan Practice

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Working on coloured grounds is one of the significant innovative features in the evolution of Western European painting technique. The appearance, during the course of the 16th and, increasingly, the 17th centuries of coloured grounds was a feature partly linked to the emergence of canvas as the dominant support for painting. Among Italian and Spanish artists, the visual effect of the coloured ground on the tonality of a composition and its role in the execution of a painting was realized, and one of the places where this feature was often exploited was 17th-century Naples.

A number of paintings on canvas by artists working in Naples and Rome during the 17th century from the Statens Museum for Kunst (SMK) collection has been subjected to technical investigation, with a view to identify patterns and/or differences in the range of practices employed by painters in what was an important artistic centre during this period. The investigation includes works by artists such as Giovanni Lanfranco (1582-1647), Domenico Gargiulo (c.1609-c.1679), Salvator Rosa (1615-1673), Girolamo Troppa (1630-c.1710), Luca Giordano (1632-1705), Paolo de Matteis (1662-1728) and Nicola Vaccaro (1640-1709), several of them active in or with links to Rome and Naples during the 17th century.

A main focus has been the characterization of materials and ground layers structure, a topic which, as regards Neapolitan painting in the Italian baroque context, has been little researched or published in the past.

The experimental results collected by optical microscopy and spectroscopic techniques (such as SEM-EDXS, FTIR and Raman) indicated that a complex mixture of materials had been used by the artists. They not only demonstrated the practices applied by the painters but also, in some cases, the consistency or evolution of a particular artist's technique. Despite variations in their colour, stratigraphy and morphology, ground layers in paintings from different artists or within the same artists' production clearly share a similar elemental and molecular composition. In fact, Si, Al, Ca, K, Fe were consistently found as major components detected by SEM-EDXS, together with variable amounts of silicates, quartz and pigments identified by FTIR and Raman spectroscopy.

The regular occurrence of specific components in grounds of different dates within an artist's production could be related to the existence of professional primers in the city, while variations in the practice may point to influences from outside, as many artists of the period were periodically migrants. For instance, at that time Naples was under Spanish rule and consequently affected by Spanish culture. However, Neapolitan painters of the period also absorbed influences from other Italian centres and developed a style of their own.

Results obtained from the study will be used in association with a large-scale project to compare practices and interchange between Northern and Southern European artistic circles from 1500 to 1700 [1-3].

[1] J. Dunkerton, M. Spring. Studies in Conservation 43.sup1, 1998, 120.

[2] R. Enggass, J. Brown. Italian and Spanish Art, 1600-1750: Sources and Documents (1970). Northwestern University Press.

[3] M.D. Gayo, M. Jover de Celis. Boletín del Museo del Prado, Tomo XXVIII nº 46, pp. 39-59, 2010.

In-situ and laboratory spectroscopic study of the mural **painting of Ribera de Valderejo (Álava, Basque Country)**

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This work concerns the study of some wall paintings preserved in the church of Saint Stephen located in the village of Ribera de Valderejo (Álava, Basque Country). Thanks to the use of portable instrumentation, X-ray fluorescence and Raman spectroscopy, it was possible to perform a characterization of plasters, of antique pigments used by artists (hematite, goethite, vermilion, orpiment, gypsum and carbon black) and of modern materials employed during past restorations in modern era (arylamide yellow, phtalocyanine green, ultramarine blue, red manganese, barium sulfate, carbon black and anatase). The analyses were mainly carried out on some of the painted areas that appeared unusually grey in order to identify if the color is caused by an intentional act or by the degradation of raw materials. The results obtained by portables technique do not allow to clarify some important aspects but they permitted to perform a selective sampling to continue the study by laboratory analyses. The elemental maps with SEM-EDX and successively the molecular analyses by Raman spectroscopy highlighted the inadequacy of restoration works carried out in the past and the use of a highly toxic substance, dangerous both for the environment and for human health too, such as magnesium arsenate used as a biocide product, which was not documented. This paper demonstrated the importance of the use of diagnostic techniques for the study of materials belonging to Cultural Heritage in particular to suggest to restorers the best non invasive intervention and compatible with the original appearance of the paintings because the mentioned grey area was restored in green colour. However, this are was never green in the past.

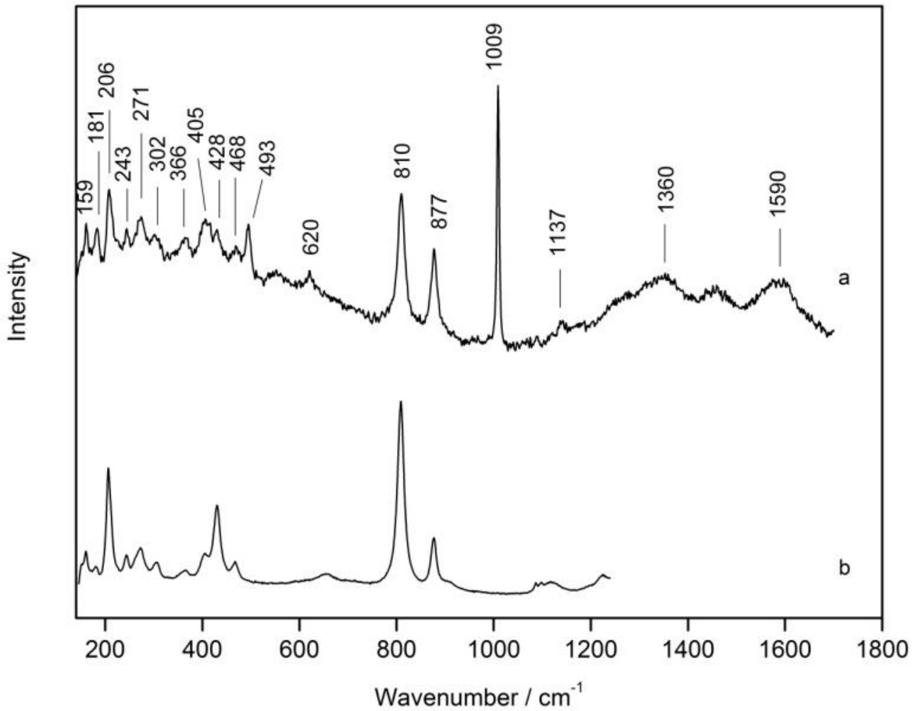

Figure 1. Raman spectra of the compound found in the wall painting (a) with the features of gypsum and carbon black and the spectra of mineral hornesite (b)

Identification of organic dyes and pigments in ukiyo-e Japanese woodblock prints by non-invasive and mobile techniques

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Japanese ukiyo-e works refer to woodblock prints or paintings produced between the 17th and the late 19th century. They reflect the social and economic changes in Japanese society during the Edo period (1615-1868) and the Meiji era (1868-1912). With Japan's economic opening in the beginning of the Meiji era, the techniques and materials used by artists changed. Chemical pigments imported from the West enrich the available colour palette mainly composed of natural organic dyes and pigments, such as safflower or indigo.

The aim of the study is the identification of organic colourants employed by Japanese printers in a collection of ukiyo-e prints preserved in the Zaragoza Museum. As prints are fragile artworks, various non-invasive analytical methods were employed as hyperspectral imaging in the visible range (HSI) and colorimetry. However, the reflectance spectra in the visible region characterize the colour on the print which can vary according to different parameters: mode of extraction from the plant, pH, fillers to which they are fixed (alum, carbonates), mordants for the indirect colouring agents...

The present work focuses on the results obtained in the infrared region by combining fibre optic reflectance spectroscopy in the near-infrared range (FORS NIR) and mid-infrared spectroscopy (MIR). In the FTIR spectra, bands are specific to the vibrations of chemical functional groups which are helpful to determine the chemical family of the colouring agent. However, some difficulties have been encountered like, for instance, the attribution of the combination and overtone bands in the NIR range or derivative-like shape bands in the MIR region. Pre-processing smoothing or derivative as well as treatment like Principal Component Analysis (PCA) or Kramers-Kronig Transformation were applied.

The first step consists in the building of a database in the different spectral regions thanks to model samples made in laboratory using reference pigments (indigo, carmine, dragon's blood, safflower, gamboge) and different kinds of Japanese papers (kozo, mitsumata, gampi).

In situ measurements on Japanese woodblock prints in the Zaragoza Museum were performed and the results were compared with the database.

Identification of inorganic mordants from liquid extracts of madder lakes by laser induced breakdown spectroscopy

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Most of the natural dyestuffs used for the preparation of organic pigments are of the mordant type and are co-precipitated with an inorganic substrate to form a lake pigment, in which they form very stable and difficult to dissociate complexes. Historically, alum was the main used substrate. Other metal salts, including those containing iron, tin, and chromium, can also be used in place of alum to give madder-based pigments of various colours. Generally, reverse-phase liquid chromatography is the method of choice for the analysis of dyes after a wet sample treatment, since most of their chromophores are polar and water-soluble compounds.

The sample preparation for the extraction of dye components from lake pigments is commonly based on the hydrolysis of the complexes in a methanolic solution with hydrochloric acid, necessary to isolate the organic dyestuff from its mordant metal [1]. Different authors tried a number of mild extraction methods based on chelating agents and moderate acidity conditions with conflicting results. It has been demonstrated that the mild extraction methods are preferable. The hydrolyzed organic fraction is often purified by extraction into an organic solvent, and analysed by HPLC-DAD or -MS, while the aqueous portion is usually discarded as waste, thus loosing any information on the inorganic fraction of the lake pigment.

In this work, the aqueous fraction from the micro-extraction of madder lake was analyzed by Laser-Induced Breakdown Spectroscopy (LIBS) for trace elements identification. The assessment of the inorganic components of the lake can indeed be helpful in the characterization of organic pigment lakes, since the recipes used in their production varied in time and depended on the availability of raw materials. Their knowledge can thus provide important information for dating a work-of-art or locating its geographical origin.

The analysis of the aqueous fraction by LIBS was thoroughly optimized. In particular, the direct laser irradiation of microdroplets shows lower precision and sensitivity compared to the laser irradiation of microdroplets dried on solid substrates. The choice of substrate material is thus critical to the success of the LIBS analysis. In this work several materials (glass, aluminium, graphene oxide, silicon and Teflon) were tested as substrates for LIBS analysis of aqueous residues of the dyes extracts. The preconcentration of the liquid extracts enables us to effectively identify the nature of the inorganic mordants, to distinguish among madder lakes identical from the colorimetric point of view, and to rationalize the difference in colour of lakes having the same organic composition.

[1] J. Wouters, J. Stud. Conservat 30, 1985, 119.

Differentiating natural and amorphous arsenic sulfide in painted artifacts by means of Raman spectroscopy

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In heritage science studies, elemental point analyses and imaging techniques (SEM-EDX or MA-XRF) provide a relatively rapid identification of the mineral pigments used by artists based on the characteristic elements. Combined with the color of the analyzed area, this is often enough to draw conclusions on the pigments present. However, in the case of arsenic sulfides, elemental analysis is insufficiently specific since several natural pigments (yellow orpiment, As_2S_3; yellow pararealgar, As_4S_4; or red realgar, As_4S_4) as well as amorphous arsenic sulfide, a man-made product also used in works of art, have identical/very similar chemical compositions.

Even though described in literature since Cennini's *Libro dell'Arte* [1], amorphous arsenic sulfide has often been misidentified. Its identification in artifacts by means of Raman spectroscopy was only reported recently, based on its characteristic spectrum that is different from that of the crystalline compounds [2, 3, 4]. Based on satellite Raman contributions, in certain cases, the sulfur content or manufacturing processes described in artists' treatises and literature (sublimation of natural pigments, melt/quench of arsenic oxide and sulfur mixtures) can also be deduced from the Raman spectra.

This work will present a study on both references and diverse historical samples in which Raman spectroscopy allowed to differentiate between natural and amorphous arsenic sulfide. In some historical samples, Raman spectroscopy permitted the identification of the manufacturing processes such as partial sublimation of natural orpiment and possible sublimation of realgar or pararealgar, a process in agreement with literature.

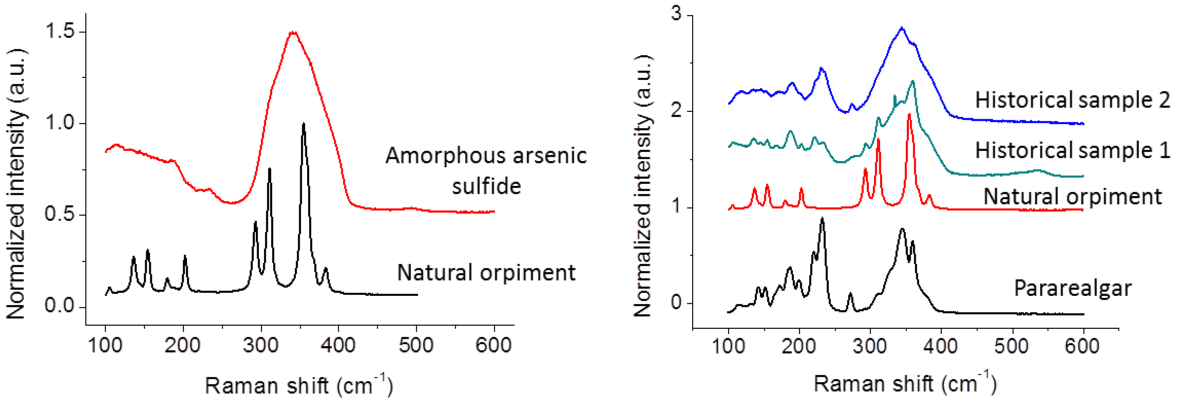

Figure 1. Raman spectra obtained on reference materials and historical samples and presenting the characteristic scattering of both compounds.

[1] Cennini C d'Andrea. The craftsman's handbook: the Italian "Il libro dell'arte." New York: Dover Publ; 1960.

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[3] Luo Y, Basso E, Smith HD, Leona M. Heritage Science 4, 2016.

[4] Panayotova S, Ricciardi P. Colour: The Art & Science of Illuminated Manuscripts. Cambridge, 2016.

Colours and pigments in late *ukiyo-e* paintings: a non-invasive study of a series of woodblock prints by Shuntei

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Colorants and pigments in traditional Japanese woodblock printing inks have been used from the late 16th century to the beginning of the 20th century (Meiji era, 1868-1912) in paintings in the *ukiyo-e* style. Many pigments were used throughout the period, but some were not used during the early years, or were introduced in the later period [1]. Sometimes works from the end of the 19th century has been unjustly considered to be from a declining period. However, the introduction of new pigments and the extraordinary quality of the works could demonstrate a Silver Age of Japanese *ukiyo-e*.

This study presents the results of the series *Bijin jni kagetsu* ("Beauties of the twelve months") by Miyagawa Shuntei, edited in Tokyo and dated in 1898-1899. In twelve triptychs, women and children wear traditional Japanese kimono clothing at their leisure time in beautiful landscaped gardens. Miyagawa Shuntei 宮川春汀 (1873-1914) was a neo-traditional Japanese illustrator specializing in the genre of *bijin-ga* (portraits of beautiful women). The series belongs to Federico Torralba Asian art collection at the Museum of Zaragoza.

Pigments on woodblock prints generally require specific analytical methods because the amount of pigment available from a print is substantially less than that available from a painting. Diffuse reflectance spectroscopy (DRS) has been chosen as a portable, non-invasive analytical technique to identify pigments and colorants used in these woodblock prints. The spectra of more than 190 points sampled throughout the artwork were recorded between 360 and 740 nm. Different pigments were characterized and identified by comparison with reference pigments. Traditional compounds in Japanese paintings, like indigo, azurite, malachite, vermilion, red lead, gamboge, and yellow and red earths, and others like safflower red, orpiment, copper greens and blues, Prussian blue and ultramarine, were identified. A number of pigment mixtures were also used on these prints. Colour combinations included red with blue to give purple, yellow with blue to give green, or red with yellow to give orange.

[1] E. West Fitzhugh, in Pigments in later Japanese paintings, Smithsonian Institution, Washington, 2003, 1-56.

Non destructive study of the pigments and the watermarks of engravings in North European Chiaroscuro

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E. Laval(1), R. Mathis(3), M. Menu(1), E. Pagliano(1), R. Pillay(1), X. Salmon(2),
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The "CLARO" project deals with the analysis of the pigments and the watermarks of color engravings carried out in Germany, France and the Netherlands between 1508 and 1640 [1, 2]. This non-destructive archaeometric study of prints is of particular interest for those artworks still unfamiliar with this type of approach. The characterization of pigments is indeed an essential question for a better understanging of the materiality of the engravings. Although such analyses were recently published on Italian prints [3], this study for engravings produced in northern Europe is unprecedented.

The methodology consists in the complementary use of imaging and spectroscopic techniques. On the one hand, false color infrared photography [4] and reflectance hyperspectral imaging [5] allow a first evaluation of the pigments and dyes present. Furthermore, infrared reflectography (IRR) [6] highlights materials that do not reflect infrared (as is the case of carbon black). On the other hand, fiber optics reflectance spectroscopy (FORS) [7], X-ray fluorescence spectroscopy (XRF) and Raman spectroscopy [8] allow the characterization of inorganic pigments and in some cases organic dyes. Finally, the study of watermarks by transmitted light provides information about the origin of the paper support.

We will present the corpus, the methodology applied and the first results obtained on the prints in chiaroscuro. Through the material characterization, the objective is to determine the know-how and possible specificities of engravers' workshops and even artists in northern Europe. In addition to bringing new knowledge in Art History, the results obtained will also help in the localization and dating of anonymous engravings. Those informations will be discussed with the historians and curators, partners of the project, in charge of these prints.

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Characterization and photostability of red synthetic organic pigments in alkyd and acrylic paints

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In the 19th and 20th centuries a great variety of organic synthetic pigments (SOPs) was synthesized and introduced into the paints and coatings market [1]. Due to their excellent properties in terms of light and weathering fastness, many SOPs have found application in outdoor conditions. Nevertheless, these new pigments were used even shortly after their discovery by artists unaware of the stability and durability [2] and of the possible interactions of the various paint components under environmental conditions.

In contemporary art, artworks are often designed for outdoor presentations. Here, among other environmental influences (e. g. T, RH, etc.) the solar radiation plays an important role in the mechanism of deterioration. Especially, the energy of the UV light is within the Bond Dissociation Energy (BDE) of many synthetic organic materials and in combination with oxygen it can cause photooxidative degradation [1].

So far studies were performed on the identification and photostability of phthalo blue and green pigments in alkyd and acrylic binders [3, 4] commonly used by contemporary artists. To study red synthetic organic pigments, we focused on three different chemical classes of SOPs, such as naphthol AS (PR112), quinacridone (PR122 and PV19), and diketopyrrolopyrrole (DPP) (PR254 and PR255). To investigate the identifiability of the pigments in aged paint layers and to study the photostability of the paints, e. g. alkyd and acrylic, pigment powders and paint mock-ups were exposed to accelerated artificial solar radiation. As the photooxidative degradation is generally occurring on the uppermost area of the materials, surface sensitive analytical methods such as µ-Raman spectroscopy, Fourier Transform Infrared Spectroscopy in Attenuated Total Reflection (FTIR-ATR), Secondary Ion Mass Spectrometry with MeV ions (MeV-SIMS) and UV-Vis spectroscopy were selected.

The results showed that pigments were stable under the used ageing conditions and they could be clearly identified also in aged paints. Moreover, a relative enrichment of pigments, due to photodegradation of the binder, was registered by FTIR-ATR and MeV-SIMS on the surface of the aged paints. Chemical changes characteristic for alkyd and acrylic paints were detected in the aged paints by FTIR-ATR, and the quinacridone pigments resulted to influence the photodegradation of the paints the most. In addition, MeV-SIMS analysis (both, spectral mode and molecular imaging) were successfully applied for the exact identification of the pigments in real samples taken from artworks exposed to outdoor conditions.

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‘Do you see what I see?’ A non-invasive multi-analytical study of the limits of detection of smalt in ultramarine mixtures

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A hierarchical use of blue pigments has been identified in several 15th century Venetian manuscript fragments by a combination of non-invasive analytical methods. Interestingly, the X-ray fluorescence (XRF) data suggest that while the blue draperies of the main figures were painted with pure ultramarine, in background areas and border decorations the precious pigment was mixed or layered with smalt. Notably however, this difference would not have been discovered had Raman or reflectance spectra (350-2500 nm) alone been collected: the smalt-containing areas do not show the typical Raman peaks or reflectance characteristics of cobalt (II)-containing pigments.

To assess the limits of detection of smalt mixed with ultramarine – and better contextualize the results from the manuscripts – a series of ultramarine-smalt mixtures of known composition painted on parchment were analysed by the non-invasive analytical methods typically used to study illuminated manuscripts: XRF, UV-vis-NIR reflectance spectroscopy, Raman spectroscopy, FT-IR spectroscopy in external reflectance mode as well as multi- and hyper-spectral reflectance imaging. Samples containing a layer of ultramarine (both thin and thick) over smalt were also analysed. Notably, it was found that while XRF could identify the presence of cobalt (Co K peak) in all samples containing smalt, most other techniques could detect the smalt component only in the samples with higher smalt content.

Overall, the data suggest that only a small amount of smalt may be present in the manuscripts analysed, and that the determination of the presence of smalt needs to be made carefully. Due to its glassy nature, the identification of smalt in Venetian art has particularly significant meaning in the context of technology transfer between manuscript illuminators and other categories of artists and craftsmen.

The implications of the detection limit data presented will be discussed in light of the prevalence of these non-invasive techniques in the examination of illuminated manuscripts. The practical challenges involved in developing an analytical approach capable of detecting these and other types of pigment mixtures will also be addressed.

Synchrotron study of micro-structure and luminescence of lead carbonates: revealing the Old Masters pigments qualities

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The lead white pigment, composed of two main mineral phases (cerussite $PbCO_3$ and hydrocerussite $2PbCO_3.Pb(OH)_2$) has been synthesized and used in paintings since the Antiquity. The study of historical sources reveals that there existed a large variety of lead white qualities that painters could select, characterized by different degrees of synthesis sophistication. This work, based on the combination of micro-structural and optical characterization, using Synchrotron radiation, has permitted a better understanding of those pigment qualities.

A cristallo-chemical study was performed in the laboratory to specify the formation mechanisms of the crystalline phases during the antique synthesis, based on the corrosion of metallic lead. The impact of post-synthesis processes on the composition and the microstructure of the pigment were highlighted. By combining several Synchrotron-XRD analysis configurations (ESRF, ID22 and ID21 beamlines) with Rietveld refinement, it was possible to gain insight on those parameters within paint layers of prestigious paintworks of the Louvre Museum. New results obtained on a corpus of artworks by Leonardo da Vinci (1452-1519) will be detailed.

Those results have been completed by photoluminescence (PL) study of lead white pigments. After defining the main PL mechanisms using benchtop instrumentation, Synchrotron UV photoluminescence (SOLEIL, DISCO beamline) was implemented on historical micro-samples [3] to evaluate the results obtained at macro-scale. Hypotheses on the connection between optical properties, structural parameters, and post-synthesis processes used to obtain high quality pigments in the past have been proposed: luminescence can be used as a probe of the pigment history.

This research demonstrates potential for novel instrumental developments (for example UV fluorescence mapping at high spatial resolution), and provided new evidence which allows the connection between synthesis processes of the past and the presence of defects detectable by structural or optical spectroscopic methods.

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A Multi-Analytical Approach to Identify Historic Carbonaceous Media on 19th Century French Drawings

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Historically, works of art on paper have proven challenging objects for scientific study. Due to the lower concentration of materials used in these works, sampling is not possible as removal of a sufficiently large sample would be visibly and irreversibly damaging to the work, necessitating *in situ* analysis methods. As a result, conservators and curators rely upon close observation—at both the macro and micro level—as their primary means of differentiating drawing media. However, because this is a subjective approach and highly dependent on the experience of the observer, this is a challenging, if not impossible, task.

With the industrial revolution of the 19th century came a diversification of drawing materials and methods available to artists of the time, such as Georges Seurat and Odilon Redon. The works of these artists, deceptively simple in appearance, represent complex mixtures of black media including charcoals of varying hardness, assorted crayons, natural and fabricated chalks, ink, and pastel. To address the problem of accurate characterization of black drawing media curators, conservators, and scientists at the J. Paul Getty Museum and Getty Conservation Institute have initiated a collaborative study of 19th century French drawings. Specific research questions include: Can carbonaceous pigments be distinguished and correlated to particular types of black drawing media, such as charcoal, chalks, or pastels? Is it possible to distinguish different types of black drawing media based on binder or clay content? Did the artist apply fixative to their drawing and, if so, what type?

To develop an effective, noninvasive, analytical framework for the study of 19th century drawings, studies were first conducted on mock-ups prepared with historic and modern drawing materials using a suite of techniques to characterize the materials present and understand the complex media-substrate interaction. Micro-Raman spectroscopy was used to identify carbonaceous materials by examining two characteristic spectral features, the graphitic G band and the defect-associated D band. The vibrational frequencies of these two bands, as well as their intensity ratio, can be matched to reference pigments for proper identification [1,2]. Fourier Transform Infrared (FT-IR) spectroscopy was used to aid in characterization of organic binding media and fixatives, and to support the black media assignment made using Micro-Raman spectroscopy [3]. X-ray fluorescence (XRF) was used to identify inorganic elements such as aluminum in chalks. *In situ* x-ray diffraction (XRD) was used to characterize minerals in clays. Multivariate statistical analysis of the data provided a means to further distinguish classes of drawing media. Collectively, these analytical techniques successfully characterized the materials used by the 19th century French artists, providing insight into the development of modern drawing. Additionally, this work provides a framework to address the broader need within cultural heritage studies for noninvasive analytical methods to study low concentration materials *in situ*.

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Large volume imaging of cultural heritage with optical coherence tomography

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Optical coherence tomography (OCT) is a nondestructive imaging technique capable of imaging 3D images of thin layered structures up to a few millimeters deep. Applications within the field of material science research and cultural heritage studies are structural and stratigraphy analysis of layered objects and varnish layers [1].

Our OCT imaging system (Ganymedes, Thorlabs Gmbh) has an axial (depth) resolution of 3.0 µm and a lateral resolution of 4 µm in air. The system is capable of imaging high resolution cross-sectional images of varnish layers. Sample properties such as stratigraphy, layer thickness, attenuation coefficient and refractive index are accessible from the OCT signal.

Current OCT systems work by scanning the beam over the sample using galvanometric mirrors tipically yielding scanned areas of 10x10 mm^2, much smaller than many works of art. This limits the practical usabililty of the thechnique

In this work we present a setup, consisting of scanning stages and the OCT device, that enables us to scan up to 20 x 20 x 0.2 cm^3 volumes of cultural heritage. Specifically designed software regulates synchronised scanning, dynamic focus control, image registration, image segmentation and user friendly image rendering. The resulting image enables conversators to asses the condition of layers in a large volume of an object and judge the results of (restaurative) interventions.

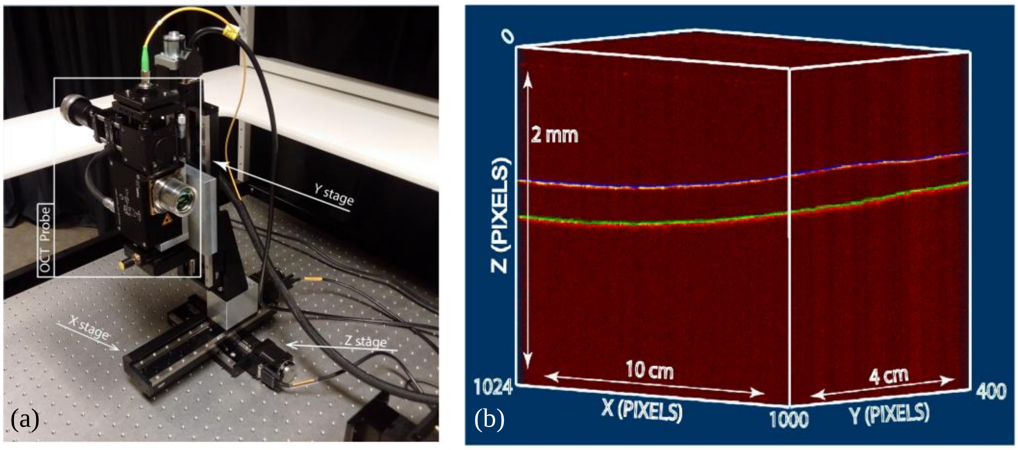

Figure 1. (a) Picture of the integrated OCT probe and scanning stages. (b) 3D image dataset measuring 10cm x 4cm x 0.2cm, depicting a transparent coating on a metallic substrate. The interfaces are segmented in the rendered image.

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Macroscopic X-ray powder diffraction imaging: highly specific pigment mapping using mobile equipment

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In the last decade, Macro X-ray fluorescence scanning (MA-XRF) has become an established method for noninvasive investigation of painted surfaces [1]. The distribution of pigments in, or below the surface of paintings from well-known artists such as Van Eyck, Memling [1], Rubens, Rembrandt [2], Magritte [3] and Van Gogh [4] have been examined. Since XRF only provides information on the presence of a range of chemical elements (phosphorus and upwards), in some cases, identification of a number of pigments needs to be done by combining information on the elemental content of an area of the painting with its color and/or with other spectroscopic information. The lack of specificity of MA-XRF also becomes apparent when areas of artworks are considered in which degradation phenomena have altered the appearance of the paint.

In order to arrive at a more compound-specific way of chemical imaging, we have recently implemented a macroscopic X-ray powder diffraction scanner (MA-XRPD). In addition to recording X-ray fluorescence signals, either in transmission or in reflection geometry, patterns of coherently scattered X-rays are recorded by means of a large area photon counting camera at each examined point. The augmented possibilities and limitations of using such a scanner in a number of situations will be discussed, using as case studies works of art painted by Vermeer, Velázquez, De Heem, Van Gogh and/or their circle.

In a number of these paintings by J.D. De Heem (1606-1684), including 'Flowers and Insects' (Royal Museum of Fine Arts, Antwerp, B) and 'Festoon of Fruit and Flowers' (Rijksmuseum, Amsterdam, NL; see figure), it was also possible to record maps of pigment degradation products, with which it was possible to confirm recently established degradation pathways of As-based pigments [5].

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FT-IR investigation of painting cross-sections

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The general aim of this work was optical microscopy (OM) and Fourier-Transform Infrared (FT-IR) spectroscopic analysis of famous 16th century painting The Coranation and Assumption of the Blessed Virgin Mary (author unknown, Convent of the Sisters of St. Catherine Orneta, Poland).

Figure 1 shows The Coranation and Assumption of the Blessed Virgin Mary together with marked spot of sampling, the cross-section of the micro-sample, and the exemplary FT-IR spectrum. The obtained results allowed us to identify ground layers, admixture of pigments present in the individual layers, binders, and degradation products.

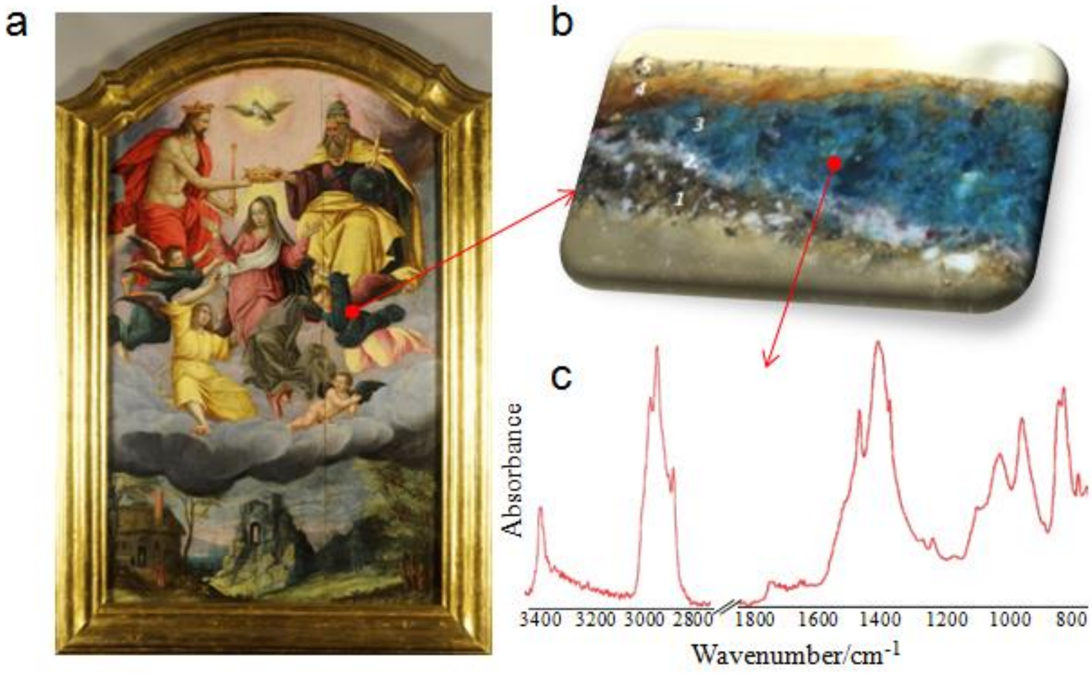

Figure 1. *The Coronation and Assumption of the Blessed Virgin Mary* together with marked spot of sampling (a), the cross-section of the micro-sample (b), and the exemplary FT-IR spectrum (c) (the photo taken by Zuzanna Rozłucka, (UMK, Toruń)).

Interestingly, the composition of the painting reveals many similarities to the famous *Coronation of the Blessed Virgin Mary* by Hermann Han (1580-1627/8) or Bartłomiej Strobel (1591-1647). The performed analysis allowed for identification a rich palette of pigments, e.g. azurite, ultramarine blue, lead white, protein binders, and degradation products such as moolooite.

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Capabilities of *in-situ* Spectroscopic Imaging for Visualizing Traces of Antique Polychromy

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In the Greek and Roman Antiquity buildings and statues were often painted in brightest colors. Few traces of this splendor remain today, but their study allows gaining insight in this world of Antique Polychromy. For this the surface of an object is commonly surveyed with a microscope employing visible light, IR and UV illumination. Paint remnants identified in this fashion are studied by spectroscopic spot analysis, e.g. by X-ray Fluorescence Analysis (XRF), as the taking of samples is generally discouraged [1]. Next to being labour-intensive and comparably slow, this method is limited to remnants of antique polychromy, which are visible on the surface of the marble.

Spectroscopic imaging allows for a comparably rapid and semi-automatic survey of large surfaces (several hundreds to thousands of square centimeters). It has been established in the last years for the investigation of historical paintings in the form of XRF imaging [2] and hyperspectral imaging in the visible and near IR range [3]. We could recently show that XRF imaging allows detecting previously unknown traces of antique polychromy on the surface of the well studied Frieze of the Siphnian Treasury at the Delphi sanctuary in Greece [4].

XRF imaging allows to clearly visualize traces of pigments different in elemental composition from the marble support or surface contaminations. Hematite (Fe_2O_3), which is even in traces on the surface clearly visible by the bare eye, is only weakly detectable by XRF. However, hyperspectral imaging in the visible and near IR range (300-1000 nm) allows a clear visualization of it and revealed previously unknown pictorial details.

In this contribution we will show how these two methods of spectroscopic imaging allow for new insights in the painting technique and pigment use in antiquity, discuss their shortcomings and capabilities and highlight their complimentary nature on examples from the Frieze of the Siphnian Treasury.

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p-XRF analysis of lapis lazuli for provenance studies

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Despite the Badakhshan Province (Afghanistan) remains the most plausible hypothesis for the lapis lazuli used in antiquity, alternatives proposed in literature are worth to study to confirm or disprove their historical reliability [1]. In the last years we have proposed and successfully applied to lapis lazuli objects a protocol to identify the provenance of the raw material by means of micro-analytical non-invasive methodology [2-4].

In this study, portable X-Ray Fluorescence (p-XRF) analysis was carried out on lapis lazuli to search provenances markers, then overcoming the problem of the not portable instruments used in the current protocol. Until now, 55 lapis lazuli rocks of known provenance from 5 quarry districts have been analysed, creating a database that, to the best of our knowledge, is probably the widest in provenance studies on this material using p-XRF. Our database is composed by: 20 samples from Badakhshan in Afghanistan, 4 samples from Liadjura-Dara in Tajikistan, 11 samples from Lake Baikal area in Siberia, 8 samples from Coquimbo region in Chile and 12 samples from Mogok in Myanmar. Samples from Tajikistan and Siberia are georeferenced, i.e. GPS coordinates are known. On the basis of trace element contents it was possible to distinguish some of the origins of the lapis lazuli.

Data obtained by means of p-XRF were compared with those obtained on carved lapis lazuli artefacts kept at the Egyptian Museum of Florence, the second most important Egyptian museum in Italy. The collection in Florence has a great historical value and includes several lapis lazuli pendants, scarabs, small statuettes and amulets ascribable mainly to the 1st millennium BC. In particular, 14 of these artefacts were analysed by means of p-XRF technique.

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Multidisciplinary non-invasive image diagnostics based on mobile techniques of 15th century paintings from Sicily

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Four paintings on wooden panel, dating back to 15th century and pertaining to the artistic background of Sicily have been studied at the Museum of Palazzo Bellomo, in Siracusa, during the 2016 edition of the IPERION CH.it / E-RIHS.it Training Camp, devoted to PhD/master students in Art and Applied Sciences and young conservation scientists and restorers. Here the results are presented of the image diagnostics performed with different instruments, following the multi-disciplinary approach informing the whole study.

Figure 1. Detail, visible light

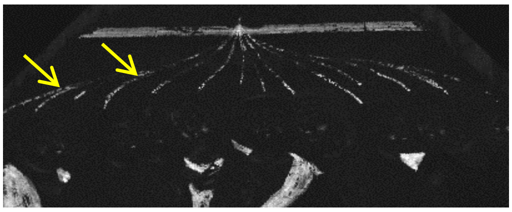

Figure 2. XRF scan for Mercury L-peak

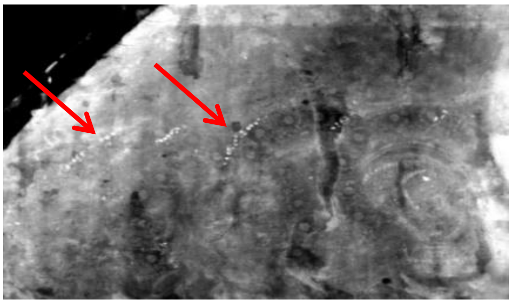

Figure 3. X-Ray detail of the left corner

Multispectral and Hyper-Spectral imaging have been performed with a 8.3 Megapixels Chroma C4 scientific camera using six interferential filters (centered at 400, 450, 550, 600, 750 and 1.050 nm, with band-pass ± 25 nm) in front of the CCD sensor and with a scanning device acquiring simultaneously 32 channels on wavelengths from 400 up to 2500 nm. Full size digital radiographs of the paintings have been accomplished by the mobile scanner equipped with CMOS detector. Macro-XRF scanning was carried out with the instrument based on a novel real-time technology enabling a fast continuous scanning over a 110×70 cm^2 area with a speed of 100 mm/sec.

The following images are a valuable instance of the powerful potential of the cooperation among these non-invasive imaging techniques. In this *Madonna with Child, and Pentecost*, the descent of Holy Spirit as flames, represented in a former version of the painting and now not visible, is unveiled by X-Ray radiography and referred to as cinnabar (mercury sulphide) by the XRF elemental image.

Acknowledgments: The authors gratefully thank the Directorate and the entire staff of the Regional Gallery of Palazzo Bellomo, Siracusa, providing help and support for the realization of the diagnostics program and the Opificio delle Pietre Dure, Florence, for the precious collaboration.

Non-invasive analysis of mural paintings from a Republican house (1st century B.C.) in Ostia

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This paper is a comprehensive analytical study of the murals belonging to an ancient Roman house through the characterization of materials. The project focuses on the wall paintings of the Domus dei bucranes, a house of the end of the Republican era discovered on the site of the Schola of Trajan in Ostia. This Domus has undergone several phases of development in the 1st century BC before being destroyed around 20 BC. A new house was immediately rebuilt after a major change from the ground, which allowed exceptional preservation of the decoration system. The results complement our knowledge of Roman painting techniques during the 1st century BC and also provide a comprehensive multidisciplinary approach to the problem of conservation of wall paintings. These two related objectives have been studied using non-destructive testing methods (MA-XRF, FTIR and Raman spectroscopy). The analyzes have been performed in situ using our mobile systems. The different set-ups had to be modified in order to be able to work on horizontal surfaces, specially our XRF scanner. The study of the pictorial layers address various issues in the field of archaeology: what technique has been implemented? Does the same technique was used in both phases of the development of Domus? Do they correspond to the techniques described by ancient writers? These responses are compared to those observed in other sets of murals dating from the 1st century BC.

Characterization of Arsenic Sulfide Pigments in Japanese Prints of the late Edo Period

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Arsenic sulfides, ranging from vivid yellow to red, have been used as pigments throughout history. The arsenic sulfide orpiment (As_2S_3) has been identified as a yellow pigment in Japanese woodblock prints from the mid-17th to early 19th centuries. [1] The use of natural orpiment as a pigment for commercial woodblock print production is curious due to its relative high cost. Recent work by Luo *et al.* uncovered the use of a less costly, synthetic orpiment known as alacranite (As_8S_8-As_8S_9) in Japanese prints of the Meiji period (1868-1912). [2] Herein, we extend the work from Luo *et al.* to the characterization of arsenic sulfide pigments used in Japanese prints of the late Edo period (1615-1868). We focus on the yellow, orange and green areas of select prints and determine if the arsenic sulfides used were of synthetic or natural origin. Analysis by polarized light microscopy, Raman spectroscopy and scanning electron microscopy confirms the presence of alacranite and orpiment in Japanese prints tentatively dated to the 1820s and 1830s. Period literary evidence suggests the manufacture of alacranite in Japan in 1846 and therefore our findings potentially reveal the use of alacranite nearly 20 years prior. Additional period literature cites the use of an imported Chinese 'second grade' orpiment used primarily for painting. The detailed chemical characterization of arsenic sulfide pigments from Edo period Japanese prints in combination with period literature will provide further insight into yellow pigment usage and production in Edo Japan.

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Time-resolved ATR-FTIR as a tool to monitor chemical reactivity in oil paint model systems

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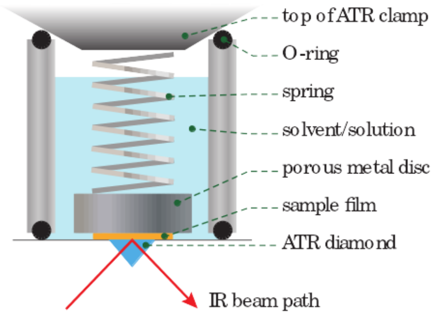
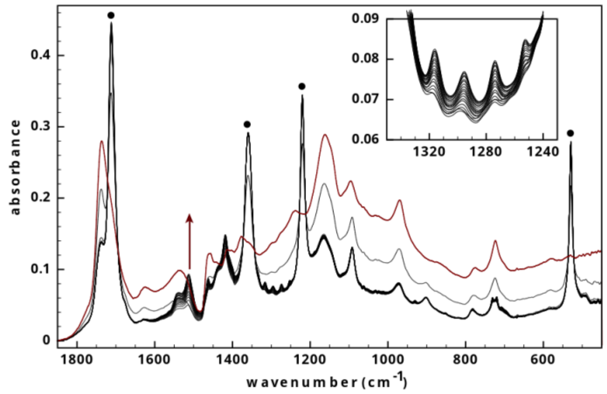
The influence of cleaning action on paint is one of the most challenging topics in the field of paintings research. This raises the important question if exposure of an oil paint to solvents triggers or enhances reactions beneath the surface of the paint. Ideally, one would study the influence of solvents using time-resolved measurements. Traditionally, solvent extracts, paint swelling, paint elasticity and change in heat capacity were studied and taken as a measure for the impact of solvents on a paint layer. These techniques have the limitation that they either analyze the bulk but lack chemical specificity, or analyze a small part of the paint which does not necessarily reflect the bulk. More recently, single-sided NMR was used to quantify the increased stiffness of the paint as a result of cleaning action [1] and to study the diffusion of water in acrylic paints [2]. Although this technique enables time-based measurements, the time-resolution is insufficient for monitoring fast-diffusing solvents and chemical specificity is lacking. However, time-resolved attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) is capable of monitoring the molecular composition of a paint surface upon exposure to solvents or solutions on a timescale of seconds [3,4].

We have developed an analytical method based on time-resolved ATR-FTIR in order to study the diffusion of solvents and the kinetics of crystalline metal soap formation in model systems of aged oil paint (see figures). These model system consist of zinc and lead ionomers that mimic mature oil paint binding medium and feature molecularly dispersed metal carboxylates in a polymerized linseed oil matrix [5]. The diffusion coefficients of solvents are obtained using an adapted version of Ficks law, extending the method to polymer films of varying thickness using a custom-built sample cell on a standard ATR-FTIR setup. It is shown that, when exposed to solvent, free unsaturated fatty acids (FAs) easily react with metal ions of zinc and lead to form crystalline metal soaps within the model paint film. The kinetics of this crystallization process are studied and complemented with a mechanistic mathematical model. These measurements show the potential of time-resolved ATR-FTIR spectroscopy in monitoring the chemical composition of a mature oil paint binding medium over time.





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IBA and FORS mappings applied to the analysis of cultural heritage artefacts: Last improvements on the AGLAE facility

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Ion Beam Analysis (IBA) is a powerful technique to reach the chemical composition and distribution of the elements at the surface of the objects and can give key information to Cultural Heritage questions: How old is it? Is it a fake? Where does it come from? How was it made? At the AGLAE facility, IBA techniques (PIXE, PIGE, IBIL and RBS) can be performed on several-cm-sized maps with down to 10µm resolution thanks to the multidetector end-station [1].

If IBA gives fundamental information, sometimes another level of knowledge is necessary on the same area of interest with a resolution close to the ion beam techniques' – for instance the oxidation state of metals. Fiber optics diffuse reflectance Spectroscopy (FORS) is one of the methods that can give information and can be implemented at the AGLAE end station.

Therefore, a system of micro FORS has been developed to complement the IBA analyses. It is able to perform FORS measurements on the very same area and the same scale in size and time as the IBA measurements.

A supercontinuum source is used as a white light source ranging from 350 nm to 950 nm with not only a small spot at the ion-beam size around 50µm to be able to analyse the same precise area than IBA but also high luminosity even at small size to have enough luminosity to get fast recording of reflectance spectrum. Spectra are recorded through a custom optical fibre with a spectrometer with 3 nm resolution FWHM and 8 ms acquisition time. This device allows fast mapping of the reflected light. Thus, maps can be performed in which, for each pixel, all IBA spectra and reflectance spectrum are recorded.

Examples of the application of the techniques on Cultural Heritage artefacts and questions will illustrate the talk.

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Advanced techniques of photo-luminescence microscopy for the analysis of precious semiconductor-based painting layers

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UV-induced fluorescence microscopy, based on the use of a conventional epi-fluorescence microscope and a mercury arc lamp as the light source, is an established method for the analysis of painting cross-sections. Indeed, the analysis of the faint and heterogeneous optical emission from trap state levels in semiconductor pigments is not straightforward with conventional set-ups.

Here, we discuss the complementarity of two advanced photoluminescence (PL) micro-imaging techniques through analysis of illustrative examples of stratigraphic micro-samples from precious Russian modern paintings, characterized by the presence of zinc white, titanium white and cadmium yellow/orange painted layers. The employed set-ups comprise a synchrotron-based PL micro-imaging set-up [1], with sub-micrometer resolution and detection of the optical emission in different spectral bands, and a time-resolved PL microscopy set-up, which allows analysis of the emission decay kinetic from the nanosecond to the microsecond regime [2]. The combined approach allows the differentiation of semiconductor pigments and the analysis of crystal defects on the basis of their spectral and decay kinetic emission properties. An example is here reported (Figure 1): spectral images of the PL emission allow the detection of sub-micrometers luminescence particles ascribed to different crystal defects in two white painted layers. Time-resolved PL microscopy highlights the microsecond decay-kinetic behavior of the emission, confirming the trap state nature of the luminescence centers and allowing the discrimination between the white painted layers.

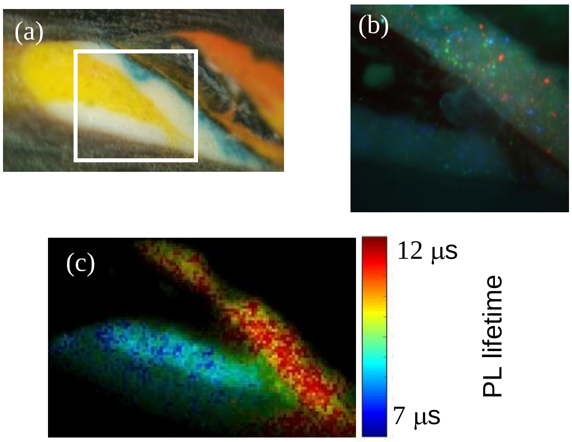

Figure 1. PL microscopy analysis of a stratigraphic sample from a Russian modern painting (N. Goncharova, 1913). (a) Visible image; (b) composite color image achieved by combining the PL emission at 410-440 nm (blue channel), 450-490 nm (green channel) and 800-870 nm (red channel); (c) emission lifetime map following analysis of the emission decay kinetic in the 0-40 µs timescale.

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The new "CRONO" macro-XRF scanner applied to Cimabue's masterpiece

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In recent years, commercial relatively compact macro-XRF scanners have become available, opening the way to a new research field and establishing the technique as one of the most powerful non-invasive method for the investigation of polychrome surfaces. Thus, chemical maps related to the elemental distribution within the analyzed area may provide crucial information for the definition of a proper conservation campaign. Moreover, the possibility to scan large surface with a reduced acquisition time allows a reliable documentation of the investigated artworks, reducing costs of the approach and enlarging the number of possible applications. The present research work is focused on the study of the "Madonna Enthroned with the Child and Two Angels" by Cimabue (1240 – 1302), held in Chiesa Santa Maria dei Servi in Bologna, Italy, to reveal new details on the paint technique adopted by Cimabue, through an accurate documentation of artworks. Thanks to the recent introduction of the "CRONO" macro-XRF scanner, a considerable area of about 1,38 m^2 was analyzed with a 2 mm resolution in about 5 hours and 45 minutes as measurement time.

CRONO, developed by XGLab SRL, is composed of a main XRF unit and of a motorized stage system to implement the scanning. The excitation source is a Rh tube with adjustable maximum voltage (up to 50kV). The X-ray excitation light is collimated to 0.5, 1 or 2 mm, software selectable by the user. A 50 mm^2 Silicon Drift Detector performs the fluorescence photons detection. The sample can be scanned at a maximum horizontal speed of 42 mm/s and the resulting output data are compressed in a HDF5 file. An internal microscope video-camera with dimmable light allows the user to monitor the system alignment and to document the scanned areas. The CRONO XRF acquisitions allowed a detailed visualization of elements ascribable to pigments used by the artist and a precise localization of several retouched areas referred to different restoration actions. For the first time the state of conservation of the masterpiece and its conservation history was evaluated considering the entire painted surface, disclosing new knowledge. Moreover, a particular attention was addressed to the characterization of the throne decorations. Elements, such as Cu, Pb, As and Ag were identified and their presence was linked to different ornaments, suggesting the application of various painting techniques and new questions on the originality of some decorative paint effects.

A multi-analytical approach to the painting technique and the green and blue pigments used in Andean colonial wall paintings

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This work shows the results of the application of different analytical techniques to characterize the green and blue pigments and investigate the painting technique in Andean colonial wall paintings. Studies were carried out on microsamples extracted of murals from the churches of Soracachi, Curaguara de Carangas, Corque, and Santiago de Callapa in Bolivia. These colonial churches were located on an ancient commercial road linking the cities of Potosí in Bolivia with Arica in Chile, known as the Silver Route (S.XVI-XVIII). To approach these goals, an integrated investigation comprising Raman and FTIR-ATR spectroscopy, optical microscopy, scanning electron microscopy with X-ray spectroscopy (SEM–EDS), and mass spectrometry (MS) was carried out. The study revealed a very simple painting technique consisting on the application of a thin pigment layer on a white ground layer on the adobe wall. Previous investigations on the wall paintings of the church of Our Lady of Copacabana de Andamarca in Bolivia indicated *a secco* technique [1]. The Raman analysis of the ground layer in the cross-sections of the samples showed characteristic bands of calcium sulfate compounds with different levels of hydration: gypsum, basanite and anhydrite [2]. Regarding the green pigments, Cu-based minerals, such as brochantite and antlerite, both basic copper sulfates, were identified in most of the green samples. These pigments are uncommon in colonial art and have been recently reported in a wall painting of a church in Bolivia [1]. Among the blue pigments, indigo was identified by micro-Raman spectroscopy and direct insertion mass spectrometry [3]. This MS technique also gave information on the binder mixed with the blue pigment. The characterization of the materials used in the manufacture of the wall paintings together with the pictorial technique constitutes a significant contribution to the study of the Andean artistic heritage, which is in many cases the result of the fusion of pre-Columbian knowledge with practices of European painting.

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The Giotto's workshop in the XXI century: looking inside the "God the Father with Angels" Cusp

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God the Father with Angels (about 1330, a tempera on panel, 76 x 71 cm) by Giotto, is the cusp of the altarpiece of Baroncelli Chapel in the Franciscan church of Santa Croce in Florence, but very few is known about its history since the mutilation of the Baroncelli Polyptych [1]. Now held in the San Diego Museum of Art, the cusp was never studied by means of scientific methods before our team took the opportunity when the panel was brought back to Italy in the context of the exhibition "Giotto, l'Italia" (Palazzo Reale, ~~of~~ Milan. September 2, 2015 – January 10, 2016). All the non-invasive analyses (compact and portable MA-XRF, FORS, IR refelectography, IR false colour) have been performed with portable instruments and with times compatible with closing hours of exhibition (five diagnostic campaigns, five hours of work/campaign, no interruption of exhibition).

Exploiting the integration of different knowledge, technologies and resources of our team, we were able to provide data for understanding the organizational model of a Giotto's workshop. The achieved results confirm the well-known painting technique based on different layers of pigments, a painting technique already used by Giotto [2]: combining the effectiveness of scanning p-XRF with the responsive of image spectroscopic analysis, we move step by step toward the discovery of Giotto's palette for the flesh tones in God the Father with Angels.

The imaging data support the hypothesis of a detailed underlying drawing, including a drawing characterized by bigger brush signs; by applying image segmentation and pattern recognition algorithms to the collected reflectograms, the use of patrones for the face of "God the Father" and the use of the sketches for the faces of angels could be thought.

Acknowledgments: The authors would like to especially thank Michael A. Brown, Associate Curator of European Art at the San Diego Museum of Art. The research has been supported by Fondazione Cariplo, grant n° 2015-2293.

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Pigment identification in historical samples of Matisse Cut-Outs

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In the last fifteen years of his career, Matisse turned to paper as his primary medium and produced a whole body of works usually referred to as the Matisse's Cut-Outs. He produced these artworks between the early 1940s and mid 1950s by cutting shapes out of large sheets of paper pre-painted with gouaches of vibrant colors that he would arrange and pin down into lively compositions.

The characterization of the gouaches he used for his Cut-Outs is of major relevance for their preservation, in particular from potential damage caused by exposure to light, and for their conservation if treatment is deemed necessary. To this day, however, only a few studies have been published on the condition of these works and the characterization of the gouaches [1,2].

Pigment identification was carried out on a set of seventy nine historical samples of Henri Matisse's "gouache" papers taken from left overs of the original sheets used by the artist and preserved by his family (image 1). This study set was assembled to best represent his color palette and is composed of varying tonalities of violet, blue, teal, green, yellow, orange, red, magenta, pink, brown and blacks.

The organic and inorganic pigments present in the samples were identified using Dispersive Raman, Surface Enhanced Raman (SERS) and Fourier Transform Infrared (FTIR) spectroscopies. Microfaedometry (MFT) was performed as well to assess the lightfastness of the colors. The analysis was carried out in parallel with X-ray fluorescence (XRF) and Reflection Infrared (r-FTIR) spectroscopies. The results were compared to validate the use of a noninvasive approach for the study of artworks in the museum collection. A case study is presented to illustrate the value of the information gathered from this study set for the preservation of Matisse's Cut-Outs.

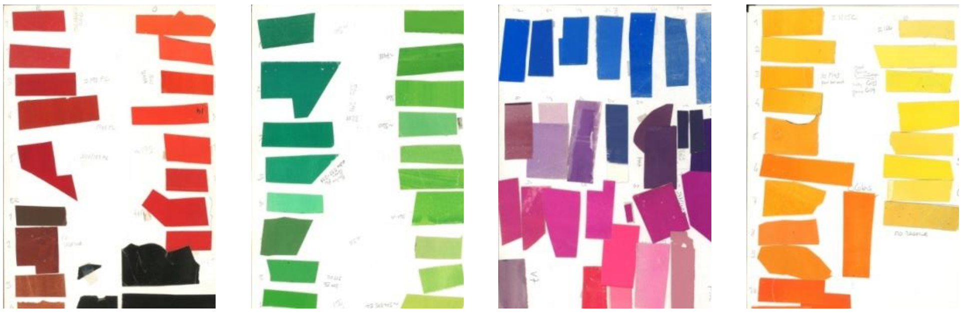

Figure 1. Study set of painted paper samples, c. 1947–54. Gouache on paper, seventy-nine pieces. Gift of the Matisse family, 2014 (approximate sample size is 10cm^2).

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A tale of two pigments: the characterization and synthesis of Indian yellow, and zinc orange from Toulouse-Lautrec's early palette

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Historic oil-paint samples were sampled from Château du Bosc, the family home of Henri de Toulouse-Lautrec. The samples were retrieved from tin based tubes housed in a mid-to-late 19th century wooden box address to Toulouse-Lautrec. Amongst the range of pigments collected, two colours stood out: Indian yellow and zinc orange, both defunct pigments with a limited window of use. These colours were tested to confirm the presence of the indicated forms of the pigments, and at the same time, sparked new questions regarding the authenticity of the labels. Authentic Indian yellow was found, whereas a zinc orange synthetic alternative colorant was identified. Further research into these colours led to attempts to understand their synthesis, and to try to recreate them in the laboratory. A range of scientific analyses, including PLM, XRF, -FTIR, py-GC-MS, UV-vis spectroscopy and induced fluorescence, were employed to fully characterize these pigments (both original and synthesized ones). This paper will describe some of the results of these characterization and synthesis studies, and reveal interesting notes regarding late 19th century Parisian artists' palettes.

Comparative technical analysis of the medieval altarpieces by Hermen Rode in Tallinn and in Lübeck

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In the following case study, two complex and sizeable artefacts, the St Nicholas Altarpiece in Tallinn (in the Niguliste Museum) and the St Luke's Altarpiece in Lübeck (in the St Annen Museum) were studied *in situ* and in the laboratory using a wide range of technical investigation and documentation methods. All of the applied methods had been previously tested and had been commonly used separately in several cases, but in order to support art historical and conservation projects in geographically different locations this study had an exclusive opportunity to identify the shortcomings and optimise the work-flow.

During the investigation project in Tallinn (Estonia) and in Lübeck (Germany), several material and technical analyses were conducted. At first, various methods were used as documentation solutions during this study, including: photogrammetry, 3D scanning, multispectral examinations (near-infrared (NIR), ultraviolet (UV) and X-ray), panoramic photography and reflectance transformation imaging (RTI), a computational photographic method that captures a subject's surface shape and colour and enables the interactive re-lighting of the subject from any direction. Next, a non-destructive paint composition analysis with a portable X-ray fluorescence (XRF) device *in situ* was carried out. Then small paint samples were collected from the altarpieces and chemical analyses using different instrumental techniques (ATR-FT-IR, SEM-EDS etc.) were performed at the University of Tartu laboratories.

The results of this study illustrate that one of the key factors for successful results is adaptable work-flow. In material analysis and documentation, the selection of the optimal methods is based primarily on the attributes of the object, and the aims and necessity of the study. In terms of complexity and size, the two altarpieces were excellent test objects, combining polychromic sculptures and paintings, i.e. the specific attributes of two-dimensional and three-dimensional art.

Such enriched documentation may provide research and archiving information that conservation and heritage specialists can particularly benefit from when it is accessible. Combining material analysis, heritage documentation and different imaging methods on the Web is challenging and novel.

In conclusion, the results of this study demonstrate that complex artefact surveys can be successfully and cost-effectively conducted. The results obtained are informative and involve a comparison of the techniques and materials used in Tallinn and Lübeck. Such an interdisciplinary approach, which provides the opportunity for familiarisation with different research methods and the creation of synergies among specialists from different fields, can also supplement imaging and information technology solutions and make them accessible to researchers and general users. During the research, the rode.ekm.ee website was developed and published, and it contains a wide range of gathered data and successfully implemented educational materials.

Nicolas Poussin's painting technique in the scope of a mobile laboratory: X-ray fluorescence, X-ray diffraction and reflectance hyperspectral imaging

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Nicolas Poussin is known as a painter-poet. He aims in his paintings at communicating his ideas and world-view; it has been said that everything in his paintings is directed to this single end [1]. To better understand Poussin's painting technique and choices, five paintings of Nicolas Poussin from three European museums have been investigated through mobile complementary techniques: X-ray fluorescence, X-ray diffraction, X-radiograph and reflectance hyperspectral imaging (in the case of two paintings from the Palazzo Barberini, Rome). From these analyses, we will show that Poussin in his painting as a poet writes: carefully choosing each material, its location, its relation to one each other.

Non-invasive analyses, spot measurements and imaging techniques, together with reconstructions help us to understand the nature of the mixtures found, and the effects achieved through their use. We did not confine our investigations solely to investigating the nature of the materials employed, but we tried to understand their relationships to one another in the context of the work as a whole. Poussin uses a limited number of pigments in a way which suggests that their choice was ordered by more than just visual effect [2]. The pigments used and the objects depicted are linked. For example, the different paintings analysed show Poussin's very specific use of lapis lazuli, which as a pigment had a symbolic worth way in excess of its high market value.

We also focused our attention on the handling of the materials used to create the dramatic effects of light and shadow, so crucial to the general effect of the painting and to the representation of convincing three-dimensional space. We therefore attempted to better understand the material make-up of these effects by studying the evolution of particular elements.

Finally, we particularly investigated two early masterpieces by the artist, now in the Palazzo Barberini in Rome, with the whole set of equipment, including visible and near infrared hyperspectral imaging. These paintings are unique in that they are documented by a contemporary of the artist as being painted in a glue medium, and thus they are the only surviving works in this medium (at which the documentary sources tell us he excelled). This therefore provides a great opportunity to investigate the relationship of the materials and techniques deployed in comparison to his works painted in an oil medium.

As a conclusion, this first analysis of Poussin's paintings by hyperspectral imaging will be the occasion of showing the possibilities and remaining challenges of this promising technique, which is currently raising interest in the cultural heritage community.

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New insights into Indian yellow and its use in Rajasthani wall paintings – a multi-analytical study

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The previously undocumented, though widespread use of Indian yellow in 17th-century wall paintings in Rajasthan (India) was revealed by photo-induced luminescence imaging and *in situ* FTIR analysis of two painted schemes in the Garh Palace (Bundi) and the Ahhichatragarh fort (Nagaur). The results of a multi-analytical study focusing on two samples from the Bundi wall painting and reference pigments from the British Museum and National Gallery (London, UK) are presented here.

The optical properties of the samples were characterised by photoluminescence spectroscopy. Small differences in terms of spectral shift and lifetime decays were revealed and further investigated through an in-depth characterisation of their chemical composition. HPLC-ESI-Q-ToF was used with both positive and negative ionisation and confirmed the presence of euxanthic acid and small amounts of euxanthone as the main organic components [1,2]. Euxanthone-4-sulphonate was also identified for the first time in all samples. The presence of this compound opens up new interpretations regarding the production process of Indian yellow. Although the pigment is generally believed to derive from the urine of cows fed on mango leaves [3], some questions remain open. Several flavonoid molecules, such as morin, kaempferol, quercetin and luteolin, were detected in one wall painting sample characterised by a brighter yellow colour and a bathochromic (red) shift. Py(HMDS)-GC-MS was also used for the first time to characterise Indian yellow and the trimethylsilyl derivative of euxanthone was identified in the pyrograms, proving it to be a suitable marker for the identification of the pigment in complex historic samples. SEM-EDX was used to characterise the elemental composition of each sample and stratigraphic analysis of both wall painting samples revealed different white pigments within the preparation layers.

This study provides new insights into the composition and use of this fascinating pigment. Methodological advances and conservation implications are also highlighted, mainly related to the sensitivity of Indian yellow towards different solvents, thus contributing to better-informed conservation strategies.

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Portable instrumentation for the study of wall paintings: the case of S. Maria ad Undas in Idro (BS-Italy)

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The parish church of *Santa Maria ad Undas*, on the Idro Lake shores, externally looks quite simple and austere while the inner single nave possesses a rich decorative apparatus, currently mostly covered by a white lime layer applied during the seventeenth century plague period.

Its unique characteristic is the painted masonry altar, discovered in 1955 after the removal of an eighteenth-century altarpiece. It is a very rare artifact comparable only with two other altars, both located in the Brescia area. The style and the oriflamme of San Bernardino of Siena suggest that such decoration was realized shortly after 1443, when the symbol was formally canonized.

Being the altar immovable a preliminary *in-situ* study was mandatory to plan possible consequent laboratory analysis to finally assembly a valorization project also including a restoration and conservation plan.

A set of three non invasive techniques was used to characterize both the author palette and neo-formed secondary phases that may be present: Multispectral Imaging, Raman spectroscopy and Reflectance Spectroscopy (FORS).

Images acquired under UV light, in both fluorescence and reflectance mode, gave useful information about the presence of organic residual materials due to the presence of a binding medium used for the application of currently lost gilding details [1]; at the same time the readability of some details was improved with respect to what observable in visible light. Images collected in Reflected Near Infra Red (RNIR) light led to formulate initial hypothesis about some of the pigments used by the artist, such as hematite, goethite and green earths [2].

The combined use of the two spectroscopic techniques allowed to clearly identifying the pigments and the alteration phases on the altar: the red and yellow areas showed signals typically attributed to hematite and goethite, confirming what supposed from RNIR imaging. Furthermore the presence of white lead was stated by Raman spectroscopy, while the use of FORS resulted fundamental to recognize the blue and green pigments as azurite and green earths [2].

As concerning the secondary phases, quite common species such as gypsum, niter and hydromagnesite were revealed due to the detrimental effect of the average church environmental conditions, such as very high humidity and relatively low temperature. The same combination is a fundamental condition for the formation of Plattnerite as alteration phase of white lead when applied in frescoes [3]; other black areas resulted covered by a thin carbon-based layer attributable to the burning of candles.

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"Precious powder": Designing a methodology for the technical and analytical study of pastel paintings from the Rijksmuseum collection

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Since its appearance in the late 17th century, pastel paintings have always been considered as one of the most fragile works of art because the medium lays loose on the support and can be light sensitive. Between 2008 and 2016, conservators, curators and scientists collaborated at the Rijksmuseum to characterize 18th-century pastel supports, media and fixatives. This material characterization was useful to address conservation and technical art history questions, such as: what is the palette of pastel sticks available? why do some pastel colors fade? what is the role of fixatives in the protection of the pastel medium?

This paper will present first the methodology developed to study a corpus of about 20 pastel paintings from the Rijksmuseum collection, an 18th-century pastel sampler and mock-ups. As a result of collaboration with various research laboratories in Europe, spectroscopic, chromatographic and biochemical techniques were applied to analyze the composition of the supports, media and fixatives. Analytical results were then related to 18th-century written sources.

For the first time, peptide fingerprinting (ZooArcheology by Mass Spectrometry) performed at University of York provided data about the parchment species selected by pastellists, giving new light onto the remarks left in the written sources. Furthermore, the combination of micro- and macro-scanning XRF, Raman spectroscopy, FTIR and SERS resulted in a better understanding of the pigments, colorants and also fillers used by pastellists and supplied by the famous Swiss pastelmaker Stoupan. More than relating artists' palettes, it became possible to attribute the local fading observed on a few paintings to the composition of the pastel medium and to relate the results to 18th-century comments. Finally, this paper will detail the difficulties encountered when analyzing pastel fixatives. Sprayed in very small quantities to reduce surface change of the medium, fixative is only visible on historical paintings as stains made by mistake by the artist. In order to identify the correct analytical method to discriminate different fixatives, mock-ups were produced to represent the main 18th-century recipes. Traditional chromatographic techniques (GC-MS, HPLC) were combined with biochemical techniques such as ELISA (Enzyme-Linked Immunosorbent Assay) and SAWN (Surface Acoustic Wave Nebulisation) to try to detect first protein-based fixatives and, when possible, the type of protein present.

Paul Gauguin's graphic works: multi-analytical **characterization of the artist's techniques and** materials

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The Art Institute of Chicago holds one of the richest collections of works on paper by Paul Gauguin in the world, second only to the Musée d'Orsay in Paris. The collection includes 40 unique wood-block prints from *Noa Noa*, Gauguin's famed volume that he created to familiarize a Western audience with the culture, flora and fauna of Tahiti [1]. Produced in Paris upon his return from his first trip to the island (1891-1894), the group comprises a myriad of impressions pulled from 10 blocks. Although Gauguin's graphic works are among his most innovative and experimental, they have been less studied from a technical perspective than his works in other media. As such the museum's collection provides a unique opportunity for in-depth analysis [2].

Among the many impressions in the Art Institute's collection, exemplars of *Noa Noa* prints from the first stages of carving and printing in black on poor quality papers and later impressions with delicate, colorful watercolor washes or thick organic media mixed with yellow, red and green pigments are represented. No two prints are alike, yet distinct patterns of production emerge from the group. 23 impressions from the *Noa Noa* suite were analyzed using a complement of analytical techniques. Non-invasive analyses were carried out using x-ray fluorescence and scanning-XRF spectroscopy (a rare application of this technique to works on paper), Fourier transform infrared spectroscopy (FTIR) in reflectance mode, and Raman and FT-Raman spectroscopy. Selected microscopic samples were taken from the printing inks and paints for supplemental analysis by FTIR in transmittance mode, surface enhanced Raman spectroscopy and pyrolysis gas chromatography mass spectrometry. This comprehensive multi-technique approach provided new insights into the artist's experimental methods such as a two-step printing process in which colors were site-specifically applied onto glass and transferred onto paper before the inked block itself was printed onto the same sheet, and the ad-hoc mixing of oleoresinous media. In addition, analyses revealed changes in pigments such as the fading of pinks and blues and the alteration of yellows.

The findings of this study reveal Gauguin's ingenuity in the formulation of his media to obtain specific working properties, and the manner in which he applied them to a variety of papers directly or by means of paper-to-paper or glass-to paper transfer. In total, they shed light on a very personal, innovative and unique artistic gesture.

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300-400 nm UV fluorescence multispectral imaging for organic pictorial materials identification

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Fluorescence induced by UV radiation is one of the most traditional imaging technique used in the conservation practices and laboratories. It is used for detecting and mapping the presence of varnishes and previous restoration interventions on polychrome works of art and frequently on easel paintings. Furthermore, this technique highlights the distribution of some pictorial materials, such as the red lakes commonly used in Renaissance and Baroque paintings. In this sense, materials fluorescence is obtained by means of traditional UV lamps (Wood) for laboratory, which normally have 365 nm peak-emission spectra.

Here we present a new methodology in using selectively the 300 – 400 nm UV emission range in order to detect and distinguish a larger set of pictorial materials through their fluorescence in the Vis range.

The study was applied to a real palette (a 50x70 cm panel) of 420 different material combinations made with different binders and varnishes and 70 different synthetic, inorganic and/or organic pigments representing contemporary art materials.

A xenon lamp with a set of 10 band-pass filters in the 300-400 nm range were used as light source. Images were acquired with a Nikon D800e camera (7360 × 4912 pixel) filtering the UV radiation in order to exclude the reflected UV contribution. Images were then normalized to the CMOS spectral sensitivity, to the camera lens and band-pass filters transmittance.

Differences in fluorescence intensity and/or colour in the 300-400 nm range showed to be characteristic of specific materials or combinations, indicating the high potentiality of this diagnostic technique. Beside the imaging data, UV fluorescence spectra of single materials (solid samples of pure substances) were acquired with a spectrofluorimeter in order to compare and better understand the imaging results.

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A comparison of non-invasive imaging and portable techniques for the study of Old Master paintings: **Rembrandt's** *The Jewish Bride* c. 1665

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Over the course of the past four years, some twenty late Rembrandt paintings have been investigated as part of the NWO-Science4Art *ReVisRembrandt* project in order to resolve unanswered questions and to gain a better understanding of Rembrandt's enigmatic late painting technique [1]. One of the selected case studies is the *Portrait of a Couple as Isaac and Rebecca*, known as *'The Jewish Bride'*, c. 1665 in the Rijksmuseum, Amsterdam. The authenticity of the hat and the discolouration of the (now) brown background in this painting, are examples of the kind of problems encountered in late Rembrandt pictures that concern past interventions and changes in appearance due to aging of materials. This presentation will report on the results and comparison of chemical imaging and non-invasive techniques used to investigate 'The Jewish Bride' in the galleries of the Rijksmuseum. Techniques include macro-X-ray flourescence scanning (MA-XRF), hyperspectral diffuse reflectance imaging spectroscopy (HS-IRR), as well as portable XRD and portable Raman [2].

It is now well established that MA-XRF scanning has the potential to clarify many obscure features. For 'The Jewish Bride', this includes the hidden (bone black) remains of Isaac's original hat (P, Ca maps), the now discoloured smalt-rich background of the painting (Co, Ni, As, K maps), and the identification of a new pigment, a purified form of dry processed artificial orpiment in the orangey brown shadow areas of Isaac's sleeve and underpaint of Rebecca's red dress (As map) [3]. The combination of elemental mapping with hyperspectral diffuse reflectance imaging spectroscopy, in the visual to near-infrared region (400-2500 nm), also made it possible to distinguish between a variety of Fe-based pigments (ochres, umber), and to map a unique hydroxyl feature at 1417 nm associated with yellow ochres and clay minerals in the ground layer.

As with any technique, it is important to be aware of their sensitivities and limitations. Results show that the combination of elemental mapping with hyperspectral diffuse reflectance imaging in the visual to near-infrared region, makes more complete identification and mapping of artists' materials possible as not all pigments can be identified with a single technique. For pigments that have complex chemical compositions and paints that contain mixtures of several pigments, portable- XRD and Raman can provide highly specific identification. Correlation with examination of the paint surface and existing paint cross-sections aids significantly in interpretation of data.

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Two in one: Unraveling a hidden Jan Steen painting

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A work of art represents the artist's brainchild. The artist often makes adjustments during the creative process and may even over-paint an abandoned work for unknown reasons. These changes or overlays conceal invaluable information beneath the surface, so to unwrap these secrets allows us to glance at the fragments of their creations to decipher their intriguing lives.

This work focuses on a painting by the Dutch painter Jan Steen (1626-1679) *A Visit to the Village Lawyer.* The current study was performed with spatially resolved micro X-ray fluorescence (μ-XRF) using a M6 Jetstream from Bruker; and IR reflectography with the Osiris IR image system. Jan Steen is known for using humorous approaches to incorporate didacticism into his paintings. *A Visit to the Village Lawyer*, collected by Chimei Museum, portrays a peasant couple exchanging a gift for documents interpreted by a village lawyer. In it, various traditional motifs are depicted to satirize the immorality of the lawyer [1].

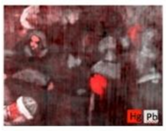
Using the M6 Jetstream a series of high resolution scans were captured and collaged. The distribution map of Pb-L (lead L-alpha line) associated with the pigment lead white exposed a distinctive composition of a crowd around a table, rotated 90° clockwise, from the upper right of the painting. Information obtained from the Hg-L (mercury L-alpha Line), most likely vermillion, revealed changes in the assistant figure on the upper painting. The initial draft of his pose was first portrayed facing towards the door, but later changed into glancing backwards with an insinuating facial expression, conveying more amusement and sarcasm. The combination of the lead and mercury maps allowed the underlying composition to be identified as clearly related to another Jan Steen painting – *Pleasures of Fatherhood* [2], where the characters are in the same positions suggesting an almost identical composition. However, the one hidden beneath *A Visit to the Village Lawyer* is unfinished.

The IR reflectography images captured by the Osiris IR image system reveal a very roughly sketched draft. With very little but representative strokes, the draft can be identified as also corresponding to the composition of *Pleasures of Fatherhood*, where the artist marked off the principle character and items.

Recent developments in multispectral analysis now provide the possibility to image larger areas; which in addition to the visualization of chemical information provides a huge support to the interpretation of paintings analyzed.

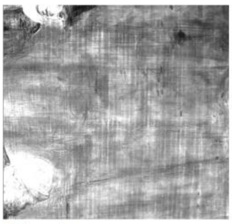
A Visit to the Village Laywer
Jan Steen
Oil on panel
62 x 52 cm

Mi-XRF element map of Pb-L



Mi-XRF
element map of Pb-L, Hg-L
Rotate 90°

Pleasures of Fatherhood
(Partial)



IR reflectography
(Partial)

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[1] The information of Jan Steen and *A Visit to the Village Lawyer* is acknowledged from the research in 2011 by Dr. Li Pen, Yu, Assistant Professor, Department of Art History, Tainan National University of the Arts.

[2] The painting is presently in the collection of Hamburger Kunsthalle.

Micro and Macro Scale Chemical Imaging on Van Eyck's Ghent Altarpiece (1432)

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The Ghent Altarpiece, a large polyptych retable completed in 1432 by the Van Eyck brothers, is considered as one of the pinnacles of Western mediaeval art. The last major conservation treatment was carried out in 1950 by the KIK-IRPA (Brussels, Belgium). More than 60 years later, in 2012, a long-awaited conservation campaign was initiated by the same institute. As part of an accompanying extensive technical study, the entire surface of the panels, measuring over 15m², is now subject to chemical imaging experiments, performed by the University of Antwerp. Early 2017, all outer panels and the lower register of the inner panels were measured by means of Macro X-Ray Fluorescence (MA-XRF) scanning

In this work, we discuss how supplementing these non-invasive macro scale imaging experiments with microanalysis had a direct impact on the choices made during the conservation treatment. In particular, the elemental maps demonstrated how the paintings on the verso panels had been largely overpainted during an early restoration campaign. The extent of this intervention had never been detected with traditional imaging techniques such as X-Ray Radiography and Infrared Reflectography. Although this overpainting closely follows Van Eycks's original composition, the scans revealed sharper forms and a more sophisticated modelling in the underlying composition.

SEM-EDX and synchrotron radiation based µ-XRF measurements on a limited number of cross-sectioned paint samples allowed refining the interpretation of the MA-XRF images by providing secure and accurate information on the layer build-up and composition. In addition, MA-XRF maps established unequivocally the relative good condition of the original scenes by visualizing the paint losses in the concealed original paint. This finding sustained the much debated choice for removal of the overpaint. In this way, an integrated combination of MA-XRF with cross-section analysis assisted in bringing Van Eyck's original paint to light after several centuries.

Concealed features in Botticelli's fresco unveiled by multispectral visible-near infrared and X-ray Fluorescence imaging

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Analytical tools provide excitingly new and crucial information about paintings and artworks, generally not visible to the naked eye. In order to maintain the integrity of the examined artworks, innovative non-invasive and non-contact methods are under constant development.

In this contribution, we demonstrate the complementary analytical capability of two research-grade portable devices: visible-near infrared multispectral (designed by INO-CNR) [1] and X-ray Florescence (XRF, designed by LABEC laboratory at INFN) [2] scanners. The joint analyses have been carried out on a Botticelli's detached fresco (*Sant'Agostino nello studio*). This artwork is conserved in the *Ognissanti* church in Florence and has recently been restored at the *Opificio delle Pietre Dure* [3]. Mural paintings represent a relatively little explored niche and therefore the subject of the survey has been a challenge in proving the analytical potential of the two imaging methods.

In this work, we show that both methods provide key information on the presence of fresco's surface and subsurface features and thus allow for much deeper insight into the painting structure (e.g., *pentimenti*, painting technique and conservation state) as compared to standard single point analyses. Moreover, the combined use of the two techniques enables an in-depth mapping of materials constituting the masterwork by Botticelli. Exploiting the materials' spectral fingerprint in visible and infrared light and X-ray fluorescence emissions we can obtain the complementary molecular and elemental data.

Figure 1. *Sant'Agostino nello studio*

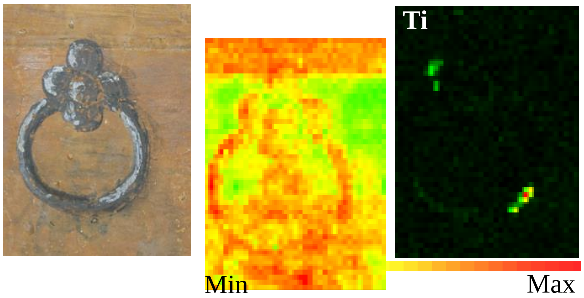

Figure 2. XRF elemental maps of an area of interest (right). A *pentimento* of the handle in the Ca map and restorations in the Ti one are visible

[1] R. Fontana, M. Barucci et al. Interpretation of fine art's analyses in diverse contexts (2014) pp. 5-16. ed Academy of Fine Arts in Prague, revievew. ISBN: 978-80-87108-48-2

[2] C. Ruberto, A. Mazzinghi et al., Microchemical Journal 126, 2016, 63-69

[3] F. Bandini, G. Lanterna et al., OPD restauro 26, 2014, 14-34

Analytical and Technological Investigation of the Paintings and other Decorative Elements of the Holy Aedicule of the Holy Selpuchre in Jerusalem

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The Holy Tomb of Christ, according to Christian tradition and belief, is placed within the Holy Aedicule of the Holy Selpuchre Complex in Jerusalem. The Holy Aedicule has undergone many construction and restoration phases throughout its two millennia history. The latest restoration was undertaken by architect "Kalfa" Komnenos in 1810 after a destructive fire in 1808 [1]. The deformation of the Holy Aedicule demanded immediate actions to ensure its structural integrity and preserve the values interconnected with the tomb of Christ, ultimately aiming towards a sustainable rehabilitation. A study was conducted by the NTUA Interdisciplinary Team for the Protection of Monuments headed by Prof. A. Moropoulou, after initiative of his Beatitude, Patriarch of Jerusalem, Theophilos III. Based on the study results, a Common Consensus Agreement, for the first time after 200 years, was reached among NTUA, the Greek Orthodox Jerusalem Patriarchate, the Franciscan Custody of the Holy Land, and the Armenian Patriarchate in Jerusalem.

Within this context, and during the diagnostic study that incorporated the investigation of the preservation state of all the building materials of the monument, in order to plan, suggest and apply compatible and sustainable conservation interventions to reveal and preserve the monument's values, paintings and other decorative elements were studied. The aim of the study was the identification of pigments and their substrate components, the investigation of the employed production and application technologies, as well as the evaluation of the materials preservation state. The analysis was carried out using the non destructive techniques of Fiber Optics Microscopy (FOM) and Micro Raman Spectroscopy in situ, whereas Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS), along with Fourier Transformation Infra-Red Spectroscopy (FTIR) and X-ray Diffraction (XRD) were used in lab on samples collected from the areas under investigation.

The wall painting depicting the Myrrhbearers, Angels Michael and Gabriel, as well as Virgin Mary, located at the Holy Tomb Chamber; the paintings of the outer and inner cupolas of the onion dome that crowns the Holy Aedicule structure; as well as decorations on the stone architectural surfaces of the monument's internal and external façades, comprise the investigation areas. In all the examined cases mineral pigments like lead white, ochre, hematite, orpiment etc were identified, whereas the bedding mortars of the paintings are of calcite matrix reinforced by hair/fibers and straws. Moderate to poor preservation state is diagnosed and traditional technologies, widespread in the Middle East during the 19th century, appear to have been employed.

[1] M. Biddle, The Tomb of Christ, Sutton Publishing Limited, ISBN 0-7509-1926-4, 1999.

On-site analysis of paintings by means of portable XRD

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We have been developing a portable powder diffractometer suitable for the on-site analysis of cultural heritage. Identification of paint components requires structural information, in addition to the chemical composition. Powder diffraction analysis is especially useful for the analysis of paintings, because paints often contain inorganic pigments. We already reported analysis with a preliminary model of this device, a θ–θ diffractometer based on a Cu X-ray tube and an SDD detector that allows measurements in reflection mode with XRF function, at the Rijksmuseum in 2015. We have revised the software and diffractometer to decrease the minimum 2θ angles from 30 to 25°. This new diffractometer, along with portable μ-Raman and UV-VIS spectrometers, was brought to Amsterdam with the purpose of analyzing paintings at the Rijksmuseum. The diffractometer is optimized for on-site analysis. It is easily transportable because of its light weight (only 5.5 kg). The X-ray beam size is 2 mm in diameter. XRF can be done at the same spot using the same instrument.

The analyzed paintings were *Portrait of Marten Soolmans* (Rembrandt, 1634), *Portrait of Oopjen Coppit* (Rembrandt, 1634), *Adoration of the Magi* (Garofalo, 1530s), *Judith and Holofernes* (Jan de Bray, 1659), *Festoon of Fruit and Flowers* (De Heem, 1660-70), and *Still life with Fruit and a Lobster* (Copy after De Heem, 1640-1700?). For measurements in the conservation studio, the painting was placed on an easel and the diffractometer was placed on a lab jack on a Z-stage to adjust the distance to the painting.

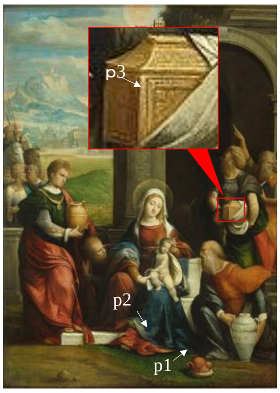

Figure 1. Analyzed points

The most unusual discovery is the possible identification of Egyptian blue in *Adoration of the Magi* (Fig. 1). Fig. 2 shows the diffraction data of the blue pigment at spot p1 of Mary's blue dress[1]. This is in agreement with the strong fluorescence peak excited by red light (632 nm) (Fig. 3). It is very rare to see Egyptian blue in 16thC paintings. It is said that following the collapse of the Roman Empire, the use of Egyptian blue declined sharply and from about 800 AD virtually disappeared from art [2]. An exception is reported in a painting from 1524 by Benvenuto, a contemporary of Garofalo, and also from Ferrara [3]. Another interesting result is the possible presence of lead tin antimony yellow in *Still life with Fruit and a Lobster*, while lead-tin yellow is used in Festoon of Fruit and Flowers, since the first-mentioned painting is considered a later copy after De Heem. These observations may be consistent with a transition of the use of yellow pigments with time. Lead-tin yellow is replaced by yellow lead antimony pigments in the 18th C.

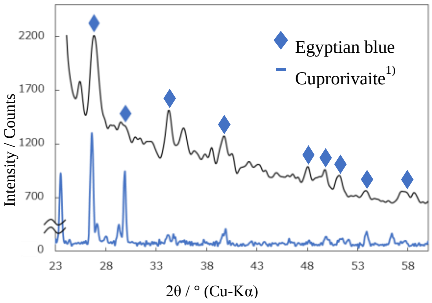

Figure 2. XRD result with reference data [1]

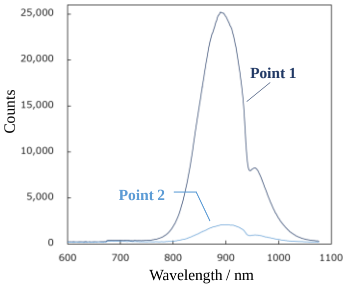

Figure 3. Fluorescence spectrum

[1] Y. Abe, et al., Anal Bioanal Chem, 395, 1987 (2009).
[2] P.McCouat, J. Art Soc.(2017) http://www.artinsociety.com/
[3] Bredal-Jorgensen et al, Anal Bioanal Chem 401, 433(2011).

The use of smalt in Rembrandt's *Homer* – new research combining MA-XRF, quantitative microanalysis, paint reconstructions and OCT

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In the NWO Science4Arts *ReVisRembrandt* project (2012-2018), novel chemical imaging techniques are being developed and applied to the study of Rembrandt's late paintings in order to gain a better understanding of his late experimental painting technique [1]. One of the unique features in his late paintings is his use of excessive amounts of smalt, a cobalt glass pigment, often in combination with lakes, earth and black pigments [2, 3]. Since most of these smalt paints have discolored over time, we can now only guess how these paintings may have looked like originally and what the role of smalt was in these paints.

Figure 1. Cobalt

This paper will report on various new aspects regarding the use of smalt in Rembrandt's *Homer* (1663), Royal Picture Gallery Mauritshuis The Hague [2]. Since its last conservation treatment in 2005/06, the painting has been scanned with MA-XRF. The resulting elemental distribution maps of Co/Ni/As/K, associated with smalt, were correlated with the cross-sections from 2005/06. This provided new information about the use and distribution of smalt in this painting. To investigate the role of smalt in the pigment mixtures, paint reconstructions were carried out based on the pigment proportions calculated from the cross-section analyses using ImageJ. We compared the effect of different percentages of smalt on the overall color, the drying properties, translucency and texture of the paint. The paint reconstructions were evaluated with the help of color measurements and drying tests. Furthermore, Optical Coherence Tomography (OCT) was used to determine the translucency and stratigraphy of the paints.

[1] P. Noble, A. van Loon, G. Van der Snickt, G, K. Janssens, M. Alfeld, J. Dik, Preprints ICOM Committee for Conservation 17th Triennial Meeting, Melbourne, 15-19 September 2014.

[2] A. van Loon, P. Noble, J.J. Boon, Preprints ICOM Committee for Conservation 16th Triennial Meeting, Lisbon, 19-23 September 2011.

[3] A. Roy, Rembrandt: approches scientifiques et restaurations, Technè 35, 2012, 6-13.

Jan Davidsz. de Heem: a technical examination of fruit and flower still lifes combining MA-XRF scanning, cross-section analysis and technical historical sources

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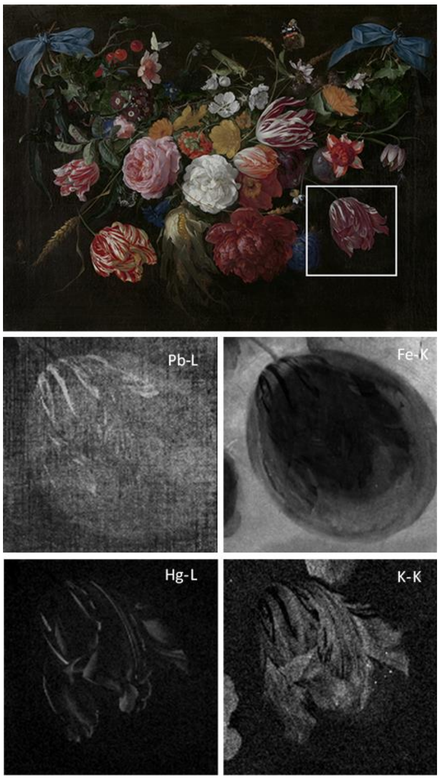

This work discusses the technical examination of five flower and fruit still life paintings by the seventeenth century artist Jan Davidsz. de Heem (1606-1684). The painter is known for his meticulous composed and fine detailed still life paintings and is a master in imitating the surface textures of various fruits, flowers, and objects. Macro X-ray fluorescence (MA-XRF) scanning experiments provided information on the distribution of key chemical elements present in painting materials and made it possible to recapture evidence of the different phases and their sequence in the artist's refined working method: from the application of colored ground layers, to the typical underpaintings, and finally, the superposition of multiple paint layers in the working up of the paintings. SEM-EDX analysis of a limited number of paint cross-sections confirmed and complemented the chemical images. In addition, the results from this technical examination were compared with seventeenth century recipes and paint instructions, in order to obtain a better understanding on the relation between written sources and the actual painting technique of Jan Davidsz. de Heem.

Amongst other practices such as the combination of a blue copper pigment with yellow lakes to obtain the well-preserved deep green colors of the foliage, chemical imaging visualized in great detail de Heem's practice of applying abstract patches of underpainting. After indicating the overall shapes of the composition (e.g. the curved form of a garland), the artist applied oval underpaintings in monochrome colors (such as lead white, vermilion or ochre) below the main flowers. These opaque egg shapes, usually exceeding the outline of the final subjects, did not only mark the position of the flowers but also served as a dead layer shining through superimposed glazes. Apart from degraded orpiment, this sophisticated modus operandi resulted in intense and particularly permanent colors that still look exceptionally fresh today. Apart from this, this interdisciplinary approach uncovered additional new information on de Heem's artistic practice and demonstrated the complementarity of the methods employed.

A New Innovative Sampling Technique for Analysis of Microorganisms on Angkor Temples in Cambodia

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The temples of Angkor monuments including the most famous Angkor Wat, and Thom and Bayon in Cambodia and surrounding countries were constructed with sandstone exclusively. They show severe deterioration caused by physical, chemical and biological processes and, among them, the active growth of microorganisms on the sandstone surfaces leading to biodeterioration cannot be ignored, but knowledge on the microbial community and composition of the biofilms on the sandstone is not available from this region. This study investigated the microbial community diversity by examining the fresh and old microbial biofilms on the sandstone bas-relief wall surfaces of the Bayon temple by analysis of 16S and 18S rRNA genes-PCR amplified sequences. An innovative sampling procedure used in this study allow non-destructive sampling at a specific location using adhesive tape for more than 30 times. A comparison of the microbial communities showed that the bacterial (prokaryotic) community of old and fresh biofilms was very similar, but the eukaryotic communities were distinctly different between them. This information illustrates the dynamic processes of formation and succession of microbial communities on sandstone in tropic region.

Because biofilms are detrimental to the bas-reliefs engraved on the surface of sandstone, information about the microbial community is indispensable to subsequent control of biofilm colonization. The non-destructive sampling of biofilms with different colors revealed novel bacterial groups of predominantly Rubrobacter in salmon pink, Cyanobacteria in chrome green, Cyanobacteria and Chloroflexi in signal violet, Chloroflexi in black gray, and Deinococcus-Thermus, Cyanobacteria, and Rubrobacter in blue green. Multiple samplings at selective locations by layers over depths with adhesive sheets of a thick biofilm revealed a stratified structure: the blue–green biofilm associated with serious deterioration was very rich in Cyanobacteria near the surface and Chloroflexi in deep layer below. In addition, nitrate concentrations were high where the blue–green biofilm was apparent. The characteristic distribution of bacteria at different biofilm depths provides valuable information on not only the biofilm formation process but also the sandstone weathering process under the tropical climate conditions.

Ammonia-oxidizing archaea (AOA) amoA gene was amplified and investigated from Bayon temple, Angkor Thom. The results confirmed the detection of three large clusters, namely the Soil/Sediment, the Nitrososphaera gargensis, and the Water Column/Sediment. Obtained sequences fell into all three clusters and most of the clones were in the Soil/Sediment cluster. The diversity of AOA amoA gene in Bayon was significantly high, indicating their contribution to production of nitrate from ammonia. AOB amoA gene-based PCR primer failed to generate any target DNA fragment bands after PCR amplification. AOB 16S rRNA gene was then used to amplify and detect AOB existence and abundance. AOB in all of the three samples from Bayon were much lower than AOA. The information collectively suggests that microorganisms are widely present on surface of sandstone temples and they are responsible for the different colors on surface, and their activity is responsible for biodeterioration through nutrient cycling.

[1] Kusumi A et al., 2013. *Microbs Environ*. 28, 422-431.

A comprehensive study of the effects induced by brown rot fungi on archaeological waterlogged wood

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The archaeological site of Biskupin (Poland) is a prehistoric settlement dating to the 8th century BC, situated on a marshy island. Excavations started in 1934 and a considerable amount of wooden artifacts was found sunken in the water of the lake. Unfortunately, during many years of archaeological excavations, wooden remains deposited in the trenches were exposed to degradation process and underwent decomposition. Among the main causes of wood degradation, fungi and bacteria were the most destructive ones.

The chemical effects induced by fungi and bacteria on wood are not well known or studied. For this reason, we present here a study of a set of wood samples (*Pinus sylvestris*) buried in the Biskupin site, reproducing the burial conditions of the original archaeological wood. The samples were then removed from the burial environment after 4, 6, 8 and 10 years of deposition in two monitoring stations (wet peat and lake water). After removal from the burial, the samples were exposed to laboratory controlled attack by a brown rot fungus *Coniophora puteana.* The final aim was to evaluate the effects of fungal activity on the wood substrates with different degrees of natural degradation. The study is part of an experimentation designed to evaluate the short-time effects of the *in situ* conservation strategy adopted for the Biskupin archaeological woods.

Various techniques were used to assess the physical and chemical degradation of the wood. Physical properties, such as moisture content and conventional density were determined on the basis of the mass of absolutely-dry wood and the volume of the sample in the state of maximal saturation. An attempt to distinguish between the morphological changes induced by the fungal attack and by the exposure to the burial environment itself was carried out through scanning electron microscopy (SEM) examination of the transverse, radial longitudinal and tangential longitudinal sections of the samples The chemical state of preservation was evaluated by using infrared spectroscopy (FTIR) and analytical pyrolysis coupled with gas chromatography and mass spectrometry (Py-GC/MS) with *in situ* silylation. All the results were compared with those obtained for reference materials, including sound pine wood and contemporary and archaeological pine wood attacked by *Coniophora puteana.*

6.2 PARALLEL SESSION B

A novel methodological approach for the assessment of surface cleaning of acrylic emulsion paints

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A successful protocol for surface cleaning of acrylic paintings aims to remove dirt without compromising the integrity of the original painted surface. This has proven to be a challenging task in terms of the effectiveness of the cleaning agents, as well as concerning the proper evaluation of the efficiency and degree of invasiveness of the cleaning treatment. So far, the research carried out on the cleaning assessment has mainly focused on the examination of the paint surface and the detection of changes occurring after treatment, the analytical characterization targeted mostly towards modification of water soluble components, like the polyethoxylate type non ionic surfactants, and pigments on the paint surface [1, 2].

In the present study a novel methodological approach was followed for an integrated assessment of the treatment of acrylic emulsion paintings using various cleaning agents. This was achieved through the analysis of the cotton swabs used for the cleaning tests by Pyrolysis – Gas Chromatography / Mass Spectrometry (Py-GC/MS). A simultaneous detection of all the main organic components of the acrylic emulsion paints - binder, surfactant, and pigments -, possibly removed during treatment was carried out. Furthermore, Scanning Electron Microscopy (SEM) was applied in order to document changes occurred on the surface morphology before and after cleaning treatment.

The experimental protocol included samples prepared in films, using acrylic paints from two commercial brands (Liquitex and Rembrandt) based on four organic pigments (PY3, PR264, PB15 and PG7). Samples of the paints were subjected to accelerated thermal ageing and artificial soiling. Seven cleaning agents were chosen for the cleaning tests including aqueous systems with buffered water and chelating agents of ethylenediaminetetraacetic acid (EDTA and triammonium citrate (TAC), water in oil sorbitan-based microemulsions, and a pickering type emulsion based on Velvesil Plus.

With the aim of integrating the information obtained from the macroscopic assessment of the cleaning tests with the Py-GC/MS results, a statistical analysis was carried out. Thus, it was possible to correlate the degree of soil removal and the aesthetic appearance of the paint surface after cleaning with the extraction of paint components. The results of the present study are expected to contribute to the development of safe and reliable cleaning protocols for acrylic paintings.

[1] B. Ormsby, E. Kampasakali, C. Miliani, and T. Learner. e-Preservation Science 6, 2009, 186.

[2] E.A. Willneff, S. LM. Schroeder and B.A. Ormsby. Heritage Science 2 (25), 2014,1.

Insight on colour change and chemical alteration of green copper-based organometallic painting pigments

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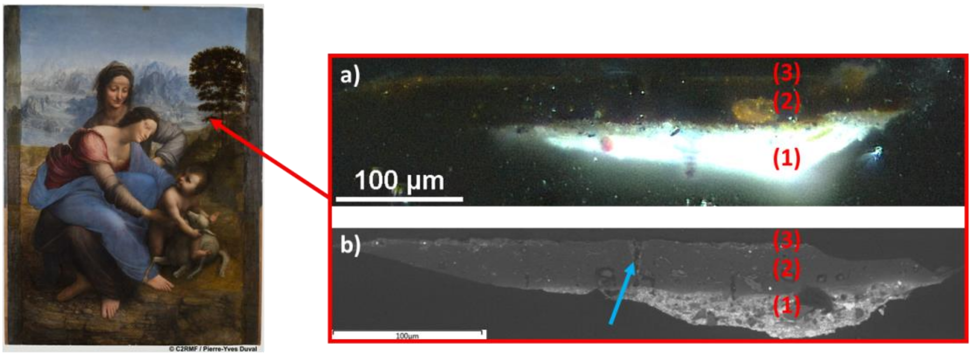
Green copper organometallic pigments (verdigris and copper resinate) were widely used in easel paintings from the 15th to 17th centuries, for their advantageous optical properties. However they often undergo chromatic modification, manifesting as a browning or a darkening of the green layers as the painting ages. It is important for painting conservation issues to understand the alteration mechanism of this phenomenon.

In a recent work, a darkening mechanism has been proposed. Degradation would be caused by ligand-to-metal charge transfer induced by light and the formation of peroxy-Cu complexes under atmospheric O2 [1].

The objective of the present work is to validate this mechanism by analyzing complex and multi-layered samples taken from historical masterpiece paintings. A set of complementary analytical techniques are used. Cross-sections from paintings are observed by optical microscope and FEG-SEM/EDX to study the evolution of alteration along time, the repartition of copper in altered/non altered areas, and the potential incompatibility of green copper organometallic pigments with other pigments (such as lead white or lead-tin yellow). The influence of the organic matrix on the alteration is investigated by UV-visible fluorescence, using both conventional and synchrotron sources. Raman and FT-IR microspectroscopy measurements provide structural information on organometallic pigments and binder. Furthermore portable UV-visible spectroscopy is also used on paintings under restoration to collect data on the alteration products without sampling. EPR analyses are performed to follow the transformation of the Cu-complex structure during ageing.

Results obtained on complex paintings are compared to the ones gathered on model samples (verdigris/resinate mixed with raw/cooked linseed oil). Analyses of historical samples reveal that alteration develops along cracks within the pictorial layers, from surface to depth, reinforcing the hypothesis of O2 diffusion. Simultaneous presence of copper green and other pigments does not seem to influence the darkening of the green layers. The binder plays an important role on the alteration of copper pigments, because their reactivity depends on the unsaturation degree of oil.



Left: *Sainte Anne*, Leonardo Da Vinci (1508-1510) – Musée du Louvre, Paris
Sample taken from the foliage of the tree (red arrow)
Right: a) Optical microscope image of the sample cross section
(3) Thin yellowish layer (earths, lead white, copper)
(2) Altered green layer (copper acetate, quartz, a few grains of earths)
(1) Blue-white layer (lead white, lapis lazuli)
b) FEG-SEM/EDX image of the sample (blue arrow shows the crack in the pictorial layer from which the darkening progresses)

[1] C. Santoro et al. Applied Physics A. 114, 2014, 637.

Elucidating Daguerreotype Degradation By Surface Species Formation Using Surface Plasmon Resonance Scattering Spectroscopy

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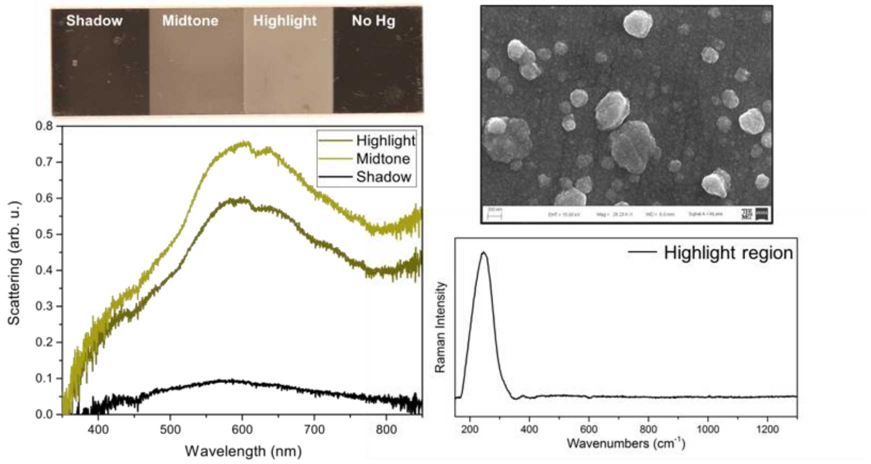
The nanostructured silver-mercury or silver-mercury-gold daguerreotype image is particularly reactive and prone to degradation by tarnishing, oxidation, and photodamage.[1-3] Treatment protocols to reverse existing signs of degradation have all but halted, as many historical efforts to clean daguerreotypes have been shown to promote further damage.[4] Conservation efforts are complicated by a lack of understanding of the composition and reactivity of the nanostructured surface that forms the daguerreotype image. Numerous studies over the past few decades have identified various surface species and have partially elucidated the mechanisms by which they react;[4-5] however, many questions remain unanswered. Using angle-dependent scattering spectroscopy, we have developed a protocol to measure nanoscale changes of the daguerreotype surface using the localized surface plasmon resonance (LSPR) of the Ag/Hg image particles, which are extremely sensitive to changes in their composition and dielectric environment. Studying spectral shifts in the LSPR of the image particles upon controlled exposure to environmental elements such as humidity, oxygen, chlorine, and sulfur provides further insight into image deterioration occurring from surface reactions. This method has been combined with other spectroscopic methods, such as Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, and scanning electron microscopy- energy-dispersive X-ray spectroscopy (SEM-EDS) to offer a more complete view of daguerreotype degradation at the nanoscale level. Until we have a comprehensive understanding of how daguerreotypes interact with their environment, these images remain in peril of irreversible damage.



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[2] S.A. Centeno, F. Schulte, N.W. Kennedy, A.G. Schrott, Appl. Phys. A 105(1),2011,55.

[3] P. Ravines, R. Wiegandt, C.M. Wichern, Surf. Eng. 24 (2), 2008, 138.

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[5] S.A. Centeno, T. Meller, N. Kennedy, M. Wypyski, J. Raman Spectrosc. 39(7), 2008,914.

Analytical challenges in studying degradation processes in paintings: ultramarine disease

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Ultramarine is a highly-valued, brilliant blue pigment naturally obtained from the mineral lazurite, which is the main component in the semi-precious stone lapis lazuli. Extracted from its accessory minerals, this natural pigment has been used across many cultures for over a thousand years and was eventually produced synthetically in the early 19th century. Used as an oil paint, ultramarine is observed in some instances to cause a degradation phenomenon known as "ultramarine sickness" or "ultramarine disease." Our research is interested in understanding the mechanism of ultramarine paint degradation and identifying markers that point to the onset of such degradation. We hypothesize that "ultramarine sickness/disease" is the result of accelerated oil degradation catalyzed by ultramarine (or lazurite), as it is a member of the zeolite class of minerals, which are commonly studied catalysts. The activities of zeolites are highly dependent on composition and structure, therefore, we suspect that pigment treatment—known by historical literature to have been varied—will influence the rates of aging reactions and possibly the resultant products. We study simplified model systems, as the degradation of oil paint is known to be a complex process involving a variety of possible reactions of differing time scales and a range of possible reaction products of varying concentrations. Using ultraviolet-visible spectrophotometry (UV-Vis), nuclear magnetic resonance spectroscopy (NMR), Fourier transform infrared spectroscopy (FTIR) with attenuated total reflectance (ATR), and electrospray ionization mass spectrometry (ESI-MS) in combination, we can evaluate product formation and determine reaction rates of key aging and degradation reactions. In this study, we monitor the oxidation and crosslinking of ethyl linoleate—a model component for linseed oil—as well as the subsequent degradation of the resulting crosslinked films in the presence of differently-treated ultramarine and commercial zeolites to determine the influence of pigment treatment. Challenges lie in the experimental design as we must overcome the slow kinetics of real-life paint systems. In addition, low yields of complex and unknown degradation products demand optimizing current methodology to ensure we have high sensitivity and low detection limits along with time resolving capabilities. To our knowledge, we are the first to intricately investigate the differences in these products, inclulding their rates of formation, as influenced by subtle variations in the preparation of ultramarine. Through such models we hope to gain an understanding of the role that ultramarine, and its preparation method, plays on the key reactions involved in the aging of oil paint.

Combining synchrotron photoluminescence imaging and microspectroscopy to study zinc white degradation in oil paint

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Zinc white (ZnO) has been commonly used as a white pigment in oil paints from the second half of the 19th century up until present day. Initially introduced as a less toxic alternative to lead white, zinc white oil paints were later found to give rise to a range of degradation phenomena [1, 2]. One critical phenomenon that has the capacity to both affect the visual appearance of a painting and severely influence the structural integrity of the paint is the formation of zinc soaps. Despite the reaction between metal oxides and free fatty acids being known since ancient times, the study of zinc soap formation and aggregation in art has only been described in the past two decades [2-4].

It has previously been shown that different manufacturing processes of zinc white can result in differences in reactivity, as well as the exhibition of clearly distinguishable photoluminescence spectra [2, 5]. In this study, we aim to elucidate this relationship by exploring a unique combination of synchrotron deep-UV photoluminescence imaging and microspectroscopy, as a high-resolution analysis technique for historical cross-sections and various model systems.

A full-field imaging set-up has been developed and employed to capture and spatially resolve the luminescence emitted by cultural heritage samples. With a lateral resolution of a few hundred nanometers, this technique allows to spatially resolve the luminescence of single zinc white pigment particles, and the different chemical phases within highly heterogeneous degraded areas. Segmenting the emitted luminescence into nine spectral bands, ranging from the deep-UV to the near-infrared, allows for new ways to highlight the spatial distribution of various chemical constituents. The complementary microspectroscopy set-up utilizes a micro-focused synchrotron excitation beam, which is scanned over the sample surface to induce luminescence. At each point an emission spectrum is recorded in a semi-confocal configuration, yielding a 2D hyperspectral map. Using this set-up, it is possible to supplement high spatial resolution imaging data with complementary high-resolution spectral data.

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Influence of lead white and cobalt blue on the degradation of Eosin lakes

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One of the main problems in the preservation of paintings is the fading of the original colors due to the light exposure. This fact is clearly evidenced in some of Vincent Van Gogh's paintings where an organic red pigment is detected: Eosin or geranium lake. This pigment was used by 19th century artists such as Vincent Van Gogh (1853-1890) or Paul Gauguin (1848-1903) due to its wide variety of possible hues, depending upon the metal used in the precipitation, which ranges from an orange-scarlet to bluish-red [1]. Both artists started to notice the discoloration in some of their paintings already several months after finishing them due to the marked tendency of Eosin to fade upon light exposure [2, 3].

The identification of Eosin and the characterization of its degradation products in paintings represents a challenge because of (i) the low concentration remaining after the aging time, (ii) the difficulty in obtaining samples for analysis, and also (iii) the different behavior when Eosin is combined with organic or inorganic pigments, binding media or varnish.

This study presents an accelerated ageing experiment of paint models in order to elucidate the discoloration process and evaluate the influence of different pigments (lead white and cobalt blue) on the lightfastness of Eosin. Cobalt blue and lead white have been detected in combination with Eosin [1]. Three different metals were used as substrates to precipitate the eosin lakes following 19th century recipes.

Paint model samples were prepared using different ratios of Eosin, lead white and cobalt blue and were characterized with several techniques before and after ageing. The influence of pigment ratios on the discoloration process was monitored by colorimetric measurements via reflectance spectrophotometry. FTIR-ATR spectroscopy was used to characterize the degradation of the binding media and provide information related to chromatic changes after the ageing process. Cross sections were characterized by optical and electron microscopies in order to observe the discoloration of the pigments and record the bromide distribution along the examined section.

Analysis of the paint models showed that the fading process due to the light exposure is limited to the top layer and clearly revealed the influence of lead white and cobalt blue on the discoloration process of Eosin. The color changes observed in the model samples can be related to the actual discoloration visible in some of the paintings of Van Gogh.

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Blanching of paint and varnish layers: from the characterization to the development of conservation treatments

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Blanching of easel oil paintings is a recurrent alteration induced mainly by humidity. It can affect varnish and/or paint layers. Depending on the degree of alteration, the paint composition can be hidden partially or totally by a whitish haze and current conservation treatments (solvents application and varnishing) are not satisfactory. The aim of the present work is to characterize the alteration, understand the physico-chemical phenomena involved in its emergence and propose an adapted, efficient and durable conservation treatment.

Our observation of circa 50 altered and unaltered micro-samples by FEG-SEM revealed a highly porous structure in both varnish and paint altered layers [1]. For the blanching of paint layers, deeper investigations performed by X-ray phase contrast nanotomography on the new nano-imaging beam line ID16A-NI at the ESRF highlighted that pores are located in the binder. Therefore the degradation processes take place in the organic matter [2]. Since the pore size is ranging from 50 nm to 4 µm, the Mie light scattering theory explains the blanching appearance, what was corroborated by computational modeling (resolution of the radiative transfer equation by the 4-flux model) [1, 3].

To identify the physico-chemical phenomena involved in the pore formation, the alteration dynamics was followed during 12 to 22 hours by small angle neutron scattering at the ILL. It evidences that the water diffusion is progressive (Fick's law). Besides, varnishes prepared with turpentine (more polar) are more sensitive to humidity than those prepared with white spirit and the rate of alteration is faster for dammar resin than for mastic resin. Our hypothesis is that the pore formation is induced by the micro-segregation of polar regions and cations during the hydration.

Conservation treatments will be efficient and sustainable only if they resorb or durably fill the pores, in order to reduce the light scattering. The inefficiency of current conservation treatments has been shown by X-ray phase contrast nanotomography. A new treatment based on a highly viscous perfluoropolyether has been developed and tested on mock-ups of varnish and paint blanched layers. The first results are very promising in terms of efficiency, reversibility (analyses by X-ray absorption microtomography) and short-term stability (one year of natural ageing). Moreover, the product has the advantage of being completely safe for conservators. Its long-term stability (artificial ageing) as well as its efficiency on ancient paintings are currently under study. These results will undoubtedly have a major impact, fullfilling a real requirement for the conservation of blanched easel oil paintings.

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Role of defects in the reactivity of Cd-yellow

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The cadmium yellow paints used in impressionist and modernist paintings in early 1900s are undergoing several deterioration processes, including whitening and discoloration. The origins of such chemical and physical alterations are still under debate. The presence of structural defects and impurities like Se and Mn in CdS, may play a role in the degradation process. In general, their presence in the pigment alters the electronic structure by creating shallow and/or deep levels in the gap. When, particularly, the surface contains such defects we notice an enhancement of the reactivity in terms of adsorption of external agents (oxygen, water ...).

We present a combination of theoretical ab initio simulations and photoluminescence spectroscopy on commercial CdS samples to interpret the presence of observed deep levels in the gap and a preliminary study of the influence of impurities in the complex mechanism of cadmium yellow deterioration.

PL spectroscopy has been performed on hexagonal CdS-based pigment by employing a compact spectrometer and UV-laser excitation focussed in a circular spot of 1 mm in diameter on the sample surface. All the calculations are performed within the framework of the Density Functional Theory (DFT) in the Generalized Gradient Approximation (GGA-PBE) with the use of ultrasoft pseudopotentials.

Design of Experiments – Investigating the effect of paint formulation on degradation rates of TiO_2-based oil paints

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Design of experiments (DoE) is a statistical tool commonly used in industry to, among others, understand the effect of the formulation of paint on its properties such as viscosity or gloss. DoE allows to investigate the effect of multiple factors, while keeping a manageable number of samples. It is generally considered more efficient and robust than the OFAT (one factor at a time) method. One great benefit of the DoE method is the ability to investigate not just separate factors but also more complex interactions that can occur in paint [1, 2]. Research into many aspects of artist's paint degradation require 'model samples'[1] in addition to observations done directly on paintings. In this work we present an example for the use of DoE in the investigation of the degradation rates of TiO_2-based oil paints.

Titanium white paints exist in a wide range of formulations [3], not only the formulation varies but also the quality of the separate components. The quality of the titanium dioxide (TiO_2) component [4] and its interaction with other paint components is expected to have an important influence on the degradation rate of these paints under UV exposure.

We carried out three designs focusing on: i. the effect of photocatalytic TiO_2, photostable TiO_2, ZnO and their relative amounts in mixtures, with or without aluminum stearate (A); ii. the effect of fillers $CaCO_3$ and $BaSO_4$ mixed with photocatalytic TiO_2 (B); and iii. the effect of TiO_2-type (C); on the degradation during UV exposure. The degradation is evaluated by the change in gloss, which eventually leads to chalking[2] [4].

Initial analysis of the results illustrates that degradation rates are, as expected, strongly determined by the paint formulation and that interactions may be more complex than initially assumed. *DoE-A* indicates that a linear model describes the design space when aluminum stearate (categorical factor) is excluded. Within this model we can predict among others the initial gloss of a paint and which paint formulations are likely to chalk. Interestingly, when this reactive component is included in the mixture, the design space can no longer be properly modelled. This indicates either that complex reactions are taking place or that uncontrolled experimental parameters that were not included as a factor in the design, play a significant role. This study shows the potential of DoE and challenges that can come up when working with it; such as the importance of building the proper design and what aspects to take into account during execution and analysis of the design. With this in mind, DoE may support and improve future model studies to better understand, predict and prevent degradation of cultural heritage.

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[2] Chalking is the end stage of photocatalytic degradation where the pigment appears unbound at the paint surface due to binder degradation.

Portable non-destructive handheld Mid-infrared FT-IR analysis of three diverse antiquities for spectral analysis combined with multivariate chemometric analysis and assessment of potential benefits in art cultural heritage studies

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The primary aim in art conservation is to extend and prolong the aesthetic life of an object or artwork. This is often complicated when the exact materials used to create the object are unknown, previously the use of diamond ATR was successfully used for the positive material identification of a range of historical and common polymers including nitrocellulose based semi-synthetics which pose a potential fire hazard if stored inappropriately [1]. More recently, the non-destructive authentication of canvas grounds from the reverse face using handheld FTIR and the diffuse reflectance interface has enabled a team of talented Italian researchers to classify and discern 16 types of ground formulations spanning the 14th-19th Century [2].

One of the current challenges for all involved in art conservation, whether a small private collector or a world renowned museum, is the issue of condition assessment combined with on-going monitorisation combining material identification, authentication and environmental storage [3]. To address this, we have developed an application to examine and assess three different art pieces leveraging the adaptability of the Agilent Technologies portable FTIR system and using the most appropriate external reflectance accessory to guarantee non-destructive and orientationally ambivalent spectral analysis. The three items are a large batik painting (6m x 2m), glass framed canvas painting and a salvaged shipwrecked pottery bowl. The spectral examination was combined with chemometric analysis techniques enabling spectral segmentation by condition and area. With this application study for portable FTIR we have demonstrated that such systems are a suitable tool to identify, authenticate & monitor the artwork, enabling archivists of all levels to tailor storage conditions to suit the artwork question.

Figure 1. Author and colleague non-destructively collecting FTIR diffuse or specular reflectance spectra with the 4300 Agilent Technologies FTIR for a variety of art objects. Spectral collection time 25 seconds.

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Characterization and provenance study of Pompeian red and yellow ochre pigments

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The study of old pigments can provide useful information about the ancient practices and cultures, for example the origin of the source materials to obtain the raw pigments and the trading routes of them. In this work, an elemental and molecular characterization and provenance study of three yellow ochre and four red ochre raw pigments recovered from the burial of the archaeological site of Pompeii were performed. For the elemental analysis, micro energy dispersive X-ray fluorescence (μ-ED-XRF) was employed and for the molecular characterization, X-Ray Diffraction (XRD) and Raman spectroscopy were used. For the study of provenance of these pigments, lead isotopic ratio analysis was performed.

The obtained elemental results showed considerable concentrations of W and Sn in two particular red ochre pigments. These high levels agree with the ones of the hematite ores present in the Elba Island (Tuscany, Italy) [1], pointing out the possible use of these ores to prepare these two analyzed raw red ochre pigments. Apart from W and Sn, all the analyzed red ochre pigments showed higher concentrations of As and Sb than the yellow ochres. The higher presence of As in red ochres could suggest its provenance from the oxidation zone of an iron sulfide (FeS) deposit [2]. Ores from Elba Island have FeS [1], suggesting once again their provenance from this island. Moreover, the Principal Component Analysis (PCA) performed using the net counts of the elements detected by μ-ED-XRF (at 1 mm lateral resolution) showed similarities between two red ochre pigments chracterized by W, Sn, and As, among others, and between the yellow ochre pigments with Al, Si, K, Mn and Rb as characteristic elements. The additional two red ochres showed also similarities between them with Cl as the characteristic element. Therefore, this statistical analysis based on the obtained results of elemental composition results allowed a clear discrimination between both colors and the possible different origins of the red ochre pigments. Nevertheless, to confirm this hypothesis and therefore to study the provenance of all the ochre pigments under study, lead isotopic ratio analysis was performed.

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Real-time diagnosis of collagen-based artworks by thermal shrinkage imaging

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Collagen, the major fibrous protein of skin, provides structural support, chemical and mechanical stability of skin-derived materials, i.e. parchment and leather. During time it can become altered as a result of a range of environmental factors such as light, humidity, mechanical, biochemical and thermal stimuli. The collagen degradation plays an important rôle in deterioration progression of historical and archaeological parchment and leather. Therefore, the ability to monitor the effects of environmental factors on parchment and leather *in situ* and the derivation of appropriate qualitative and quantitative parameters for their "health" condition assessment would allow proper control and guidance of the conservation activities and management.

Collagen induced thermal denaturation is a complex process which can be used to study and quantify collagen degradation [1]. Since its impact can be observed throughout the collagen's hierarchical structure, thermal microscopy is an ideal tool for visualizing the shrinkage motion of fibers subjected to a controlled temperature program. To date shrinkage has been evaluated by visual examination using the Micro Hot Table (MHT) method [2]. However, a precise understanding of the relationship between all shrinkage parameters and chemical and physical alterations occurring during collagen degradation are yet to be established. The primary objective of our study was to qualitatively and quantitatively characterize parchment and leather degradation using collagen shrinkage imaging. To this end, collagen alteration in parchment and leather was induced under controlled conditions by accelerated ageing treatments. New, artificially aged and historical samples of parchment and leather were used for measuring the shrinkage intervals and statistic analysis by various ANOVA models (one-way, n-way, factorial, ANCOVA, MANOVA) was performed to determine the most significant ageing-induced variations [3]. Image processing algorithms for the automatic detection of the shrinkage intervals of collagen fibers and software for the automatic diagnostic of parchment and leather were developed [4]. A portable hot table incorporating these intelligent systems has enabled us to deliver real-time diagnosis of valuable historical documents *in situ,* at the Romanian Academy Library in Bucharest, Marciana National Library in Venice and State Archives in Turin. This new diagnostic method is illustrated using some relevant examples, e.g. the testament of Marco Polo.

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Micro-spectroscopy of rock art paintings from the Cueva Mayor of the Atapuerca site (Burgos, Spain)

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The Atapuerca archaeological complex in Spain, a UNESCO World Heritage Site, is considered to be one of the 20th century's most important scientific discoveries. Micro-spectroscopic studies of rock art paintings from the Cueva Mayor of this complex have been carried out in order to characterise the composition of the pictorial materials, substrates, accretions, possible signs of deterioration as well as mineral specimens from an iron mine close to the cave in order to ascertain possible sources of the pigments used. In situ and in-lab Raman microspectroscopy (µ-Raman), a powerful tool for this task [1], combined with scanning electronic microscopy and energy dispersive X-ray spectroscopy (SEM/EDX) have been applied for this purpose.

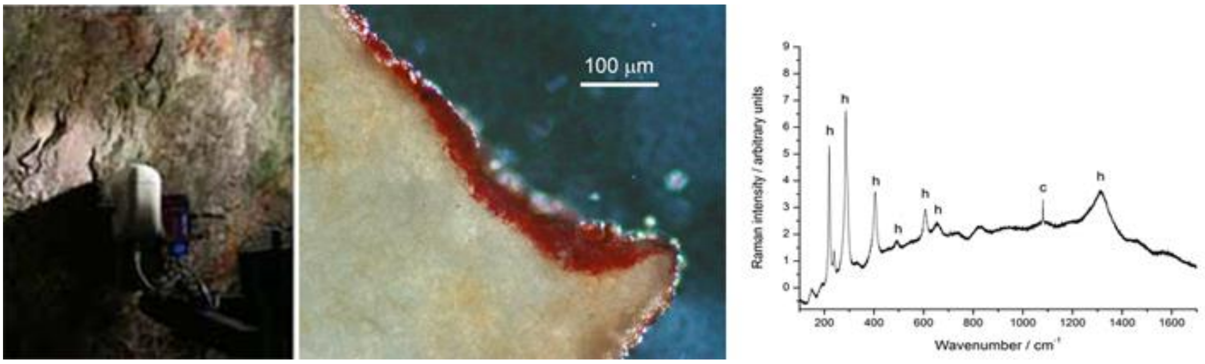

Figure 1. (Left) In situ µ-Raman study of the zoomorphic pictograph from El Portalón of the Cueva Mayor. (Centre) Microphotograph of a cross-section of pigment from this pictograph. (Right) Raman spectrum from a specimen of pigment from this figure showing bands of haematite (h) and calcite (c).

A previous study [2] on the zoomorphic figure from this cave, Fig. 1, is significantly improved by our results. The components of the pigments used in different pictographs of this cave have been definitively identified. Haematite is the dominant component; goethite and amorphous carbon, anatase and -quartz have been detected as additional components of the pigments. Cellulosic fibres impregnated with pigment have also been detected in the zoomorphic figure. Some hypotheses on the origin of fibres are suggested. Calcite is the main component of the substrates. Accretions of biological origin are observed on the surface of some painting panels.

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Non-destructive analysis of Still Bay (>70 ka) pointed artefacts from Sibudu Cave, South Africa

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In South Africa, numerous archaeological sites were found with extensive artefact archives that demonstrate modern human cognitive abilities. Sibudu Cave is an important site located in northern KwaZulu-Natal. It was occupied during a long time period from Pre-Still Bay to Iron Age [1]. Sibudu yielded numerous examples of modern human technology such as bedding constructions [2], preparation of complex mixtures [3-5] and innovative bone [6] and stone technologies [7, 8]. This paper complements the archaeological research performed with optical light microscopy of micro-residue traces on stone tools [9] by providing physico-chemical evidences. Raman spectroscopy and scanning electronic microscopy have been used to confirm the presence of ochre on the Still Bay bifacial tools from Sibudu Cave. Ochre was also detected on areas called brown stains; this showed that different qualities of ochre were utilised for the use process of the tools. Other mineral species were highlighted by Raman spectroscopy such as amorphous carbon and manganese oxides which were not recognised visually by using optical light microscopy.

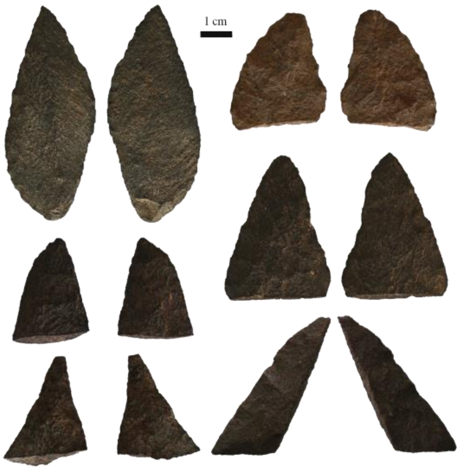

Figure 1. Examples of Still Bay pointed artefacts from Sibudu Cave

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Advanced characterization of new nanostructured stone treatments for the conservation of European Architectural Heritage

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According to the literature, the introduction of inorganic nanoparticles such as SiO2, TiO2, ZnO or Ag in polymeric blends offers different advantages compared to traditional protective treatments. Nanoparticles can help to reduce the surface wettability of treated stone and provide additional properties (photocatalytic, antifouling, antibacterial) [1, 2].

In the context of the EU-Horizon 2020 project "Nano-Cathedral", a set of photocatalytic protective treatments were formulated with different TiO2 nanoparticles, solvents and silane/siloxane systems. The innovative products were applied on 6 lithotypes (Ajarte fossil limestone, Balegem sandy limestone, Obernkirchen and Schlaitdorf sandstones, St. Margarethen calcareous arenite and Apuan marble), selected among the stones used in five medieval cathedrals (Vitoria-Gasteiz, Ghent, Cologne, Vienna and Pisa) and a contemporary opera theatre (Oslo Opera House). The six places are also representative of the different European climates and environments.

The products were chemically characterized by Fourier Transform Infrared micro-spectroscopy (µ-FTIR) and Transmission Electron Microscopy (TEM), in order to evaluate the distribution of nanoparticles in the blends.

In parallel to the assessment of the effectiveness of the treatments applied on stone specimens (capillarity water absorption and static contact angle), the stone surfaces were investigated by Environmental Scanning Electron Microscopy (ESEM-EDX) to evaluate the morphology of the nano-TiO2-based treatments on lithotypes characterized by different mineralogical composition and open porosity. In addition, the stone surface topography and roughness were analyzed on a nanometric scale by Atomic Force Microscopy (AFM) [3].

Finally, in order to evaluate the stability of the pure polymeric matrices and in presence of photoactive TiO2 nanoparticles, an accelerated ageing in solar box was performed. The behavior of the different formulations applied on silicon wafers was verified by means of FTIR spectroscopy.

Only a multitechnique approach allows to characterize the complex system "treatment/nanoparticles/stone substrate", studying the stability of the treatments in parallel with its consolidating/protective efficacy in order to maximize the exploitation of the physical-chemical features that nanocomposites offer.

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The first use of portable Raman instrumentation for the analysis of Patagonian prehistoric rock art paintings: pigments, accretions and substrata

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Archaeometrical studies in Patagonia (Argentina) reveal useful information about the materials used by the population that inhabited the area. The North Patagonian region was occupied by hunter-gatherer populations since the transition between late Pleistocene-early Holocene (at least 10.000 years B.P.) to the last century. When crossing the landscape from West to East, relatively low temperatures (in the Andes region) are found, followed by the wet forest of the mountains, dry steppes and, finally moderate temperatures and humidity of the Atlantic coast. In Patagonian archaeological sites lithic materials, pottery and faunal remains are commonly found, as well as paintings or engravings on rocks, pottery, leather, and textiles. Rock art paintings are relatively common in the Patagonian scenery and thus they play an important role in understanding the population dynamics of local hunter-gatherer groups. [1]

Portable Raman spectroscopy was applied for the first time on rock art paintings, from hunter-gatherer populations, on seventeen sites, in two different environmental regions of Patagonia, the forest at Neuquén and Río Negro and the steppe at Chubut. The selected archaeological sites were examined, revealing the pigments used from the native population. Alteration products and accretions were also investigated to obtain valuable information for a better conservation and preservation of these magnificent works of art. During a single research campaign, sixteen shelters and one cave were investigated which makes this study as one of the most condensed expeditions on measuring rock art paintings. The current research focuses only on the pigments used, accretions and substrata of the rock art paintings and serves as sequel of our previous studies on the evaluation of the use of our portable Raman instrument on the analysis of rock art under extreme conditions in Patagonia, where several improvements were proposed, to maximize the quality of the research [1].

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Investigation on construction materials and their environmental interaction at the Panamanian UNESCO sites

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Two UNESCO sites belong to the Panamanian isthmus. Specifically, on the North coast, examples of military fortifications face the Caribbean Sea: the Fortresses of Portobelo Bay and Fort San Lorenzo (XVII-XVIII cent.); while, on the opposite shore, the first Spanish settlement arises on the Pacific Ocean: the nowadays called Monumental site of Panamá Viejo (XVI cent.) [1,2].

In order to improve the knowledge on the materials characterisation [3,4] and to evaluate the state of conservation related to the environmental impact, specimens sampled at the sites underwent mineralogical-petrographic, physical and chemical analyses (Stereomicroscope, PLM, XRPD, SEM-EDX, XRF, MIP and IC), highlighting at Panamá Viejo, masonries mainly composed of polygenic breccias, tuffites, basaltic andesites, rhyolites and sporadic rhyodacites. Considering Portobelo fortifications, coral limestones and sandstones have been identified as principal building materials, while basaltic andesite has been observed only at Fuerte de San Fernando. Finally, at Fuerte de San Lorenzo, tuffites and grainstones have been detected in the masonries; these latter ones were mainly utilized for realizing corners (as ornamental parts of the portals and the base blocks). Furthermore, potential quarries of raw materials have been identified and sampled, in order to define the provenance of the stones employed in the fabrication of buildings, and to compare the differences between the preservation of the rocks utilized in the masonries with the outcropping ones.

Lastly, this study allowed us to investigate the past, present and future interaction between these materials and the environment, utilizing dose-response functions for evaluating the damages due to the surface recession, salts cycles and biomass growth [5-7].

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New *in situ* non invasive analytical methodology to determinate the state of preservation of prehistoric rock art sites

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A novel *in situ* non-invasive methodology has been tested and carried out to determine the state of preservation of prehistoric rock art pictographs and substrata over a period of time. This methodology was developed within the framework of the multidisciplinary research project "4D · arte rupestre" that has been carried out from 2013 onwards in six rock art sites with Levantine and Schematic rock paintings [1] included in World Heritage List since 1998, under the name of Rock Art of the Mediterranean Basin of the Iberian Peninsula. This project was oriented to the monitoring over time of rock art sites using different approaches to reach a comprehensive control of the deterioration processes that are affecting their preservation. Cutting-edge technologies were used to produce accurate high-resolution 3D models, precise color renditions, huge gigapixel images, remote sensing techniques, enhanced color versions of gigapixel and 3D models, comparison over time of these products (4D), geological and biological analyses, and spectroscopic *in situ* analyses.

The spectroscopic methodology combined different analytical techniques such as a portable Raman spectrometer (RS) and a hand-held energy dispersive X-ray fluorescence (HH-EDXRF) analyzer. The objective was to characterize paintings and substrata in selected points to compare with subsequent analyses in the same points in order to identify any chemical change over that period of time. It was expected that any detected change could provide clues about the alteration processes in every site. This way the methodology could be helpful for preventive preservation decisions.

In this communication an overview of the application of the proposed methodology to post-Palaeolithic Levantine pictographs of Solana Covachas VI (Albacete, Spain) is included. This is an open-air rock-shelter with different types of weathering, including biological and chemical ones. This shelter has been monitored for four years and in three fieldwork campaigns (2013, 2014 y 2016). Haematite is the pigment used in the red pictographs. The substratum is calcareous. The results of the different campaings were compared by means of chemometrics in order to identify changes over time.

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The investigation of calcium carbonate formation using micro-Raman spectroscopy

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Calcium carbonate ($CaCO_3$) has got significant importance in nature and in several industrial processes. In its different mineral modifications, calcium carbonate is highly abundant in the earth crust, occurring as calcite, aragonite and vaterite (anhydrous crystalline polymorphs) or ikaite (calcium carbonate hexahydrate), calcium carbonate monohydrate, (hydrated crystal forms) and amorphous calcium carbonate (ACC). The $CaCO_3$ can be formed during the process of biomineralization or synthetically with using gas diffusion method or mixing supersaturated solutions containing calcium cations and carbonate anions. The so-called carbonation reaction, plays a crucial role in hardening of lime mortars, a class of binders of relevance in culture heritage conservation. During this process, the $CaCO_3$ is formed from $Ca(OH)_2$ that uptake atmospheric CO_2 in aqueous medium. This contribution is focused on the investigation with micro-Raman spectroscopy of $CaCO_3$ modifications appeared during the synthesis from supersaturated aqueous calcium chloride and potassium carbonate solutions, under different reaction conditions [1], as well as during the carbonation reaction [2,3].

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X-ray photoelectron spectroscopy of pictorial samples

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X-ray photoelectron spectroscopy (XPS) is a surface-sensitive spectroscopic technique which can provide the elemental composition, chemical state and electronic state of the elements present within the first 1-10 nm of a material. XPS is routinely employed in many areas of materials science; and in the particular case of pigments used in artworks, this analytical technique has been occasionally employed to identify aging effects as well as mechanisms of degradation including X-ray induced damage [1]. In fact, radiation damage is considered an important issue in the characterization of painting materials with synchrotron X-rays [2] and particle-induced X-ray emission (PIXE) [3]. Furthermore, the observation of degradation during the characterization of materials by radiation sources has recently motivated the study of radiation damage mechanisms in the field of cultural heritage and the development of mitigation strategies [4].

In this work, XPS was used to analyze X-ray effects on pellets of azurite, malachite and alizarin pure pigments and on azurite and alizarin tempera paint mock-ups, where the pigments were mixed with egg yolk. X-ray radiation damage was assessed by comparing successive high-resolution spectra acquired on the same spot. The spectra of the pure pigments show low radiation sensitivity and reactivity under the selected X-ray irradiation conditions, although some differences among them were detected. Whereas alizarin does not experience surface chemical changes during the prolonged irradiation experiment, a slow progressive chemical reduction of azurite and malachite (copper-based pigments), together with the formation of cuprite, is observed. On the other side, tempera paint mock-ups are sensitive to X-rays and alterations of the egg yolk binding medium are displayed in a shorter time scale than the induced chemical modifications of the pure pigments. Besides, XPS allows to determine that the azurite pigment and the binder interact chemically. Azurite is partially reduced in the tempera paint from the beginning of the irradiation experiment and the subsequent X-ray exposure induces further reduction.

XPS was also used to evaluate the damage induced by ion irradiation. The model samples were irradiated with Ar+ at low energy (1 keV) for consecutive short intervals of few minutes and XPS spectra were acquired after each treatment. The spectra present similar characteristics as the ones acquired after prolonged X-ray exposure but the ion irradiation effects are already detected after few minutes. The present study is complemented with a discussion of the involved chemistry and some proposed strategies to obtain high-resolution spectra of enough signal-to-noise ratio while minimizing the radiation damage in these pictorial materials.

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From micro to macro: A multiscale Raman mapping approach for the analysis of inks and pigments on paper, panels and walls

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Raman spectroscopy has been widely applied for material analysis in work of arts, thanks to its high chemical specificity [1]. Often the high spatial heterogeneities of artworks benefit from non-invasive imaging analysis for a complete characterization [2]. While micro-Raman (μ-Raman) mapping is commonly used to study heterogeneities in micro-scale samples, Raman mapping of extended surface is less diffuse due to the constant need of refocusing and its long execution time. We present recent applications of a macro-Raman (MA-Raman) mapping device capable of detecting the Raman signal at a long working distance (30 cm) from non-perfectly planar surfaces, without the need for refocusing [3]. The device can map a maximum area of 5x5 cm^2 with a spatial resolution of 500 μm in a reasonable acquisition time (32 min for an area of $1cm^2$). MA-Raman mapping measurements on different scales (millimeter to ten centimeters) yields spatial distribution maps of the main component present in the heterogeneous artworks. Further high-resolved μ-Raman spectra on select point strengthen material characterization. The MA-Raman device has been successfully applied for the characterization of archaeologic mortars (fig.1), ink-written documents and paintings. Examples will be presented as a validation of the effectiveness of MA-Raman mapping device and demonstrate how data from Raman spectra can be used to understand complex materials through the integration between MA-Raman mapping approach and other complementary techniques including X-ray fluorescence mapping and Fourier Transform Infrared Spectroscopy. Challenges and ideas for future research and development will be presented.

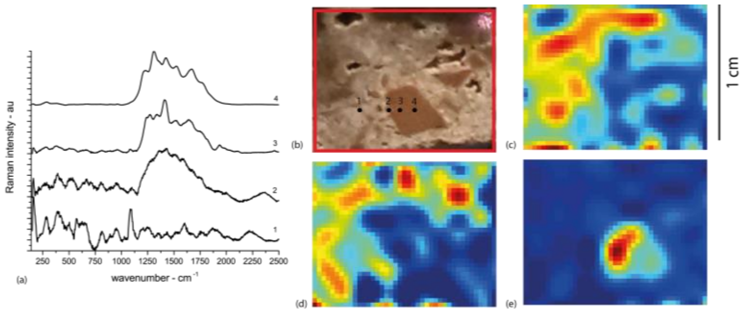

Figure1. Raman analysis archaeological mortars from *Palazzo Vernazza* (Lecce, Italy)
(a) μ-Raman spectra of different points inside the mortar marked in figure 1(b).
(b) RGB detail of mortar. (c-e) MA-Raman maps (12x18 mm): spatial distribution of calcite (280, 1083 cm^{-1}) (c), feldspar (510 cm^{-1}) (d), aragonite (1393 cm^{-1}) (e).

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A system for scientific microscope color calibration at the Rijksmuseum for the Paint Sample Database

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The Rijksmuseum Amsterdam is currently engaged in a large project to make an online database of its extensive collection of cross-sections from paintings, frames, and sculptures. This project is one of the first of its kind in the world. As part of this process, digital photomicrographs are collected from each of the 2700 embedded paint samples. To enhance the scientific value of these images, it is important that a standardized imaging technique is used and that color accuracy of the images is ensured. In the absence of an existing solution for reflected light microscopy color management, we developed a modular multi-step system for producing an input color profile for a given microscope digital camera and a set of standardized lighting conditions. Additionally, we developed a simple drag-and-drop web-based tool with which raw digital images from our microscope can be instantly processed to produce calibrated TIFF files expressed in an industry-standard color space (ECI RGBv2).

There is a strong need for accurate color capture for our Paint Sample Database since it enables meaningful comparisons: within an artwork at different places and times, and across different artworks. Ideally such comparisons should not be dependent on a particular microscope or institution. Accordingly, we have modularized and open-sourced our approach in order to promote its easy use across in other institutions.

In a typical digital photography color management workflow, an input color profile is made by first photographing a color card with patches of known color. However, in microscopic photography, it is impossible to capture an entire color card in a single image and even custom-made miniature color cards are too large. It was therefore decided to photograph each of the 140 patches in an X-Rite ColorChecker Digital SG card under the research microscope with reflected light using standardized lighting conditions at the lowest magnification of 25x (once for bright field with crossed polarizing filters and once for dark field illumination). The raw camera output for each of the images is then analyzed by our custom open-source software to first find the square region with the most uniform illumination and subsequently statistically analyzed to remove those pixels covering microscopic flaws on the cards such as speckles or scratches. These uniform filtered square image patches are then analyzed to obtain raw mean red, green, and blue values for each patch. When this procedure is applied to each patch, the result is a ground-truth colorimetric value and a corresponding raw measured RGB triple for each patch and each illumination type. From this point, the workflow can proceed exactly the same as with a normal digital photography color management workflow.

An easy to use web-based raw image conversion system enables a standardized approach across all the microscopes in the museum and it allows for application of color calibration with virtually zero additional overhead relative to standard microscopy.

The aggregation of lead and calcium carboxylates on experimental models. A combined analytical approach for their sampling, identification and characterization

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The formation, diffusion and aggregation of metal soaps in oil paint films is a well-known issue in conservation that affects not only the stability of oil paintings and oil polychromies in sculptures but also their aesthetic perception.

From a scientific perspective, there are many questions still open regarding the carboxylate behaviour such as the design of a convincing theoretical model to explain their occurrence in a paint film and the understanding of the conditions, reactions and mechanisms that make them aggregate to each other or change phase. From a conservation perspective however, it would be interesting to understand in which conditions, the reactions and phenomena of formation and aggregation of carboxylates could contribute to a dramatic decay of some specific oil paint films or, on the contrary, to stabilize oil paint films acting as plasticizers, adhesives or surfactants.

Although protrusions have been identified in many works of art, the occurrence of aggregates of metal soaps on experimental models are more difficult. In this study, mock-ups consisting of a lead white oil paint film applied on pinewood and on sandstone were prepared. After three years of natural ageing, the aggregation of lead and calcium carboxylates was observed on the surface but also at the interface film-substrate of both experimental models. For comparison purposes, mock-ups with the same paint film on microscope glass, alabaster and primed canvas were prepared.

In this research the aggregation of lead and calcium carboxylates have been identified and characterized on experimental mock-ups by means of the combined use of UV-VIS light microscopy, SEM-EDS and micro FT-IR spectroscopy in transmission (with a diamond cell anvil) and ATR modes. The sampling method under microscope, the use of the diamond cell for the performance of micro FTIR analyses and the SEM-EDS mappings undertook have been critical for the identification of calcium and lead carboxylates in the experimental models.

Considering the specialized literature and after the discussion of the analytical data obtained from the experimental models, it's possible to hypothesise that formation, diffusion and aggregation of metal carboxylates in oil paint films are deeply influenced by the substrate nature (chemical-mineral composition and porosity), the availability of free fatty acids in the film and the eventual presence of water in contact with it.

MA-XRF imaging spectroscopy on the Archaic painted panels from Pitsa (6th c. BC, Corinthia, Greece): New evidence on their original polychromy and their iconography

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The Pitsa panels represent today the earliest examples of panel paintings to survive in Greece. They were discovered in a cave dedicated to the Nymphs near Corinth, and are currently on display at the National Museum of Athens. Based on stylistic criteria and the form of the letters in the Corinthian alphabet, the panels have been dated to the second half of the 6th BC. They fill an important gap in our knowledge of ancient Greek painting, and give us an idea of the Corinthian style at a time when vase-painting had ceased to be representative of the local tradition.

The paintings were executed on four thin wooden panels, over a white preparation of gesso (calcium sulphate) using a variety of pigments, including carbon black, calcium carbonate white, Egyptian blue, red and yellow ochre, cinnabar, orpiment and realgar. The application of a novel MA-XRF imaging spectrometer based on a real-time technology [1] on the painted surface of the tablets brought to light extremely interesting information regarding both the distribution of pigments in the compositions and their identification. Enhanced information was also revealed regarding the association of certain minor/trace elements with raw pigments, whereas in certain cases quantitative information was gathered with respect to specific paint layers. Elemental mapping of copper, iron, mercury and arsenic allowed us to distinguish iconographic elements that were not visible with naked eye, considerably enhancing our evaluation and interpretation of those unique testimonia of Archaic painting.

Figure1. MA-XRF elemental distribution image of Fe-As-Cu obtained at the National Archeological Museum of Athens on one of the panels.

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The Glass beads as markers of the trade to Southern Africa from the 8th to the 19th century AD

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Glass beads have been produced and traded for millennia all over the world, to be used as everyday adornment, ceremonial costumes or objects of barter. The preservation of glass beads is rather good and large hoards have been found. The variety of shape, size and colour as well as the composition and production technologies of glass beads motivated efforts to use them as markers of exchange pathways, from/around/through/to Indian Ocean, Africa, Asia, Middle East, Europe and America and as chronological milestones. The present review addresses the methodology of identification (morphology, elemental composition, glass nanostructure, colouring and opacifying agents, and secondary phases) by means of laboratory and mobile instruments exampled on glass beads excavated from Southern Africa sites [1-8]. In concluding the review, the potential information that could be extracted with advanced portable methods of analysis is discussed.

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A novel tool for Cultural Heritage material analysis: Transmission Electron Microscope (TEM) 3D Electron Diffraction Tomography and Orientation/Phase Mapping applied to ancient Roman glass tesserae

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A large collection of Late Roman colored mosaic glass *tesserae*, excavated in 2008 at the sanctuary of Isis and Sarapis, an archaeological site of ancient Messene, SW Peloponnese, Greece, were analysed by a Scanning Electron Microscopy coupled with an Energy Dispersive Analyzer (EDS) aiming at the characterization of its base glass composition and colorant minerals[1].

The aim of the present study is to extract advanced information regarding the mineralogy of the opacifying and coloring agents of glassy materials with the use of novel Electron Diffraction Techniques operating at nm scale while it operates in a quasi-desctructive mode during the sample preparation by Focused Ion Beam (FIB). Precession Electron 3D Diffraction Tomography (ADT 3D) is a Transmission Electron Microscope (TEM) based technique [3-5] and enables to determine precisely unit cell parameters, crystallographic symmetry and exact atomic crystal structure of mineral phases (of nm or micron size) present as precipitate in the glass. This novel technique can be considered as a very reliable alternative/complementary analysis to SEM/EDS, EPMA, Raman-IR, SIMS and XRF techniques for very accurate characterization of ancient artifacts.

In the present study we applied ADT 3D technique to analyze different minerals found in the blue glass *tesserae* collection; the study resulted to the accurate characterization of the crystal structure (unit cell, space group and atomic coordinates) of different calcium antimonite opacifiers, which in the presence of copper and cobalt minerals, produce the observed colorations. By using advanced precession diffraction based orientation /phase mapping techniques (ASTAR) at nm scale [3], we can identify orientation relations between different crystalline precipitates and differentiate between the amorphous and crystalline phases of the glass artifacts.

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Study of a modern Chinese cloisonné vase by means of EDXRF and Raman spectroscopy

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Cloisonné is one of the Chinese famous traditional handicraft artworks with history of more than 500 years. It refers a technique of creating designs over metal vessels surface with coloured-glass paste placed within enclosures made of metal wires, which have been bent and shaped into intricate patterns by hands and tweezers. Known as cloisons (French term for "partitions"), the cell enclosures generally are either soldered onto the metal body of copper or bronze, or even sometimes on precious metals such as silver or gold. The glassy enamel, is coloured with metallic oxides and inserted into the closed areas of the design. Objects are also gilded, often on the edges, in the interior, and on the base. The vessel is usually fired at a relatively low temperature, about 700-800 °C.

The enamelled cloisonné wares were highly appreciated and promoted by the emperors of the Ming (1368–1644) and the Qing (1644–1911) dynasties. The objects made by cloisonné technique were intended primarily for the furnishing of temples and palaces, because their flamboyant splendour. This sophisticated technique has been maintained up to now, and modern cloisonné objects reproducing same patterns and shapes than the old ones can be found.

In this work we studied the features of a modern Chinese cloisonné vase by means of small-spot energy dispersive X-ray fluorescence (EDXRF) and portable Raman spectroscopy. Quantitative elemental results of enamel have been obtained after calibration of EDXRF instrumentation with certified reference materials. Up to eleven different coloured enamels have been recognized and analysed (black, pink, red, white, yellow and three shades of both blue and green). Enamel paste is mainly formed by lead oxide based flux and the main identified colouring agents are chromium, manganese, cobalt, copper, antimony and cadmium.

The body of the vase is made by copper with minor amounts of zinc and tin. Analysis of metallic decorations at the surface of the vase reveal the presence of metal coating processes applied for the embellishment of the piece. Analysis and thickness of layered metal structures have been obtained by XRF fundamental parameters assisted with data from pure metal spectra, thus revealing the gilded parts consist of a thick layer made by silver-doped nickel.

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Keywords: EDXRF; Raman; China ware; Cloisonné

Investigation of 18th-century Chinese double-walled vases in *yangcai* painted enamel

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In this work, two double-walled vases in *yangcai* painted enamel, produced between 1742 and 1744, were investigated for exploring their manufacturing technique. Having long been issues of interest, the exquisite revolving vases of Qianlong reign (1736-1795), inspired probably from double-layer vases and revolving lanterns, contain different varieties, including revolving bowl, revolving bottle, revolving brush holder, revolving hat stand, etc. The complex process of manufacturing these kinds of porcelains combines usually different techniques such as firing, underglazing, enameling, piercing and jointing, along with rotating mechanism. The very difficulties encountered are to precisely control firing temperature and accurately assemble the base and the inner and outer vases in order to assure the normal operation of the revolving system. Due to the precious and undetachable character of these revolving vases, it is hard to investigate their inner structure and fabrication technique in detail.

In recent years, a homemade and versatile X-ray cone-beam micro-CT scanner has been developed at the National Palace Museum (NPM), Taipei, with the aim of studying different types of artifacts for conservation, restoration and technical study purposes. As a nondestructive and powerful tool which permits of scrutinizing the inner structure of artifacts, this CT scanner was thus employed to investigate the two double-walled vases mentioned above.

Besides, as the exploration of the relationship between various types and different names of painted enamels on porcelain, including *falangcai*, *yangcai* and *fencai*, are highlighted in the field of Qing dynasty porcelain study, we also used a handheld XRF to preliminarily analyze the elements contained in the glaze of these two vases and discuss their possible ingredients.

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The magic of colour of medieval stained glass windows. Insights into composition of red and violet flashed glasses

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Stained glass windows were one of the most important and precious features of medieval architecture, especially due to the application of impressive colour and light. Manufacturers of medieval stained panels used different components and applied specific techniques to receive complex and multi-layered glass structures. Presently, technology and provenance of the glass objects can be elucidated by information about elemental composition of various layers and components of glass. The determination of changes in the elemental composition, which occurred due to deterioration processes, is vital for the proper evaluation of the condition of glass. Such information is also very important to establish an appropriate conservation treatment [1]. Many analytical methods can be applied for the investigations of glass samples [2]. However the characterization of flashed glass is particularly difficult due to its multi-layered structure and low concentration of colouring elements [3].

The main aim of the study was to reveal composition and structure of the medieval flashed red and violet glass from three different periods. The stained glass windows from the oldest Polish collections: Roman stained glass windows from Adampol (beginning of 13th century), windows of the Dominican Monastery in Krakow (13th to 15th century) [4] and the so-called Grodziec Collection (dated to 1420-25) were investigated. Elemental composition of bulk glass and external layers of glass samples was determined by X-Ray Fluorescence spectrometry (XRF), Scanning Electron Microscope coupled with an Energy Dispersive X-Ray spectrometry (SEM-EDX) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). Morphology of the deteriorated glass was investigated through SEM-BSE images of the cross-sections. Moreover, the longitudinal concentration profiles were determined by LA-ICP-MS measurements in order to provide information on trace elements content in each layer of glass.

Results show that stained glass panels reveal characteristic elemental composition of wood ash glass produced from 1000 to 1500 AD in Central Europe. Differences in elemental composition detected for minor or trace elements were strictly connected to colour additives. LA-ICP-MS concentration profiles and BSE-SEM images revealed specific layers in the translucent glasses, decorative paint layers and drawings. Considerable differences between the composition of healthy bulk glass and the deteriorated surface of glass were also detected.

Acknowledgements: LA-ICP-MS measurements were supported by National Science Centre of Poland from funds granted within post-doctoral internship based on decision no. DEC-2013/08/S/ST4/00560.

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Mycenaean Glass from the Argolid, Peloponnese, Greece: A Technological and Provenance Study

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Mycenaean glass is acknowledged to be of outmost importance in archaeological science and archaeometry studies due to both its 'elite' identity and its widespread distribution in palatial and funeral contexts. Within the framework of a large research program, glass collections from 16th - 13th c. BC Late Bronze Age/Mycenaean sites in North-East Peloponnese, Palaia Epidavros and Ancient Asine in the Argolid [1], have been studied analytically and tailored to tackle issues related to questions such as: whether–glass was imported in the form of ingots and/or previously shaped artifacts via exchange routes or they were produced in local glassmaking workshops.

The aim of this paper is to identify the technology and source of the primary glass used and, thus, to appoint the Mycenaean glass industry of the Argolid within the broader Mycenaean, Mediterranean network and further Egypt and Mesopotamia.

The study resulted in the chemical fingerprinting of the collection with the use of the totally non-invasive techniques of XRF, SEM/EDS and PGAA. The statistical analyses provided technological evidence~~s~~ for compositional similarities amongst the samples that form two major compositional groups, both associated with artifacts originating from Eqypt. Regarding their coloration at least two cobalt colorants can be identified with respect to their arsenic content and other cobalt- associated impurities.

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Historic conservation materials on stained glass windows in the Naumburg cathedral

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The long life cycle of conservation applications constitutes a challenge for studies on ageing of conservation materials. The stained glass windows in the gothic Naumburg cathedral (Saxony-Anhalt, Germany) incorporate interventions from the past two centuries, thus offering a rare opportunity for investigating the long-term behaviour of conservation materials aged under real conditions.

Parts of the original windows of the Naumburg cathedral, dating back to the early 13th century, are preserved and count to the oldest in Germany. They coexist with panels from the late medieval period and with panels replaced in the mid-19th century. At that time, first restorations were performed as well. They were followed by a number of conservation interventions from the early 20th century until the 1960s.

Over 100 samples collected from the windows of the Naumburg cathedral are examined in a multi-analytical study, in which FTIR is combined with Raman spectroscopy, EDX, GC-MS and thermoanalytical methods. Next to protein-based materials and cold-painting, polyacrylic resins – some of which have been on site for nearly a century – are found to make the majority of the samples. In addition to lab analysis, a portable Raman and an FTIR spectrometer are tested on their performance in non-invasive *in situ* spectroscopy.

The results improve the understanding of the ageing of polymers in conservation applications and at the same time cast light on aspects of the history of conservation in the Naumburg cathedral.

Figure 1. Medieval stained glass window with aged polymer

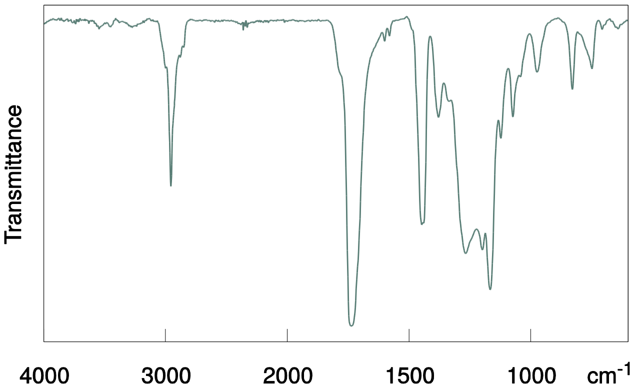

Figure 2. FTIR spectrum of aged polyacrylic resin

Characterization of glaze ceramics from the archaeological site of La Alcazaba, Almería (Spain)

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"La Alcazaba de Almería" is one of the most impressive mediaeval remains in Al-Andalus. The importance of its defensive walls is expression of the economic and strategic relevance that the city acquired during middle Ages. It was the sea port of the Córdoba Caliphate and, afterwards, the capital of a "Taifa" kingdom. In the course of archaeological excavations in this monumental area, several glazed ceramic remains were found in the palatine area so-called second enclosure. They come from different archaeological contexts dated back between the X-XV centuries.

The found glazed ceramics correspond to small fragments on which different patterns and colours can be identified: blue, white, red, green, black, yellow, etc. The aim of this work is to study the composition of the different colours and try to distinguish the manufacture procedures, as for example the employment of different raw materials (source of blue pigment, opacifier, etc) and different methods to separate colours (typical Islamic "cuerda seca" method, colour overlapping, etc).

For this purpose, the multi-elemental and non-destructive PIXE (Particle Induced X-ray Emission) analytical technique was employed in order to preserve the samples. Protons of 2.9 MeV and 1 mm spot size were used in an external beam line at Centro Nacional de Aceleradores (Seville). Helium atmosphere was created along the path from the analysed point to the X-ray detector so elements with atomic number over 11 (Na) could be quantified. Phosphorus, tin and lead appear in the glazes as opacifiers and main flux components. Cromophores are also identified: cobalt for blue, manganese for black, iron and copper for green, copper for red, etc. Both glazes and pastes were analysed and compared with other Islamic samples of the same type.

Assessing the firing temperature of Uruk pottery in the Middle Euphrates Valley (Syria): bevelled rim bowls

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Among geochemical studies on ancient pottery, knowing its technological production has been one of the main interests in the last 25 years. Assessing the firing temperature of ancient pottery have been attempted by different methods, from the study of physical parameters (e.g. porosity) to molecular compounds (e.g. minerals) and other physico-chemical properties (e.g. atomic-level changes) [1]. One of the most successful methods have been studying mineral phase transformation sequences produced during firing of clay and raw materials, although very little knowledge exists about such transformations in mixtures, and other parameters than temperature are critical, namely the original raw materials, firing duration and re-dox conditions during firing [2]. These methods have provided imprecise but valuable results in a number of study cases of different periods (from the Neolithic to Middle Ages) around the world [3,4,5,6]. The most used methods to assess mineral composition is X-Ray Diffraction (XRD) and optical microscopy (OM), usually combined with some spectroscopic methods (infrared or Raman spectroscopy) or thermal analyses. In this work, we used XRD and OM to assess the firing temperature of a particular type of pottery from Mesopotamia. The Middle Uruk phase in Mesopotamia (3600-3500 BC) has been characterized by the massive production of the so-called bevelled rim bowls (BRBs). They are very similar in shape in Mesopotamia and surroundings, but their production method is unknown, including the scarce knowledge on their firing temperature, although short recent studies in samples from two sites of the Middle Euphrates Valley (Syria) showed that they were fired at mild temperatures probably below 600-700ºC [7]. Recent studies of BRB samples from the same sites have also shown very similar elemental and mineral composition [6], being either manufactured in a same production center, or due to the homogeneous composition of the raw materials in the Middle Euphrates Valley. In any case, assuming the use of the same raw materials the mineral composition of the BRBs would depend on the firing temperature. In this work, we analyzed the mineral composition of a significant number of samples from 4 Uruk sites of the Middle Euphrates Valley (Syria), after comparing their geochemical composition, to assess if the firing temperature were similar in all of them. Results indicate very similar geochemical composition due to the use of the same raw materials and very similar mineral sequences that can be attributed to a same firing temperature probably below 600-700 ºC.

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Use of small angle neutron scattering and X-ray powder diffraction with the Rietveld method in the assessment of firing conditions in historical fired-clay bricks

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It is well-known that the description of the complexity of fired-clay bricks can be tackled only by integrating information from different analytical techniques [1]. At the same time, a nondestructive or low impact approach, aimed at the conservation of cultural heritage objects, is prompting for the search of new analytical methods for their characterisation. As a widely accepted practice, in restoration works, the best compatible materials should be employed. To this aim, the characterization of the original bricks is essential in order to choose the most suitable replacement material and prevent further damages. Mechanical properties and performance of fired-clay bricks are directly related to their microstructure and mineralogical composition, which in turn depend upon the employed raw clay and firing temperature.

In this work, the potential of small angle neutron scattering (SANS) and X-ray powder diffraction (XRPD) with the Rietveld method (including the quantification of the amorphous fraction), is evaluated in the investigation of historical fired-clay bricks.

SANS is a powerful tool for the characterization of the microstructure of porous solids. In bricks, XRPD allows to identify and quantify the minerals and the amorphous fraction, in order to describe the phase transformations taking place during firing [1,2].

Bricks produced from 2 raw clays have been fired at 5 temperatures (from 800 to 1100 °C) in laboratory. Results have been used to derive information on the firing process experienced by a number of historical fired-clay bricks produced in Czech Republic.

SANS allowed to retrieve the pore size distribution, characterise the fractal surface of pores as well as suggest an empirical relationship between surface area per unit volume of pores and firing temperature. The fractal quality of the surface area of pores is also suggested as a method to distinguish between bricks produced from different raw clays. Unit-cell parameter of spinel and amount of hematite (phases detected in the fired bricks) from XRPD are proposed as indicators of the firing conditions.

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XRF analyses of the Serra d'Alto pottery (Matera, Italy)

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During the Middle Neolithic period (between 5000-4500 BC) the Serra d'Alto Culture was particularly widespread in trenched villages located in the eponymous hill of Matera and in the neighboring Apulia region. Serra d'Alto pottery wares consists both of a very fine-granulated paste, defined *figulina*, and of a medium/coarse paste. Fine paste cups and bowls are decorated with geometric patterns painted with black pigment. Their vertical strap-like handles are often enriched on the top by zoomorphic plastic applications. Coarser wares, typically necked-shape vase, are enhanced with engraved decorations and plastic applications.

In this paper, the X-ray Fluorescence (XRF) analyses of 120 samples of black painted decorated pottery are reported. We analyzed samples from seven archaeological sites of Matera's area: Murgia Timone and Murgecchia [1], Tirlecchia [2], Serra d'Alto [3], Setteponti [4], Trasano [5] and Saldone [6].

The results show that on each sample the decoration has been obtained by the use of a dark pigment based on manganese oxide. The ubiquitous presence of this material suggests a deliberate technological choice and defines a proper characteristic of Serra d'Alto's pottery manufacturing.

This study is part of an interdisciplinary project on painted pottery in the central and southern Italy, from Early to Middle Neolithic period [7].

Figure1. Serra d'Alto pottery wares: *figulina* painted with black pigment

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'Not too white': an investigation into the influence of the use of calcium carbonate-rich imported marls on 17 - 18th century Dutch tin-glaze tile production

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Although approximately 10 million Dutch tin-glazed tiles were produced and extensively exported during the 17th and 18th century, no significant research has been undertaken into the raw materials and techniques used in their production. From the early17th century, Dutch delftware tiles were produced using local clays mixed with calcium carbonate rich 'marl' clay imported from Flanders and England. Archival evidence from England and the Netherlands not only documents this trade and the raw material sources, but also provides recipes for the clay mixes and glazes used at the time. It is generally assumed that the imported marl was added to increase the coefficient of expansion of the ceramic to prevent crazing of the glaze, but this research indicates that a central factor for its use was the reduction of production costs due to its influence on the ceramic colour (a light body needs less tin oxide in the glaze) and mechanical strength (enabling the production of thinner tiles). The possible problems encountered by using an excess of marl are suggested where a contemporary potter comments that the clay mix must 'not be too white' as this leads to 'cracking'.

In this project, archival research is combined with the physicochemical analysis of sourced clays and marl (SEM-EDX and XRF) together with clay-recipe reconstructions, with the aim of investigating the influence of the imported marl on the final tile product. Samples were prepared and fired between 950°C and 1100°C in reducing and oxidising atmospheres, the firing protocol being formulated from documentation on traditional firing techniques and previous research into the firing of Ca-rich clays. After firing, the sample colours (see for example below) were measured using colorimetry and the Munsel system and compared with historic tiles. The relation between the colour and firing temperature was further investigated with XRD analysis in order to assess mineralogical changes, notably the development of calcium silicates and in particular pyroxenes. Structural strength of the ceramic samples was measured using three-point flexural testing (MOR).

The sourcing, preparation and firing of the marl clay pastes gave important insight into its working properties, especially when compared with samples made with a synthetic marl. While the physicochemical characteristics of the fired ceramic are primarily determined by the $CaCO_3$ w% in the clay, the firing process (temperature and atmosphere) were shown to significantly influence the colour and mineralogy of the fired ceramic. The limited parameters within which changes were observed show the skill of the 17th century potters.

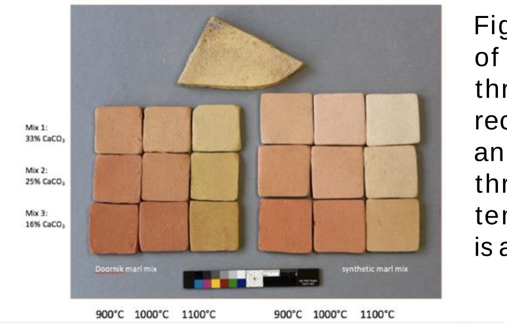
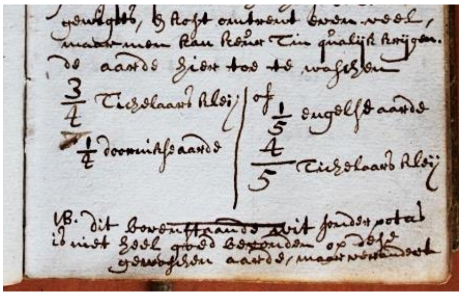


Figure 1. The results of colour tests of three different clay recipes using natural and synthetic marl at three different temperatures. Above is a 17th century tile



3/4 Tichelaars klei | of 1/5 engelsche aarde
1/4 doorniksche aarde | 4/5 Tichelaars klei

Figure 2. 18th century clay-mix recipe

Jun Ware – A Technical Study

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Chinese Jun Wares were everyday ceramic objects made in large quantities from the 10th-15th centuries. They can be divided into three sub-categories: Classic, Splashed and Numbered. Chronologically Classic Jun is the earliest, whilst Numbered Jun was only produced later and is believed to date from the 14th century.

Classic Jun ware has benefited from extensive analytical study to account for the characteristic blue-tinted color caused by phase separation and light scattering within the glaze [1]. Building on these data, the focus of this study are the far rarer Numbered Jun wares made specifically for the Imperial court at one or more workshops. Numbered Jun wares present clear differences in the way they are manufactured, having different and color and gloss, which may relate to chronological or geographical variations in production site and/or variations in raw materials or firing conditions [2]. However, the dating and production history of Numbered Jun remains controversial [3]. This study represents the first in-depth investigation of samples from imperial palace pieces of Numbered Jun as well as from pieces of Classic and Splashed Jun ware. Some modern replicas produced at one of the few known kiln sites were also included as these are believed to be made from traditional materials.

The aims of the present study are twofold. First, compositional differences within the Numbered Jun production will be characterized using Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). Second, the chromophores within the glazes and the firing conditions required will be elucidated using a multianalytical methodology that will utilize X-ray Fluorescence Spectroscopy (XRF), Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDX), X-ray Photoelectron Spectroscopy (XPS) and Hyperspectral Imaging. This aims to provide information on how specific phases were produced by careful choice of raw materials and kiln firing sequences.

Full characterization of the Jun ware glazes will enable identification of key differences between Numbered and other classes of Jun ware, and of differences within the Numbered Jun ware. This will clarify the relationship of Numbered Jun to earlier Jun ware ceramics and reveal any changes in production technology and/or materials. Variations within Numbered Jun ware will enable subgroups to be accurately identified and characterized. Ultimately, we hope to establish how such differences may relate to particular workshop practices and hence clarify the number of likely production sites involved.

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LA-ICP-MS multi-element analyses of blue & white tin-glazed earthenware tiles: 2D surface and depth mapping of glazes

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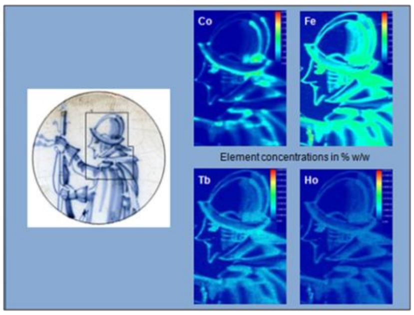
Blue and white glazed Chinese porcelain and European tin-glazed earthenware represent a very extensive and highly important component of ceramic art. In this paper we focus on cobalt-blue, tin-glazed tiles from the Netherlands and Portugal, the two main European traditions. A previously-developed protocol for quantitative measurement of 54 elements in glass and ceramic glazes [1] is combined with procedures to create 2D (lateral and depth) maps from glazed surfaces [2]. Element surface maps were generated by rastering with the laser beam over the selected surface area in line scanning fashion (pixel size, 100×100 µm), whereas multiple passes on the same line resulted in elemental information along lines with increasing depth that could be combined into pseudo cross-sectional maps (depth resolution, 2.5 µm). These LA-ICP-MS protocols produced exciting new art historical information on cobalt-blue wares.

The high dynamic range of the LA-ICP-MS allows simultaneous measurement of major, minor and trace elements, and as such can reveal relationships between the pictorial blue glaze design and 54 elements in the 2D surface maps. Association of elements with the blue colourant (cobalt) can be directly gleaned from the maps as for example shown for the outline of the soldier's head in the 17th century Dutch tile (Fig 1). Firstly, the influence of minor elements such as iron, nickel and manganese which modify the blue hue may be determined. Secondly, the role of trace elements (present in concentrations as low as part per billion and exemplified by terbium and holmium in Fig 1) can be assessed as marker elements, indicative of geological sources of the original cobalt ores.

Because the blue design is applied on top of a white tile glaze layer, the concentration of cobalt and associated elements varies with depth of the glaze. Additional compositional information extracted from 2D depth maps (Fig 2) will be highlighted such as the application thickness of the decoration (Co and Fe), the distribution of associated elements (As and Ni), the presence of unmelted glaze components (Hf and Zr in sand grains), etc.



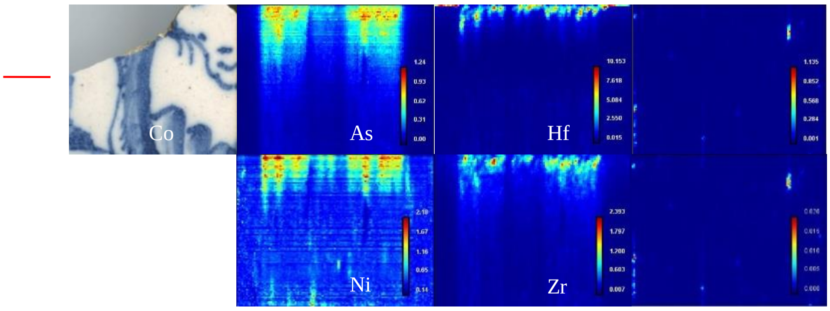


Figure 1. 2D surface maps for selected elements on
(100 passes on "red" line) area indicated.

Figure 2. 2D depth maps for selected elements

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Computed Radiography, Pixe And Xrf Analysis of Pre-Colonial Pottery From Maranhão, Brazil

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This work concerns the archaeometric analysis of ceramic fragments from archaeological excavations carried out in "Sambaqui do Bacanga", 'Sambaqui do Panaquatira" and "Rabo de Porco", located in the São Luiz city area, at Brazilian northeast. Ancient civilizations that inhabited that territory were characterized as fishing, catchers, hunters and ceramist populations. Dates obtained by thermoluminescence ranged from 6600 to 127 BP. The studied samples were sixty three representative pottery fragments selected of stratigraphic levels from the surface to 170 cm deep for all sites. The three analytical methods employed were Computed Radiography, PIXE and XRF. Computed Radiography employed an X-ray tube Philips MG 450 and a CR30-X AGFA scanner. PIXE measurements were performed with an external beam setup with ~2.4MeV proton beam in the LAMFI laboratory using three X-ray detectors, two Si-PIN detectors and one HPGe with standard spectrometry electronics; each spectrum was taken for 600s. To perform normalization between the measurements a gamma-ray scintillation detector (NaI(Tl)) was used to determine the ion beam charge. XRF measurements were performed with a Shimadzu Energy Dispersive X-Ray Fluorescence Spectrometer (EDX – 720), which consists of an X-ray tube (Rh target) to excite the samples, a Si(Li) detector and 3mm collimator. Sixteen elements were measured with good statistics in the different ceramic samples through EDXRF and PIXE analysis: Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, Rb, Sr, Y and Zr. Multivariate statistical analysis, Hierarchical Cluster Analysis (HCA) and Principal Component Analysis (PCA), of the fragments elemental composition were performed to separate and correlate the groups of the samples. Fragments of the three archaeological sites grouped into two clusters, the first is composed of samples from "Sambaquis do Bacanga and Panaquatira", and the second consists of the "Rabo de Porco" samples. This result indicates that each cluster of fragments was manufactured with different clays, and "Sambaquis do Bacanga and Panaquatira" fragments are derived from the same source or same kind of clay. The internal structure of the ceramic fragments observed by Computed Radiography revealed the presence of various sizes and types of anti-plastics in the sherds.

Self-cleaning coatings by N-doped TiO_2 on limestones

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Titanium dioxide (TiO_2) in nanocrystalline form is one of the most investigated materials in semiconductor heterogeneous photocatalysis for the degradation of several recalcitrant compounds. *Self-cleaning* properties have recently attracted much attention for the development of hydrophilic surfaces, contributing to the degradation of atmospheric pollutants which damage outdoor buildings and monuments.

This work was aimed at the analysis of several TiO_2 coatings synthesized in our lab to test their self-cleaning abilities on different limestone surfaces. In order to achieve visible light active photocatalysts, non metal doped TiO_2 were prepared by the sol-gel technique starting from different titanium(IV) precursors. Nitrogen was chosen as dopant material [1], using ammonium hydroxide and ammonium fluoride as nitrogen sources. Characterization of the nitrogen-doped TiO_2 (N-TiO_2) powders was carried out with spectroscopic and microscopic techniques. The photoinduced properties and the compatibility of the nanostructured N-TiO_2 based coatings were tested on calcitic and dolomitic Israelian limestones.

N-TiO_2 powders, obtained by drying the synthesized sols at room temperature, are mainly composed of anatase in nanocrystalline form, with a few percent of brookite phase, as highlighted by Raman and X-ray diffraction measurements. The Raman peak positions and FWHM suggest the crystallite size in the 5-10 nm range, in good agreement with XRD and TEM analyses. Diffuse reflectance spectroscopy shows a shift in the band gap towards lower energies with respect to the undoped TiO_2. XPS analysis indicates that doping yields nitrogen in substitutional positions or at least in positions that affect the immediate environment of titanium.

The N-TiO_2 coatings tested on limestone samples have proved to be harmless with respect to colorimetric change and water capillary absorption, as confirmed by analyses carried out according to the UNI-Normal protocols. The hydrophilic properties, induced by UV-VIS irradiation, are demonstrated by the increase in the wettability of the surfaces: within few minutes of irradiation, contact angle values approach the super-hydrophilicity limit. Finally, the photocatalytic activity was assessed through the degradation of organic dyes (Methyl Orange and Rhodamine B) under UV-VIS and visible light, emphasizing better photoactivity for Methyl Orange stained samples.

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Limestone chromatic changes: a microbial-mediated inorganic process

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Colour is a major argument that drives the decision of the architect in a specific architecture project and the market value of an ornamental stone [1]. As limestone and marbles are the most important commercial stones, it is essential to know how their colour is naturally achieved and how this parameter can change.

Among the rocks explored and processed in Portugal, the Jurassic blue limestone from Estremenho Limestone Massif has had a special impact on the market. This acceptance among international clients results from its aesthetic and physical characteristics, that allow a wide range of uses, always with harmonious finishings.

However, the chemical alteration of these stone materials has been shown to be a problematic issue [2]. After application, it is well known that this blue limestone is susceptible to alteration, changing its colour and causing occurrence of aesthetic patterns. This alteration has been reported in different places, both indoor and outdoor, causing costly repairs.

Considering that the main limitation of the lithological variation is the chromatic change, several techniques and methodologies were applied in this work, in order to understand and signalise the possible causes. In this way, particular importance was given to chemical and mineralogical composition, and the presence of microbial communities.

This limestone is characterised by the presence of two different colours, with similar chemical compositions, from which one of them is characterized to have more sulfur on its composition, due to presence of greater amounts of pyrite.

The multianalytical approach applied in this study showed that the colour changes may be the result of gypsum and iron oxide formation in the surface, while the culture dependent methods revealed that these altered areas are predominantly contaminated by bacterial strains, although filamentous fungi and yeast are also present in this microbial community. Furthermore, the surfaces affected by different kinds of microorganisms showed the presence of metabolic active cells whose bioactivity is correlated with the detected contamination levels. The DNA content was also evaluated, constituting another biocontamination index.

The concomitant presence of biocontamination with the alteration products detected suggests that the inorganic alteration of the rock composition seems to be mediated by microbial activity, which can enhance the degradative effect.

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Novel materials for the restoration of marble and limestone substrates based on oxalate derivatives: an experimental and DFT-theoretical approach

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The contribution of synthetic Chemistry to the development of new substrates for the protection and restoration of carbonate stones, often deteriorated by weathering and biological and chemical decay agents [1, 2], is encountering a progressive flourishing. In this context, the treatment with ammonium oxalate, resulting in an artificial coating of calcium oxalate, was proved to be a promising technique for the protection of stone items [3, 4, 5]. During the past few years, we have been testing the introduction of structural modifications on the oxalate anion as a synthetic tool for the development of novel salts aimed at the protection and consolidation of stone carbonate substrates of art-historical interest. In particular, by varying the nature of substituents in monoesters and monoamides (oxamates) of oxalic acid it is possible to tailor the solubility of the relevant ammonium and calcium salts [6, 7]. In addition, theoretical calculations carried out at Density Functional Theory (DFT) level can help predicting the structural and electronic features of the investigated compounds as well as their capability to interact with the calcium carbonate lattice. We report here an experimental (X-ray diffraction, Mercury Intrusion Porosimetry, FT-MIR and FT-Raman spectroscopy, SEM) and theoretical (PES and NBO analysis) investigation on the effects induced by the variation of the anion on the efficiency of the treatment of marble samples coming from the Cimitero Monumentale di Bonaria in Cagliari (Italy) and biomicritic limestone samples from Cava Flore (Santa Caterina di Pittinuri, Oristano, Italy).

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Analysis of typomorphic minerals applied in the investigation of origin of archeological objects and painting materials

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The identification of the origin of the raw materials used in the manufacturing of the archeological objects or applied as the painting materials became one of the issues most frequently discussed by archeologist or art historians. Analysis of typomorphic minerals would be profitable in solving this question. Typomorphic minerals are characteristic for the specific material and were formed under particular conditions of temperature and pressure which reflected the conditions present at the formation of the site. The defined set of the typomorfic minerals could be used as a "fingerprint" of geological site and might indicate the origin of the analyzed material.

For the first time we applied this approach during examination of the pottery discovered in the archeological site in the south-western Poland [1]. The petrographic and Raman spectroscopy analysis of the clay bodies revealed the presence of the syllimanit. This discovery enabled us to determine the provenance of raw material used in the manufacturing of the analyzed ceramic. Recently the analysis of the typomorphic minerals was successfully applied in the attribution examination of the paintings and origin investigation of amber. The SEM-EDS and Raman analysis led us to the identification of the iron-titanium minerals present in the raw material used to the preparation of ground layer applied in the painting. This discovery supported the attribution of the painting in the question to Silesian painter J.J. Knechtl. Moreover, the combined approach to the analysis of typomorfic minerals was accomplished during investigation of Indonesian amber. The set of minerals suggesting the origin of the amber found in Borneo was established due to the cross-examination including SEM-EDS, petrographic analysis and finally the crystallographic examinations. Results confirmed the presence of kaolinite, quartz, chlorite, calcite, creamy inclusions of tonstein and further 11 minerals. The description of the typomorphic minerals characteristic for Indonesian origin of amber might became an effective tool in the provenance investigation of archeological amber.

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New insights into the characterization of lipids in pre-Hispanic ceramics by mass spectrometry techniques

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The usual method of lipid analysis in archaeological samples involves hydrolysis and derivatization of lipids to obtain FAME (fatty acid methyl esters). Because fatty acids are unspecific biomarkers it is also necessary to study residuary acylglycerides which are better biomarkers of original source. In this study we carried out a multi-analytical approach based on the integration of three different mass spectrometric techniques: gas chromatography-mass spectrometry (GC/MS), high performance liquid chromatography-mass spectrometry (HPLC-MS) and elemental analysis-isotope ratio mass spectrometry (EA-IRMS) to characterize archaeological organic residues which provides relevant information on past human activities.

This work focuses on the lipid profile analysis of organic residues from ceramic storage and service containers from archeological sites in Catamarca, Argentina. In addition reference samples of typical plants (maize, mesquite, chañar and mistol) and animal (llama, guanaco and ñandú) food resources rich in lipids were studied for comparative purposes.

Results from GC-MS in archaeological samples indicated mixtures of plant and animal lipids, including odd carbon and branched fatty acids. Neutral lipid analysis showed presence of animal and/or plant sterols. Isotopic analysis indicated the presence of different mixtures of C_3 and C_4 plants lipids, and/or animal lipids. With HPLC-MS we identified intact mono-, di- and triacylglycerides (MAG, DAG, TAG) in the archeological samples.

A comparison between TAG profile of reference and archaeological samples allowed us to identify TAG of vegetable origin and biomarkers of South American camelids fat. The latter are characterized by having in their structure an odd fatty acid, in agreement with data from GC-MS data. The occurrence of intact TAG with odd fatty acids, both in archaeological samples and camelid samples (guanaco and llama), suggest that these compounds are not the product of contamination or post-depositional microbial degradation.

The statistical significance of the biomarkers obtained by the multi-analytical approach was estimated using multivariate statistical analysis (MCA and DA).

Lipids in the archaeological samples are largely found as TAG (even unsaturated), proving exceptional preservation. The characterization of the lipid profile and the identification of biomarkers by a multi-analytical approach in these samples could be useful to know the use of these archaeological utensils. The characterization of the acylglycerides and fatty acids in the references samples allowed us to start the construction of a database of lipids from plants and animals native to the area under study.

Nuclear Magnetic Resonance Analysis for Treatment Decisions: The case of a White Sculptural Environment by Louise Nevelson

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Solid-State Nuclear Magnetic Resonance (NMR) is a analytical technique rarely used to determine the best course of treatment in art conservation. This is partly due to the need for relatively large amount of sample (order of 50-100 mg) for solid state NMR. However, recent developments reduce the necessary amount by orders of magnitude opening possibilities for more use in the near future. Unilateral NMR is a non-invasive NMR technique that can be used to detect physical properties of materials. For example solvents used for cleaning of painted surfaces may change the mechanical properties of paint layers and will be readily detectable using this method.

In this work, both solid state NMR and unilateral NMR have been applied to investigate the paint composition and to inform the treatment decision for a white sculptural environment by Louise Nevelson completed in 1977. Within ten years of installation, the sculpture required restoration and today the painted surface is in critical condition with both the original paint and the restoration lifting and flaking. Unilateral NMR is used to determine the thickness of the different paint layers, and the composition of the original paint and the restoration is determined using solid state NMR. Measurements show that each layer is about 200 μm thick and that the original paint is an alkyd while the restoration is a PVA paint. Pentaerytritol (PE), a compound from the alkyd paint, has been identified in the restoration layer. The original alkyd paint is more stable than the restoration paint, suggesting that the migrated PE has degraded the restoration layer. The free PE may be a result of excess in the alkyd paint formulation rather than degradation of the original paint. The analytical study guided the decision to remove the highly degraded restoration paint. Cleaning systems using mechanical and physical gels are currently being investigated and potential mechanical changes in the alkyd paint will be evaluated using unilateral NMR before a final cleaning decision is reached.

Discrimination of Acacia gums by MALDI-MS: developments and applications to samples from Ancient Egypt

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In the cultural heritage field, characterization of plant gums is commonly based on their monosaccharide composition, as determined by gas chromatography mass spectrometry (GC-MS) after acid hydrolysis [1] or with pyrolysis techniques (Py-GC-MS) [2]. However, while different gums may be distinguished using statistical treatments such as chemometric data analysis, these techniques might lead to misinterpretations since the monosaccharide profile of an unknown sample can be altered by the presence of other organic or inorganic components, as well as by the effects of ageing [1,2].

Matrix assisted laser desorption ionization mass spectrometry (MALDI-MS) is an extremely sensitive technique and is relatively new to cultural heritage. MALDI-MS has already proved to be essential for protein analysis (proteomics), and a new strategy for plant gum identification was recently developed involving partial enzymatic digestion followed by analysis of the released oligosaccharides by MALDI-MS. Due to significant differences in their polysaccharide structure, gums from different plant sources can be discriminated according to their unique MS fingerprint [3,4]. However, never before has this method been applied to ancient artworks.

This analytical strategy has been used in the present work to unveil the nature of organic materials in ancient Egyptian objects after a first, and sometimes not completely informative, investigation by Fourier transform infrared (FTIR) spectroscopy and Py-GC-MS. The MALDI-MS method was adapted to the type and amount of sample available from artworks, and a new approach of enzymatic digestion of the polysaccharide material directly from the cotton swabs commonly used during cleaning is proposed. Attention was particularly focused on the study of the plant gum that is most often encountered in museum artefacts: gum arabic. This gum can be obtained from different *Acacia* species (e.g. *A. senegal*, *A. seyal*, *A. ferruginea*). Gum samples from different *Acacia* species have been studied both by MALDI-MS and MS/MS analysis and the results indicate that they can be distinguished from the presence of specifc oligosaccharides. The ability to discriminate gums from different *Acacia* species is potentially valuable to answer questions of trade and provenance in the use of Acacia gums in ancient artefacts.

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Development of a new methodology for the analysis of sterols and bile acids in archaeological soils for the characterization of species

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The interest on identifying and quantifying organic compounds from archaeological organic soil residues has increased during last decades due to the possibility of characterizing their biogenic origin [1].

The main objective of this research is to develop a new and quicker methodology for the analysis of 8 sterols and 2 bile acids in archaeological organic soil residue samples for determining their biogenic origin (ruminants, canines, porcine and humans) from a stable rock-shelter, San Cristobal, located Upper Ebro Basin, Spain.

For that purpose, microwave-assisted extraction variables (sample mass, solvent mixture volume, oven ramp time and final T held) were optimised by means of a central composite design. Optimum values were obtained when 5 g of sample were exposed to 25 mL of dichlorometane:methanol (2:1, v/v) and the temperature was increased to 150 °C with a temperature ramp of 10 min and kept for 10 min.

After the evaporation of the solvent and a saponification step with 5 mL of KOH (2 M, 90% methanol) at 120 °C for 1 h, the pH was adjusted to 2 previous to a liquid-liquid extraction (2 x 10 mL dichlorometane). Finally, a solid phase extraction (2 g of silica) clean-up step was optimised. Although 10 mL of acetone were enough to elute all the sterol, 40 mL were necessary to elute all the bile acid. Finally, acetone was evaporated and analysed by means of gas-chromatography mass-spectrometry after a derivatisation step.

Good recoveries (82-145 %) were obtained for all the analytes expect for deoxicholic acid at high concentration (47 %). All the RSD% values were below 15% and the limit of detection range was from 1.4 to 83 ng/g.

25 archaeological organic soil residue samples (strata) were analysed from San Cristobal. The presence of ruminants (use of isomeric relations and principal components analysis) in three different periods from Neolithic to Roman period confirmed the use of San Cristobal as a stable rock-shelter.

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GC-MS and HPLC-APCI-MS for the research, valorization and dissemination of the Iberian Culture

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The physical-chemical analysis of archaeological materials of the Iberians (6th-1st ct. BC) has become an area of research of special interest in recent years for Archaeometry, providing valuable information for the dissemination and valorization of the Archaeological Heritage of the Iberians. In this context, the aim of this work is to show the advances in the research in this field of knowledge: the analysis of chemical markers of contents in ceramic vessels. In particular, a methodology that combines Gas Chromatography-Mass Spectrometry (GC-MS) and High-Performance Liquid Chromatography-Mass Spectrometry with Atmospheric Pressure Chemical Ionization (HPLC-APCI-MS) is presented. The joint and coordinated use of both techniques has proven to be an adequate methodology to identify the type and origin of the residues conserved in ceramic containers. This methodology is proposed as an alternative and complement to other techniques currently applied in the field of content analysis such as GC-C-IRMS or nanoESI MS / MS. GC-MS enables to obtain lipid profiles identifying fatty acids, triacylglycerols (TAGs), sterols or wax esters. This technique also allows the detection of native sulfur. HPLC-APCI-MS can isolate and identify intact TAGs more accurately than other techniques. Thus, it is possible to associate TAG profiles with a range of fat types by HPLC-APCI-MS. First, TAGs with a high content of unsaturated fatty acids (oleic, linoleic, linolenic) are associated with vegetal fats. Second, TAGs of saturated fatty acids are associated with animals; some of them are so specific that they can be considered biomarkers of fat of specific animal species. Finally, the difference between ruminant animal fat and non-ruminant animal fat is based on the proportion of palmitic and stearic acids in the sn-2 position of TAG (P:S ratio): Ruminants show a ratio of *ca*. 60:40, whereas the ratio is closer to 95:5 in non-ruminants [1].

The ceramic group studied in this work, on which this methodology has been applied, comes from three archaeological contexts from the Iberian period and dated between 6th and 3rd centuries BC: the cemetery of La Noria (Fuente de Piedra, Málaga), the Sanctuary and the Palace of the *oppidum* of Puente Tablas (Jaén) and the battlefield of *Baecula* (Cerro de las Albahacas, Santo Tomé, Jaén). Thanks to the joint use of GC-MS and HPLC-APCI-MS, a set of chemical markers related to the presence of animal fat (mainly ruminant), vegetable fat, beeswax and native sulfur has been identified. These products appear either in isolation or forming various mixtures, possibly as a result of multiple use of the vessel during its useful life. This has led to establish different types of functions and uses of the pottery and their contents: consumption, ritual, medicinal, etc. [1,2].

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Identification of organic residues in archaeological ceramic vessels of Basque whalers from 16th to 17th century

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Analytical research in the field of organic archaeological residues found in ancient vessels has grown into a recognized field in its own right and has developed rapidly in recent decades. The characterization of such residues has led to the clarification and understanding of the encompassing history, the historical, cultural and technological context in which were manufactured and what purpose they were used for. In this sense, the identification of biomolecular markers can provide information not only about the nature of the residue but also about the transformations undertaken by the sample during the burial process.

The aim of this work is focused on the identification of the organic residues from archaeological ceramics found in a deposit in Lekeitio (Basque Country, Northern Spain). These vessels are suspected to have been used by the Basque whalers in the period from 16th to 17th Century to store whale oil. Bearing in mind our aim, different analytical approaches based on chromatography and mass spectrometry (GC/MS and HPLC-ESI-qTOF) were used to study both fresh blubber and whale oil products and the archaeological substances in order to obtain chromatographic profiles and possibly detect highly diagnostic biomarkers. Two hydrolysis approaches were used in order to compare data and obtain as much information as possible; (i) microwave assisted direct hydrolysis of the ceramic samples and (ii) microwave assisted hydrolysis of previously solvent-extracted samples. On the other side, the study of solvent (chloroform:hexane (3:2 v/v)) soluble fraction was carried out by means of HPLC-ESI-qTOF. Preliminary results led to the identification of some interesting organic compounds in the hydrolysable and soluble aliquots from the ceramic vessel such as pristane, phytane, several saturated fatty acids, hydroxyacids and cholesterol along with triacylglycerols in the solvent soluble fraction. On the other hand, the obtained results for the fresh whale oil and blubber suggested a similar lipid profile to the ones obtained for the archaeological samples. The chemical results together with archaeological data seem to indicate the vessels were used to store whale oil.

DMFDMA: a new/old GC-MS derivatization agent for the analysis of binders in cultural heritage objects

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Dialkylacetals of dimethylformamide (DMF-DAAs) have been known as GC and GC-MS derivatizing (alkylating) agents for organic acids since the 1970s [1,2]. They present substantial advantages over the prevalently used GC and GC-MS silylation derivatizing agents. They pose − in general − fewer health concerns [3], while the derivatized compounds should be stable and less sensitive to atmospheric humidity [2]. Furthermore, the derivatization reaction should be fast and require no additional solvents, as long as the compounds are readily soluble [1]. Despite these benefits, an analytical study for a GC-MS method involving DMF-DAAs and its application to cultural heritage samples has not yet been undertaken.

This paper outlines the analytical performance of a GC-MS method for the analysis of fatty and amino acids with N,N-dimethylformamide dimethylacetal as derivatization agent. Some of the parameters that will be evaluated are: stability, recovery percentage vs. amount of analyte, reproducibility of retention times and peak areas, limit of detection, etc. The method will be tested in relation to paint micro-samples from late-medieval liturgical objects, which are currently under investigation within the scope of the Norwegian Research Council-funded project, "After the Black Death: Painting and Polychrome Sculpture in Norway" [4].

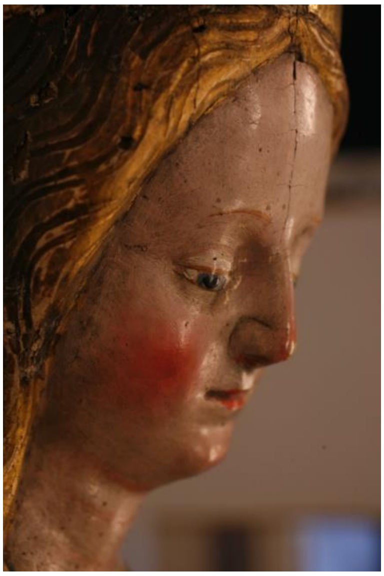

Figure 1. Detail of Nativity with enthroned Madonna from Torsken Church, KHM collection.

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Development of a qualitative and quantitative analytical method for the characterisation of mixtures of free fatty acids and metal soaps in paint samples

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The characterisation of metal soaps in paint samples is a difficult task, especially in mixture with free fatty acids. Different analytical methods based on gas chromatography/mass spectrometry (GC/MS) and infrared spectroscopy (FTIR) have been applied for the qualitative analysis of metal carboxylates, but commonly their amount and type is determined together with free fatty acids or after complex sample pre-treatments [1]. In this work we present the development and optimization of a new and simple analytical method based on the use of GC/MS for the qualitative and quantitative characterization of mixtures of free fatty acids and metal soaps in paint samples.

The characterisation of hydrolysed and saponified fractions of paint samples is very important to understand the state of conservation of a paint film and its behaviour during conservation treatments. This is especially true for modern oil paintings [1], for which the degree of hydrolysis of a paint, the relative content of metal soaps, as well as the presence of metal soaps of monocarboxylic and dicarboxylic acids, may play an important role [1,2,3] . Respect to traditional oil paint media, the formulations of manufactured modern oil paints were modified to produce suitable working proprieties such as viscosity, drying rate, and colour. This resulted in the addition of a range of oleochemicals, which included metal soaps to facilitate the dispersion of pigments into the medium [1]. Metal soaps are also formed as a product of reaction of between the excess of carboxylic groups released from the network as consequence of the hydrolysis of triglycerides and of the oxidative cleavage of long chain fatty acids, and the cations of certain pigments, such as lead and zinc.

In the framework of the Cleaning of Modern Oil Paintings (CMOP) project we developed a two step analytical method, which is based on the use of two different silylating agents for the derivatisation of the carboxylic and the carboxylate moieties: N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) for metal carboxylates, and 1,1,1,3,3,3-hexamethyldisilazane (HMDS) for free fatty acids. The reaction conditions for the derivatization of carboxylates were optimized by an experimental design using lead stearate and palmitate as model systems and the analytical method was fully validated following the ICH guidelines. This new analytical method was successfully used to characterise reference materials, model paint samples and samples from paintings.

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6.3 PARALLEL SESSION C

Advanced extraction and analytical methods applied to discrimination of different lichen species used for orcein dyed yarns

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Today, in the field of cultural heritage conservation, orchil represents one of the most intriguing sources. This name indicates a purple dye that can be obtained by means of treatment in ammonia from any of several lichen species belonging to the genus *Roccella* or other lichen genera (at least 60-70 species could be treated in order to obtain the orchil mixture). In history, the largest employment of this material coincided with the maximum request of the precious Tyrian purple and its use results in imitating the shellfish dye [1, 2].

Even if this use is well known during the history, orchil is not easily detectable in historical samples, due to its high photo-instability [2]. For this reason, many scientific works are focusing on the improving of non-invasive (such as UV-Vis fluorimetry) and micro-invasive techniques (such as SERS on fiber) and, at the same time, on optimizing analytical conditions in HPLC-MS or MS experiments to detect also traces of phenoxazone compounds [1-4].

In this paper, we present the preliminary results of a multi-analytical approach, as a powerful tool to discriminate different species of lichens, such as *Roccella tinctoria* DC., *Lasallia pustulata*, *Ochrolechia tartarea*, etc. In the first part of the research, samples of yarns dyed with the different species, prepared in laboratory after the proper raw lichens treatment [5, 6] have been extracted through the innovative ammonia methodology of extraction [7].

As preliminary step, in order to evaluate the difference between the several species, HPTLC has been applied. All the spot present on the TLC preparative plates have been analyzed through SERS (HPTLC-SERS), in order to obtain a SERS database of different compounds, which are fixed on the yarns dyed with the different species. Then, HPTLC-MS experiments have been carried out, in order to deep into the identification of compounds, corresponding to each spot. When a sufficient amount of material was available, 1D-NMR experiments have been performed, in order to clarify the chemical structures of these dyes. Taking into account that large quantity of material is not available in the real case and this approach could not always be applied, the results of the multi-analytical approach have been compared with those obtained from small scale samples, analyzed through SERS on fiber and HPLC-MS experiments.

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Identification and classification of textile fibres using ATR-FT-IR spectroscopy with chemometric methods

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Identification of textile fibres is important in conservation and archaeology, but also in industry (quality control), forensic science (identification of fibres on crime scene). Due to the abundance of textiles, their occasionally similar properties and the development of artificial fibres, which by their properties are similar to the natural fibres, the identification of textile materials has become rather complicated. Accurate methods, that can work with small amounts of sample without damaging the object, are needed.

In this study the possibility of classification of single- and two-component textile materials using ATR-FT-IR spectroscopy and chemometric methods (principal component analysis (PCA) and discriminant analysis) was assessed. Additionally, experiments for semi-quantitative analysis of mixed fibres (cotton-polyester, wool-polyester and wool-polyamide) with PCA were carried out. [1]

For the classification altogether 89 textile samples belonging to 26 different types (11 single-and 15 two-component textiles) were investigated. All measurements were carried out using a Nicolet 6700 FT-IR spectrometer with a Smart Orbit micro-ATR accessory. Homogeneity of the textiles was assessed with a Leica stereomicroscope and Nicolet iN10 MX FT-IR microscope.

During interpretation of the spectra of pure fibres, characteristic absorptions for every fibre and differences from spectra of fibres of similar composition were found. Different one- and two-component fibre samples were used for creating the PCA model and to perform the discriminant analysis. For semi-quantitative analysis PCA graphs were composed using two-component mixed fibres with different quantitative contents and corresponding pure fibres.

The developed methodology was applied to a real life sample - unknown ribbon from the memorial chaplet. The results of this analysis will be demonstrated.

It was concluded that ATR-FT-IR spectroscopy enables quick, easy and non-destructive classification and semi quantitative analysis of textiles [1]. Based on this analysis we demonstrate that classification of textile fibres (both single-component and two-component) is feasible using PCA and discriminant analysis of infrared spectra. Also, if suitable number of mixed textile samples are available, then semi-quantitative analysis with ATR-FT-IR using PCA is well possible.

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Surface Enhanced Raman Spectroscopy of Antraquinone-aluminum complexes on Dyed Fibers

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Raman spectroscopy and Surface Enhance Raman Spectroscopy (SERS) have been the tools of choice for the identification of numerous chromophores over several different substrates through the last two decades [1,2]. In particular, the identification of natural dyes on archaeological textiles has withdrawn the attention of numerous research groups who have achieved enormous advances in terms of identification of specific dyes and the sample pretreatments necessary to the extraction of the dye from the fiber [3].

It is hard not to notice that all efforts of identifying dyestuff using SERS fall short due to the high variability of the coloring matter present in raw material and the also to the presence of mordants. The presence of mordants in dyed fibers interfere with the SERS phenomenon since, as it is known that the sites where dyes interact with the SERS active substrate are the same by which dyes interact with the mordant. Using different SERS active surfaces some researchers have been able to identify mainly alizarin and carminic acid on several textiles from Peru and Chile. More recently, the SERS spectrum of pseudopurpurin was also successfully acquired by Rambaldi et al [4] offering new data to interpret SERS spectra, for example, from aqueous extracts of *Galium Hypocarpium* roots.

In order to interpret SERS spectra from several red wool samples from the north of Chile (Arica culture (1000 – 500 B.P.) and some sites in the San Pedro de Atacama archaeological complex), the Raman and SERS spectra of alizarin and purpurin aluminum lakes was recorded. Also, laboratory dyed silks (treated with HF vapors) were used as models to try to understand the observed SERS results. LDI-ToF-MS experiments were conducted as well to observe the species extracted from the fibers. The extraction of metal-dye complex along with the free dye from mordant dyed silk fibers was successfully confirmed by SERS and LDI-ToF-MS, and thus offering a new perspective into the interpretation of SERS spectra from dyed fibers.

SERS results have shown to be great for the identification of the main coloring compounds, however the usefulness of it will be always a function of the questions behind the analysis. In this regard, the use of LDI-ToF-MS shows to be a tool that could function as a complement for SERS experiments as well as a source of valuable information on its own.

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An Innovative Method for the Non-invasive Proteomic Analysis of Cultural Heritage Objects

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The identification of proteinaceous material of cultural heritage and ancient objects is a recent field of study. The methods used by the proteomics laboratory are applied or adapted to the analysis of artworks: low amount of proteinaceous materials and aged samples can be easily analyzed. But all the developed analytical procedures require at least a micro sampling from the object.

In this research we present the application of a new non-invasive method for the analysis of protein material from cultural heritage. The technique uses a functionalized film that extracts the proteins from the surface of the object. The extracted proteins are then analyzed by LC-MS/MS analysis using shotgun proteomics.

The method was then applied to several historical samples in order to identify the organic binders used by the artists. We will present the developed protocol and the results obtained from the analysis of several Italian artworks: a polychrome wooden altarpiece from the Maestro of Oropa (XIV century), a polychrome sandstone capital (XIV century), a rare polychrome alabaster (XIV century) and two wood medieval and renaissance panels, respectively from Pietro Gallo from Alba (XIV century) and Defendente Ferrari (XVI century). Our non-invasive method allowed the non-invasive identification of the main proteinaceous binders casein, skin glue and egg.

A non-invasive methodology for stratigraphy investigation of historical violins using reflection IR spectroscopy and UV induced fluorescence technique

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In the Cultural Heritage field, the stratigraphic analysis is carried out through the study of cross-sections [1]. This methodology is fundamental to discriminate the different layers composing a work of art, but it necessarily implies invasive sampling or micro-sampling with the consequent loss of precious or unique fragments. For this reason, the possibility of sampling is denied most of the time, especially in the case of historical musical instruments of the likes of Stradivari and Guarneri violins. Having been played during the centuries, these great masterpieces have undergone different kinds of degradation and wear, and subsequent invasive restorations. As a consequence, varnish layers have been thinned or even removed from the surface in different areas and other materials could have been added overlaying the original ones, with a variation in the coating thickness over time.

This research presents a preliminary non-invasive methodology aimed to identify the stratigraphy of historical stringed musical instruments, by characterizing the different layers of original and retouching varnishes as well as wood treatment materials. A combined analysis was carried out using reflection infrared spectroscopy and UV induced fluorescence (UVIFL) photography. Firstly, an experimental study on laboratory models reproducing musical instrument stratigraphy was performed. Different thicknesses of varnish covering wooden samples treated with proteinaceous material and silicates, carbonates and sulphates were considered in order to assess the sensitivity of the method. Subsequently, the procedure was applied to five historical violins hosted in the Museo del Violino in Cremona (Italy), as shown in Figure 1. The stratigraphic results allowed to build up the knowledge about the construction techniques used by ancient violin makers.

Figure 1. UVIFL photos of Antonio Stradivari ("Hellier" 1679, "Ford" 1703, "Cremonese" 1715), Guarneri "del Gesù" ("Principe Doria" 1734) and Jean-Baptiste Vuillame (copy of Messiah 1870) violins

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Complementary use of Optical Coherence Tomography (OCT) and Reflection mid-FTIR spectroscopy for in situ monitoring of varnish removal from easel paintings

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Aged varnishes and overpaints significantly impair visual perception and/or value of authenticity of easel paintings. Although the removal of such layers is one of the most frequently performed restoration treatments it is still questioned regarding its controllability and safety to the artwork. There is thus a need for developing suited diagnostic methodologies able to inform restorers on the chemical, optical and morphological aspects of cleaning.

To this aim, we have explored the possibility of complementary use of Optical Coherence Tomography (OCT) and reflection mid-FTIR. On one hand the OCT technique provides cross-sectional images with varnish layers directly visible and thus permits for direct measurement of their thicknesses. Adding many cross-sections into 3D data gives also insight into the varnish thickness distribution over a given area of the paintings. On the other hand reflection mid-FTIR allows for a chemical characterization of the surface compounds revealing the nature of the varnish and monitoring its removal. Artificially aged model samples and 19th c. paintings (from the collection of RCE and Rijksmuseum's objects donated to science) were investigated with a portable HR OCT system (built at NCU for the FP7 CHARISMA project, 870 nm central wavelength, axial resolution in the varnish = 2.2 m) and a portable FTIR system (ALPHA from Bruker, 7500 cm^{-1} – 400 cm^{-1} spectral range, spectral resolution = 4 cm^{-1}).

In the presentation the examined objects and the experiment's methodology will be described. Multilayered samples and paintings were examined complementing OCT results with chemical fingerprint from FTIR at different steps of the solvent cleaning tests. Results will be discussed in terms of comparison of sensitivity of both non-invasive optical techniques.

The combined use of OCT and FTIR techniques proved to be valuable approach to support the conservator's evaluation of tests to remove the unwanted layers one by one and leaving the original paint surface intact.

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A non-Invasive Study of Surface Coatings of Electric Guitars

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The electric guitar is an emblematic musical instrument born during the 20th century which became part of Heritage collections less than thirty or forty years ago [1]. According to the special status of this object in modern and musical history, only few and recent publications focus on its museum status [2]. Since the first instruments were made in 1939 by Charlie Christian and others, design seems to have an important value, especially the look that was obtained with a particular coating. Beyond its protective role, according to collectors and art historians, this coating of guitars seems to build up their aesthetic identity and cultural specificity. Firms' catalogues lead us to think that the surface coating is made of polymer materials [3], some of which are known for their chemical instability [4]. Despite the importance of this coating, there is a lack of academic research about chemical investigations: fewer analytical data is available on the nature of the different components than is the case for the violin for instance [5]. In this context, determining the nature of the coating components and technical guidelines for implementation can be considered of great interest from the conservation point of view in order to adapt storage conditions for exhibitions or playing conditions and to monitor evolution of guitar collections through time.

In this study, we focus on the 30 important instruments produced between 1953 and 2000 from the electric guitar collection in the Musée de la musique (Cité de la musique-Philharmonie de Paris). The aim of this study was to establish a specific methodology, with mobile and non-invasive analytical techniques in order to address the lack of bibliography about coatings and finishes. The organic part of coatings was characterized by FORS (Fiber optical reflectance spectroscopy) and FT-IR (Fourier Transform InfraRed spectroscopy) while the inorganic pigments used were studied by XRF (X-ray fluorescence spectrometry). Photographs under visible and UV light were first taken to locate inhomogenities and thus to decide where to conduct the localized analyses. For further information about the implementation of finishes, some samplings were made to observe the stratigraphy. This was also an opportunity to carry out Raman spectroscopy to complement the results. It will help to assess the validity of our methodology and to test its limits.

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Fluorination technique to identify the type of resin in aged vanishes and lacquers using infrared spectroscopy

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Infrared spectroscopy (FTIR) is a long established standard technique to characterise organic materials on micro-samples. There are, however, limitations to the technique when analysing chemically complex multi-component materials with interfering functional groups. This is particularly true in the case of terpeneous resins. Natural resins have been widely used as varnishes and additives in oil-based lacquers and paints throughout history. Once aged, these materials are complex molecular systems containing various functional groups. Within this context it is of interest to note that the different resins contain distinct structural elements that can be exploited to achieve differentiation by infrared spectroscopic techniques. The ability to correctly assign the functional groups is critical for the identification of resins. This study presents a pre-treatment technique for selective fluorination of various carboxylic acids by exposure the to gaseous sulfur tetrafluoride SF_4 [1]. The derivatisation treatment of micro-samples leads to characteristic band shifts, allowing the separation of otherwise overlapping bands. Accordingly, the IR bands of *primary acids, tertiary acids, α,β-unsaturated acids, peroxy acids, esters, ketones*, and *α,β-unsaturated ketones* are split into distinct absorption bands. Based on this technique, inert functional groups can be used as markers for the classification and characterisation of terpenes in both fresh and highly aged materials (Fig. 1). The main constituents of diterpene resins like sandarac and others possess a *tertiary carboxylic acid group*. Upon derivatisation, these show a very strong νC=O absorption band of the corresponding acyl fluoride at 1825cm^{-1}. Apart from these more recent resins, fossil resins also generally consist of polymerised diterpenes containing *ester groups* (1735cm^{-1}). Triterpene resins such as dammar and mastic contain *ketones* (1710cm^{-1}) and *hydroxyls,* as well as *primary carboxylic acids,* formed during ageing (1840cm^{-1}). Mastic on the other hand contains *aliphatic α,β-unsaturated acids* and can be identified by its characteristic signal at (1795cm^{-1}). And finally, shellac (not terpeneous) contains *cyclic α,β-unsaturated acids* (1804cm^{-1}) and *ester* groups (1735cm^{-1}). This research shows that derivatisation using gaseous SF_4 achieves separation of otherwise interfering infrared signals, enabling the analyst to trace identifying terpeneous material components, even in complex and aged material mixtures.

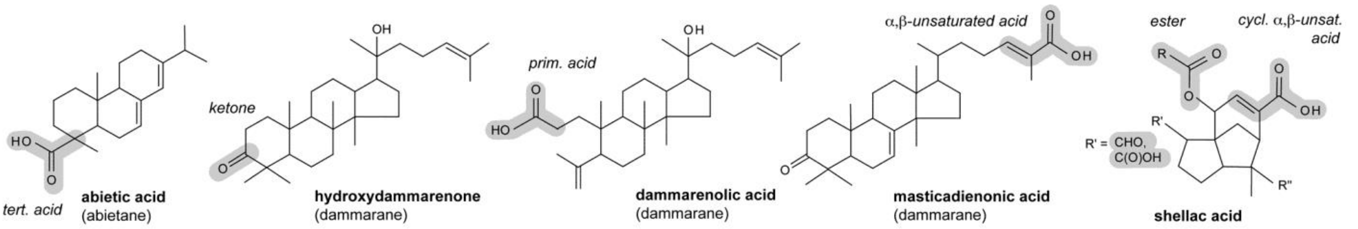

Figure 1. Different functional groups used for the identification of individual resins.

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Readability recovery in damaged ancient parchment artefacts: a comparative study among multispectral imaging techniques.

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Parchment artefacts are often affected by several biological, chemical and physical degradations, usually due to poor environmental conditions and handlings. Indeed, changes in the humidity or temperature values, daylight, air pollution, micro-organisms and humidity can be responsible for the appearance of stains, tears, fading and migration of inks and pigments, etc. Such phenomena could prevent the readability of textual elements or decorations. Moreover, manuscripts could be also altered by deliberate manipulations, as erased texts of palimpsests or in censored features of documents and illuminations.

In this work, a comparative study, aimed at recover the legibility of hidden details on damaged parchment documents, is presented. In particular, ultraviolet (UV) fluorescence (UVF), UV reflectography (UVR), infrared (IR) reflectography (IRR) and active IR thermography (IRT) analysis were performed on four ancient manuscripts, characterized by various degradations, which prevent the original readability of written texts and painted decorations. Indeed, the different penetration capabilities of each technique allowed rescuing deleted details by studying the artefacts in suitable spectral regions. Specifically, exploiting the high fluorescence of the parchment supports and the absorbing power of the iron-based inks when enlightened with an UV radiation, it was possible to recovery written characters decayed by microbial attack and water stains. In addition, good results were also obtained on a XIII century manuscript damaged by the application of plastic coating during an earlier inadequate restoration.

IRR results gave information about the nature of the employed inks, while the thermograms rescued the tracks of the writing instruments imprinted on the parchment sheet during the text realization. Furthermore, the IR analysis allowed the recovery of the underdrawings in an erased illuminated manuscript (XIV cent.) and in an historical document (XVII cent.) affected by a fading and migration of the pigments of its decoration. Interesting results were achieved by comparing the UVF images and the IR thermograms allowing to totally rescue the deleted painted decoration. Finally, it must be pointed out that the integrate use of the above mentioned techniques made possible to enhance the recovering of the lost surface and subsurface elements of deteriorated manuscripts.

Usability of spectroscopic, diffraction and microscopic analytical tools to recognize old Moroccan Jewish parchments

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The conservators of parchment collections thoroughly look for the analytical technics that would allow distinguishing ancient from modern manuscripts, in order to prevent possible forgeries and better design their storage conditions and conservation methods. Furthermore, it is noteworthy that the data collected by restorers have not been matched by a systematic study of the physic-chemical properties of parchment. A particular question that we would like to address in this study is the possibility to distinguish the ancient parchment from the modern one by conventional physicochemical techniques.

In this work, we have explored the potentiality of the vibrational FTIR spectroscopy, energy dispersive X-ray fluorescence spectrometry (EDXRF), X-ray diffraction (XRD) and scanning electron microscopy coupled to energy dispersive X-ray spectrometry (SEM-EDS) for the characterization of the natural degradation of parchment. The samples used in this work comprise 4 Moroccan Jewish historical parchments belonging to private libraries. The results have been correlated with those obtained by selected model samples including modern parchment. The aim of our investigation is to determine the changes of collagen material in response to natural aging, overall oxidation, collagen gelatinization and morphological surface changes that may be due to long time exposure to high humidity, excessive heat or further environmental conditions.

Mappa Mundi of Albi – Scientific study of the oldest map

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The Mappa mundi of Albi is one of the oldest examples of representation of the occidental world (Figure 1). The non-symbolic and non-abstract map was drawn on parchment and was probably made in the 8th century in the South of France or Northern Spain. The Mappa Mundi with the associated index of winds and seas on the adjacent page, is included in a 77 pages manuscript and belongs to the médiathèque Pierre Amalric in Albi (Tarn, France). Because it is a document of exceptional importance for global cartographic history and more widely for the history of the representation of space, the map together with the index were recorded in the UNESCO Memory of the World Register in 2015.

For the first time, a series of analysis were performed on the map from the micro to the macroscale, using mostly non-invasive analytical techniques. The aim was to identify the parchment and its degradation state and the different materials applied at its surface in order to increase our knowledge on the manufacturing technique of this unique document.

Hyperspectral imaging in the visible and near-infrared ranges (380-2500 nm) associated with statistical data treatments (PCA and SAM) provided the spatial distribution of the different components. Point spectroscopic analyses combining X-ray fluorescence, Fiber Optical Reflectance Spectroscopy (FORS) Vis-NIR, reflectance infrared and micro-Raman spectroscopies allowed the characterization of the ink, the colouring materials and organic compounds presents. The animal species of the skin used for the parchment was identified by proteomic analyses. Finally the conservation state of the collagen, main component of parchments, was assessed at the micrometer scale by nonlinear optical microscopy applied for the first time in-situ on a historic document. Unexpected results were obtained which were solved by crossing information obtained from the multi technique approach. This study will allow to take a new look at the Mappa Mundi and widen our knowledge on illuminated manuscripts in the middle Ages.

Figure 1. Mappa Mundi on the left and index of winds and seas on the right.

A multi-analytical study of the 'Hay Cookbook' Coptic magical manuscripts on leather reveal their mysteries

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This analytical study concerns a group of five leather manuscripts dating to c. 600-700 AD, all found together and apparently written in the same hand. One, the 'Hay cookbook', is a Coptic magical/medical handbook (EA 10391) said to have been found in the Theban Necropolis (Upper Egypt) with four other sheets containing templates for spells with a variety of (some startling) requests (EA 10376, 10414, 10122, 10434). Manuscripts on leather are rare artefacts and the unusual nature of the text makes these ones particularly remarkable.

Since the manuscripts were summarily documented and published in the 1930s, they have suffered slippage in their mounts, cracking and breakage, with areas of the surface appearing glossy, causing the text to become less discernable. They were mounted in a similar manner to papyrus documents - flattened between glass sheets - creating a micro-environment which appears to have contributed to their gradual decay. Continuing deterioration of the Hay cookbook and other four manuscripts, hastened the necessity for conservation, offering an opportunity to closely examine and analyse them before remounting.

A multi-analytical approach was adopted to investigate the manuscripts, including multi-spectral imaging and RTI (reflectance transformation imaging), XRF, FT-IR, GC-MS, LC-MS and MALDI-TOF (Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry).

The resulting images produced using MSI and RTI have revealed new details of the leather grain surface topography – clearly highlighting the hair follicle pattern (used to infer animal species), and remains of the ink text, even where it has worn away. Tooling and stretch marks emphasised in the RTI images have allowed us to interpret the skin processing methods and determine how the surface of the leather was prepared as a writing substrate.

The multiple analytical tools employed allow us to confirm the type of ink used to write the text, and give us a picture of the materials used to prepare the skin and convert it to leather. Substances such as vegetable tannins and oils used to 'tan' or 'cure' the leather have been pinpointed and fats and oils used for 'dressing' and 'finishing' it. Proteomic analysis of the collagen allows a positive identification of animal species'. Previously, this was only possible through comparison of follicle patterns with reference material – problematic in the case of the manuscripts because sheep and goat have follicle patterns with a similar appearance.

Never before has such attention been given to characterising the materials and technology used to create the Hay manuscripts. The results of the project deepen our understanding of the cultural context of skin technology in Late Antique Egypt. The research also emphasises the ever-refining capacity of modern imaging and analytical technology to reveal new information, and how much can be gained through collaborative study.

Non-invasive *in-situ* and SR-based imaging techniques for recovering the text from a recycled parchment

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The legibility of manuscripts can be affected by a series of factors related to their manufacture, storage, use or aging by means of physical, chemical or biological degradation [1]. In particular, recycling of parchments, a common practice throughout book binding history, is a primary agent of damage for written texts. During parchment recycling, the original text is hidden or removed, as the support is formed into other objects and/or reused for writing. Thus, reading the primary text on these compromised parchments often requires the use of analytical methods that enhance the legibility of their lost or obscured content [2].

In this study, we uncover hidden text on a parchment repurposed as the binding material for "Hesiodou tou Askraiou Erga kai hemerai" (the Greek poet Hesiod's Works and Days book, printed in Venice in 1537) using macro X-Ray Fluorescence, UV-Visible Hyper Spectral Imaging (Fig. 1) together with Synchrotron large-area based micro X-Ray Fluorescence. Overall, this combination of non-invasive techniques helped to characterize the pigments, inks, and materials used in the parchment preparation and revealed new information on the biography of the recycled and degraded manuscript. The recovered text was found to be a copy of the Institutes Justinian written in Latin. This 6th century A.D. codification of Roman Law also contained marginal comments on medieval Canon Law passages revealing new information on how texts from antiquity were copied, studied, and adopted into contemporary scholarly thinking.

By providing a comprehensive use of complementary techniques, this work provides a methodological strategy that can be implemented on similar problematic materials.

Figure 1: Visible image of the Hesiod book front book (left), overlap with eigenimages extracted from Principal Component Analysis (blue channel PC02, red channel PC03, and green channel PC04) providing enhanced vizualization of the lost text (right).

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3D Imaging of artefacts by EDXRF- Scanning

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Many artefacts have a multilayered structure, not only all types of paintings, which are composed at least by two-three layers, but also gilded or silvered metals, tumbagas, bronzes with patina, corroded silver and so on. The most useful analytical information about these multilayered structures can only be three-dimensional, in spite of the fact that the third dimension is of the order of fractions of mm for paintings and of microns for metals.

To this aim, a useful technique can be energy-dispersive X-ray fluorescence (EDXRF), which is non-destructive, non-invasive and multielemental, which can be able, in many cases, to reconstruct a 3D-map of the elemental distribution .

From the beginning of the seventy years of last Century, EDXRF-analysis started to be employed to detect chemical elements in artefacts of any type. Successively, at the end of the eighty years, when entered the market portable equipment which use small size X-ray tubes and Si-PIN or Si-drift detectors, EDXRF-analysis spread in the field of archaeometry, and is now considered the most useful analytical technique in the field. Recently, 2D scanning of paintings was systematically carried out, by using collimated X-ray beams and detectors. In such a manner maps of chemical elements in a painting are obtained, strongly increasing the level of information. 2D scanning may be carried out in the best manner by using synchrotron radiation, but it can also be done by using X-ray tubes, due to the general high content of chemical elements in pigments.

Besides to be non-destructive and multielemental, another advantage of EDXRF is that the penetration of incident X-rays in painting is generally greater than their thickness, while the path of secondary radiation emitted by the chemical elements present in the pigments is of the same order of magnitude than the pigment thickness. In the case of gilding, silvering and surface altered metals, the penetration of X-rays is generally larger than the thickness of the surface layer.

In any case, the final EDXRF-spectrum of an area of the analyzed painting or metal contains the X-ray peaks of all elements present in that area, many times independently from the depth from which X-rays of the element are coming. In several cases, and when the number of pigment layers is not greater than 3-4, this apparent independence of X-ray peaks from the depth can be overcome, by carefully processing the X-ray spectrum, in terms of elemental K/K and/or L/L-ratios. In fact these ratios depend on the location in the corresponding elemental layer, according to all the attenuation processes to which the X-rays emitted by this element are subject, i.e. self-attenuation in its layer, and attenuation by other superimposed layers.

In this paper, several examples are given of 3D reconstruction of paintings and of alloys subject to some surface alteration or discontinuity.

The processional cross of Santa Maria Maggiore at Guardiagrele: materials and techniques of Nicola da Guardiagrele investigated by X-ray fluorescence

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Goldsmith's craft is one of the most important expressions of Italian art in the period between the XIVth and the XVth century, and Nicola da Guardiagrele is one of its most prominent representatives.

This paper deals with the X-ray fluorescence investigations that were performed on one of Nicola's masterpieces, the processional cross of Santa Maria Maggiore at Guardiagrele, dated 1431, made of gilded silver pieces and enamelled plates. The study aimed at better understanding of the materials used by the master, his execution techniques and the differences respect to his predecessors. Two different spectrometers were used whose main features are good detection limits [1] and good spatial resolution [2], respectively. The former feature allowed for analysing the materials, estimating the gilding thickness and highlighting compositional differences with respect to one-century-older similar artefacts. The latter allowed for investigating the small details of the enamelled plates and performing a more accurate analysis of light elements in the enamels.

Among the other achievements, evidence was obtained concerning: the different origin - with respect to the previous century - of the cobalt minerals used for blue enamels, the thermo-chemical treatment of the plates prior to enamelling, the local abrasion of the gildings to obtain peculiar chromatic effects, the execution sequence of the pieces.

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Study of applicability of non-invasive analyses methods in archaeology

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The ED-XRF (Energy-Dispersive X-ray Fluorescence) and SEM-EDX (Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy) measurements have been made to present the quality of analyses methods and its applicability in archaeometry. The polish coin denominated 2 ***zote*** dated to 1933 was chosen as an object under study. The surface and core elemental composition was determined using SEM-EDX methods and the huge difference between Ag and Cu content was found. This result shows that X-ray spectroscopic techniques should be treated as surface analyses methods. The WD-XRF (wave-dispersive X-ray fluorescence) and XRPD (X-ray Powder Diffraction) results for surface are presented for comparison.

The spectroscopic techniques are commonly used in archaeometry. The aim of this paper was to indicate the naivety of faith in the accuracy of determining the elemental composition of objects analyzed on the surface. We have shown that the results of surface and core are inconsistent. The point is that information depth is is too short. Although X-ray radiation enters into the depths of the material up to approx. 100 microns, a feedback signal registered by detector comes from a few hundred to a few microns. The results of spectroscopic techniques can be used for the initial analyses of the elemental composition, however, archaeologists should not completely trust into the superficial measurements. Therefore, in order to obtain more reliable results of research, measurement must be done on the cut, what is practically impossible without the destruction of the artefact. Additional complication for elemental composition analyses can be irregular shape of artifacts and more complex morphology of those objects. However, because so far there is no other non-invasive method of analyses that reflects a credible elemental composition of objects under study, spectroscopic methods are the best way to preliminary archaeometry research. The problem looks deeper into the material without the destruction of the object under study can be solved through the use of neutron activation analyses (NAA). The measurements using a neutron generator and also by means of a nuclear reactor are in preparation.

Non-invasive studies on technological provenance of medieval silver jewelry form Baltic Sea region

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The scientific goal of realizing project is to investigate the source material that is crucial for understanding the contacts of the first Polish state (900-1039 AD) with the Czech state and Scandinavia. This materials are silver products which are included in the deposits - metallic treasures appearing in the Piast state since the mid-tenth century. Primarily, we are dealing with West Slavic type ornaments created in the ninth century in the first State of the Slavs - Great Moravia - which penetrated to the Czechs governance, and from there to the Piast state. This material is extremely interesting and preliminary studies have shown a very high educational value for understanding the circumstances of the Polish state. Ornaments of the treasures represent, not only in Poland but also throughout Europe, a unique huge material, but so far were examined mainly typological, not technologically.

The presented results are preliminary. They are focused on specific physico-chemical methodology which can give information about technology production of jewelery. In order to explore the technology of production, mainly soldering, 150 objects was subjected of non-invasive analyses of the chemical composition including trace elements. Joining numerous elements consisting of fine granulation and filigree was performed by use of different methods, among which, as we assume, the central place occupied soldering called *chrysocolla (gold - adhesive)* which was one of the early technological achievements of craftsmen working with metals. Additionally investigation of soldering and joining methods and also analyses of raw alloy material and technologies of decorative elements production were performed. The microscopic methods (optical and scanning electron microscopy - SEM) were used as a basis. Moreover, the analyses methods based on the specific interaction of X-rays with matter (X-ray microanalysis - EDX and and supporting fluorescence analysis - XRF:) and other spectroscopic technique (Raman for detection of solder organic material) were used to determine the elemental and chemical composition of technologically specific jewelry parts.

Electrochemical discrimination of monetary emissions: characterizing ten-cash Dragon copper coins

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At the beginning of the 20th century important changes in the Chinese monetary system took place. Old methodology for casting coinage was replaced by modern machinery for striking coins. In parallel, efforts were made for unifying the production of currency under the authority of the central Government during the reigns of Kuang Hsü (光緒) and Hsüan T'ung (宣統) (1906-1967) last Qing Dynasty Chinese Emperors. Thus, the "Regular Provincial series" of coins produced from the numerous Mints disseminated along the Chinese provinces under the influence of the provincial authorities (Figure 1) were replaced by new issues of currency for general use, the "Tai Ching Ti Kuo" series (Figure 2), which were minted between 1905 and 1909. In this further period, the Tientsin Mint was appointed to be the Head Mint, while some of the provincial establishments were to function as branch Mints under the control of the Board of Revenue (Hu Poo,) [1].

Application of the voltammetry of microparticles methodology to microparticulate deposits of copper corrosion products was used for discriminating these different monetary emissions. Upon attachment to graphite electrodes in contact with different aqueous electrolytes, nanosamples from the patina of coins produced characteristic responses of cuprite and tenorite. This methodology, which previously has been successfully used for dating archaeological bronze objects [2], permitted to establish a grouping of such samples suggesting different provenances/manufacturing techniques. Electrochemical data suggested that the monetary unification was performed in different stages involving different mints.

Figure 1. 10-cash copper coin from the Regular Provincial series minted in Canton (Kwantung,): obverse (left) and reverse (right).

Figure 2. 10-cash copper coin from the Tai Ching Ti Kuo series minted in Ngau (Hupei, 湖北): obverse (left) and reverse (right)

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A spectroscopic study of metal foils and its layering in Norwegian Medieval objects

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Gilding - the technique of applying a metal leaf to the surface of a work of art - played an important role in the decoration of medieval objects. Even though the gilding terminology originated in relation with gold, other metals have been connected to this nomenclature such as silver, tin and palladium as well as the use of two-layered leafs or metal powder applied onto the object.

The main types of traditional gilding methods are the so-called water gilding and mordant gilding. Water gilding technique provides a shining effect. A metal leaf is burnished (smoothed and polished) after application on top of a layer composed mainly by clay and iron oxide pigments and/or any other compactable material in a glue binding media, the latter activated by water to be used as adhesive. In the mordant gilding method the metal leaf is applied on top of a coloured oil layer which, due to its plasticity and stickiness, cannot be burnished and therefore has a final matt surface.

The aim of this study is to reveal by analytical means the elements, materials and methods of gilding techniques. The ambition is to make a first mapping of these techniques and to contribute to further studies related to the gilding technology and the artistic production and workshops in Norwegian medieval objects.

Circa twenty-five samples of gilding from four late-medieval objects were deeply studied in the framework of the project "After the Black Death: Painting and Polychrome Sculpture in Norway, 1350-1550". The samples were analyzed by optical microscopy, scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDXS), Raman and Fourier transform infrared (FTIR) spectroscopy. A broad group of these samples showed the presence of different qualities of gold and silver in the metal foils. Silver alone was found in a big group of samples - as was gold. Furthermore, a thin layer of metal was identified in different application forms. Raman spectroscopy and SEM-EDXS on the gilded preparation layer showed the presence of pigments such as lead-tin yellow, lead white, red lead, red-ochre and/or clay. Due to the thinness of the gilded preparation layer, difficulties were encountered in clearly identifying the biding media.

Data obtained by elemental and molecular analytical means have allowed the clustering of data from gilded samples to distinguish aspects of the gilding technology. This spectroscopic study will bring together results with the objective to shed new light on gilding techniques and workshop connections in Norwegian Medieval objects.

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Unveiling ancient gold inlay technique of a bronze belt plaque

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Belt plaques were very popular in China originated from Eastern Zhou period (770 - 221 BCE). As personal ornament, they were worn by nobles or warriors to reflect their social status. The S-shape bronze belt plaque with gold inlay and cloud pattern studied in this project was from a private collection [1]. Similar plaques can only be found in the burials during the Warrior States (475 - 221 BCE) at Shaanxi region so far. As one of the early casting metals used in history, copper with its typical alloy tin, was a popular metal used in Central Plains of China well before the 16th century BCE [2]. Bronze belt plaques inlaid with elaborate patterns in gold were certainly fashionable luxury accessories at the period.

Non-destructive techniques including microscopic surface examination, x-radiography, energy dispersive spectrometry (EDS) and x-ray diffractometry (XRD) were applied to study the fabrication techniques of the belt plaque. The highly unique stylistic form of the belt plaque combined with the archaeological information in burial context and technical examination results by multi-analytical methods unveiled the ancient goldsmith technique of that region at the period that has rarely been studied before. Elemental analysis was carried out by EDS revealed that lead containing tin bronze alloy was used. It was a common metallurgical alloy to produce ornaments before the Iron Age. The trace elements it contained reflected the metallurgical techniques and origin of the ore sources. Tiny platinum group minerals inclusions were found on the gold surface containing osmium-ruthenium-iridium alloy provided an important clue for the provenance. Surface corrosions identified by XRD were closely related to the burial and storage environment.

From the x-radiographs, the wires and edges of the sheets of the gold inlay exhibited a bright halo which indicated the areas were thicker and thus revealed the deeper grooves were made along the wires and edges of the inlay sheet. This can be further supported by surface examination in the areas where the inlays were missing. Many parallel shallow tool marks were found on grooves under the inlaid sheets that served as a rough surface to strengthen the adhesion. Inlaying sequences can be discerned upon closer examination on the overlapping areas. Large sheets were made by joining separate pieces together and the wires were inlaid before the sheets. Surface finishing was so well executed that the joins could hardly been seen in most places. Polishing and burnishing marks in different directions indicated the gold decoration, both in wire and sheet form, was applied mechanically and the smooth surfaces were produced after extensive polishing. Stamping technique was been used to create the curved pattern in relief as evidence by the repeating tool marks of the same size. Some grooves for inlay were cut before bending the bronze sheet to its final shape. No organic material had been found on the exposed grooves suggested no adhesives had been used, but the possibility of using clay for attachment cannot be fully excluded. It is interesting that there is a large amount of textile fibre in form of weaving textile pattern attached at the back side of the belt plaque which suggested it had been in contact with kinds of fabric in the burial environment. The fibres were identified to be hemp by microscopic examination.

Gold-inlaying technique was later fully replaced by the advent of the fire-gilding techniques. This study marks a start to the scientific study on the application technique of gold on tin bronze objects unearthed from the west of Central plains in China in the golden Bronze Age period.

[1] This research project is part of "Ancient Chinese gold working techniques (2014-2017)", which works in collaboration with the Art Museum of Chinese University of Hong Kong, Shaanxi Institute for the Preservation of Cultural Heritage and Chow Tai Fook Jewelry Co., Ltd. Belt plaques are generously provided by the owner of Mengdiexuan Collection of Hong Kong.

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What synchrotron radiation based experiments can tell about Poverty Point Objects (PPOs)

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Poverty Point is a prehistoric earthworks of the Poverty Point culture (1650 – 700 BC), located in northeastern part of Louisiana that is now a World Heritage Site. The majority of artifacts uncovered at Poverty Point are small, baked shapes made of loess, in different forms that are summarized as "Poverty Point Objects" or PPOs. Their uses have long been debated. Today, the commonly accepted hypothesis is that they were used in cooking. Most of the objects appear to have been made on-site. However, also this hypothesis needs further investigations as there is clear evidence for active trade with other Native American peoples.

Mainly two SR-based techniques were used for the investigation of the PPOs: synchrotron-radiation excited X-ray fluorescence (SR-XRF) allowing the (semi-quantitative) determination of the elemental composition of the samples and X-ray absorption near edge structure (XANES) spectroscopy providing detailed information about the chemical speciation of the elements of interest. In addition, some Infra-red investigations have been carried out for looking for organic materials. Experiments have been carried out at the Center for Advanced Microstructures and Devices (CAMD, Baton Rouge, LA) or at the Synchrotron Light Research Institute (SLRI, Nakhon Ratachasima, Thailand).

In this study, several PPOs from Poverty Point and a few from other nearby sites were investigated together with corresponding soil samples as references. SR-XRF spectra were recorded for all samples with an excitation energy of 15 keV and for some samples with 3 keV for improving the sensitivity for low-Z elements. Based just on the pattern of element composition one can determine with some confidence whether PPOs were fabricated from clay from the same site.

The speciation of various elements (e.g. ratio Fe(2+)/Fe(3+)) provides detailed information about the production process of a ceramic object (firing temperature, atmosphere in the kiln, duration of firing). Thus, Fe-K-XANES spectra and probably for the first time also Ca-K-XANES spectra were recorded of several of the samples. Even for samples with "identical" element distribution, XANES spectra show significant differences, for example, in the white line peak position and the position of the "edge" indicating that different fabrication parameter were used. For a reliable interpretation of these findings, additional test experiments with "model pottery" fabricated under defined conditions are carried out.

Towards non-destructive analysis of archaeological ceramics by micro X-ray fluorescence spectrometry

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The elemental analysis of ceramic pastes plays a crucial role in Archaeology. It allows discriminating among different clayey paste groups, which following the proper methodology, enable establishing the ceramic provenance according to their chemical fingerprint and help out building solid hypothesis regarding their historical implications and ancient trade networks [1]. Traditionally, several destructive techniques are employed to assess the chemical composition of the pastes such as Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) or Neutron Activation Analysis (NAA) [2]. Analytical instrumentation based on X-ray fluorescence spectrometry (XRF) implies new possibilities on the non-destructive analysis, but still have several limitations to overcome (e.g. limits of detection, reproducibility and representativeness of the analyses, etc.) [3]. In this work, a non-invasive multi-point strategy was selected to analyze 50 shards from several archaeological post-medieval sites in the Basque Country and La Rioja regions (Spain) by means of M4 TORNADO micro energy dispersive X-ray fluorescence spectrometer (μ-ED-XRF). For the analyses, a Rh tube and 1 mm collimator was used, and 50 replicate analyses on each sample were acquired in order to guarantee a representative analysis. To check the semi-quantitative approach obtained using Fundamental Parameters-based quantification methods, an iron rich clay (brick clay SRM679) and a low iron clay (flint clay SRM97b) reference materials were employed. The XRF chemical results were statistically explored by principal component analysis (PCA) and hierarchical clustering analysis, comparing them against the already-known reference groups obtained after destructive analyses (ICP-MS and NAA). Thus, the reproducibility of the former classification obtained non-destructively was assessed.

Additionally to the single point analyses, the distribution maps obtained at lower than 25 µm spot size allowed evaluating the influence of certain elements that may be transferred from the glaze into the paste, contaminations and even to understand better the technological features, which is also a crucial point when assessing ceramic paste compositions.

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Portable XRF setup with monochromatic radiation for the analysis of Cultural Heritage

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X-ray fluorescence (XRF) spectroscopy is a powerful analytical tool with a broad range of applications and has proven to be extremely useful in the analysis of artworks and archaeometry studies. In this work we present the development of a novel portable XRF setup, one of its kind, with triaxial geometry between the X-ray tube, a secondary target, the sample and the detector. This geometry significantly reduces the background of the measured spectra by eradicating the *Bremsstrahlung* produced in the tube through crossed polarization in the secondary target and in the sample. In this way, a better peak-background ratio is obtained, improving the detection limits and leading to superior sensitivity.

This setup reveals great improvements in the analysis of subjects with low-Z matrix, namely detection of trace elements in manuscripts and paper artworks. In this work, we will present the *in situ* analysis of paper documents belonging to the collection of Biblioteca Nacional de Portugal. A quantitative methodology will also be presented based on the comparison with paper standards.

Moreover, with this setup, a practically monochromatic excitation energy is obtained, allowing the evaluation of a sample's stratigraphy trough established methodologies of comparing the intensity ratios between characteristic lines of each layer. In this work, we will also present a methodology for determination of the thickness of gildings and silverings using this XRF setup.

The material characterisation of Industrial and Technical Heritage: The power plant in Levada de Tomar – Portugal

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Industrial and Technical Heritage (ITH) comprise objects, equipment and installations that are material testimonials of the industry history and technology development. In the last years, there has been a significant development on historical studies and conservation techniques to be applied to ITH objects. However, analytical studies that can support and contribute to this research are rather scarce. The characterization of the materials, coatings, lubricants, etc. can contribute to the knowledge of the Industry and Technology history and allow to establish with precision the conservation assessment.

In this work we present the material characterisation of a 20th Century power plant in Levada de Tomar – Portugal, composed by three groups of generators that produced electricity through hydraulic and diesel.

The equipment includes different materials, such as iron (steel) and copper alloys (brass) and coatings, which were characterized by *in situ*-X-ray fluorescence spectrometry (XRF). Representative samples were analysed by µ-Raman spectroscopy to obtain detailed and complimentary information about the coatings and corrosion products. Pigments red 3, blue 15, black 7 and calcite were found in red, blue, black and grey coatings. Observation under microscope revealed sometimes the superposition of 2 and 3 layers which can be related either to the use of a primary layer or to the application of new coatings. For complimentary information of the cross sections, elemental maps are being acquired by Scanning Electron Microscopy with Energy Dispersive Spectroscopy. Considering the corrosion products, *magnetite* and *goethite* were identified by µ-Raman spectroscopy and the presence of copper chloride based products is suggested by the detection of Cl in copper alloys using *in situ*-XRF.

The elemental identification carried out in a benchtop XRF setup enabled the characterization of lubricants. Fe, Cu, Zn and Pb were identified as wear metals and S, Ca, Zn and Ba as additives allowing to infer on the usage of the equipment.

The results achieved gave information on the history and usage of the equipment and allowed to define the conservation program based on the removal of corrosion products developed on the top of the coatings, maintaining the materials characteristics.

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In situ characterization of the materials and techniques of Roman Egyptian mummy portraits using combined forensic photography and spectroscopy

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Roman Egyptian mummy portraits, also known as Greco-Roman or Fayum portraits, are paintings mainly on wooden support reflecting Greek painting tradition blended with Egyptian funerary beliefs. This powerful combination of artistic skill and spiritual context results in individualistic portraits of the deceased that also provide snapshots of culture, fashion, and society within Greek (Hellenistic) Roman Egypt (1st century BC to the 4th century AD) [1]. Non-destructive evaluation of the portraits from the macro to the molecular scale using field-deployable imaging and spectroscopic techniques enabled the characterization of the materials and techniques used. Here we present results from forensic imaging investigations using multiband reflectance and luminescence photography from the ultraviolet (~350 nm) to the near infrared (~1000 nm) region, combined with fiber-optic reflectance spectroscopy (FORS), X-ray fluorescence spectroscopy (XRF) and X-ray diffraction (XRD) for compositional diagnostics of select Fayum portraits from the J. Paul Getty Museum Collection. The spatial distribution of Egyptian blue and madder lake pigments, visualized by their diagnostic luminescence at specific excitation and emission bandwidths [2] and confirmed by FORS, has revealed the selective application of these ancient synthetic pigments in the development of the individual portrait (fig. 1). FORS analyses also detected beeswax as the binding medium, suggesting an encaustic ('inburned') technique for the application of the coloring compounds. Integrated XRF, XRD and FORS data confirmed a rich array of inorganic and organic-inorganic hybrid pigments that were incorporated into the artists' palette to create lifelike portraits of the deceased. This study demonstrates the potential of an experimental user-friendly methodology that combines imaging and spectroscopy for non-invasive, in situ rapid and reliable analyses to develop a strong fundamental understanding of Greek Roman painting and technology.

Figure 1. a) Visible-induced near infrared luminescence of Egyptian blue on Fayum portrait (79.AP.141) and b) visible-induced visible luminescence of madder lake on portrait (81.AP.29) from J. Paul Getty Museum Collection.

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Rubrication in historic manuscripts

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Rubrication was one of several steps in the medieval process of making manuscripts. The practice usually involved the addition of red headings to mark the beginning of one section or to introduce the subject of the following section as well as to declare its purpose and function. Rubrication was used so often in this regard, that the term rubric was commonly used as a generic term for headers of any type or color, though it technically referred only to headers where red ink had been added.

Within the Centre of Image and Material Analysis in Cultural Heritage (CIMA) [1], established in the framework of the HRSM-project [2] with the aim of an interdisciplinary investigation of cultural heritage objects, a large variety of historical written manuscripts were investigated. The examined manuscripts were provided from many different libraries, as the Austrian National Library (ÖNB), several monasteries in Austria as well as religious foundations on mount Sinai. The selection comprises badly preserved or rewritten manuscripts (palimpsests) on the one hand, and manuscripts with a remarkable make up on the other, deriving from the 6th to the 14th centuries. As the mentioned manuscripts are very sensitive due to their age as well as due to the fact that they were in intense use, it was highly aimed that collecting data of used writing inks and parchments must involve non-invasive techniques. This means that methods with the ability to measure in-situ are required. XRF-analysis, Raman- and FTIR-spectroscopy cover the demands mentioned and can be applied under specific conditions also as air-path systems.

In most of the various investigated manuscripts, regardless the provenance, red ink is used to style a leading character with artistic loops and swirls - for headlines, capital letters or even oversized decorative initials. Depending on the origin and the century the used inks and binding media differ in their composition. XRF and Raman analyses revealed that primarily vermilion and minium were applied in red inks for initials. Mainly vermilion was detected in later Glagolitic and Greek manuscripts (12th-14th cent.), whereas early Glagolitic, Georgian, Armenian and Greek manuscripts (6th-12th cent.) usually contained mixtures of both in various proportions. Finally, purple red inks with iron oxide red could be detected solely in Byzantine-Greek manuscripts of the 12th and 15th centuries.

For an identification of binding media rFTIR-spectroscopy is the method of choice. Within these investigations strong indications for animal glue as binding medium for vermilion were found in Byzantine and Glagolitic manuscripts dating between the late 12th and 14th centuries.

[1] CIMA is an interuniversity research institution with an interdisciplinary approach to the investigation of cultural heritage. http://hrsm.caa.tuwien.ac.at/

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The presence of iron in the inks of the Valencian manuscripts from the 13th to the 17th centuries

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The significant artistic and documentary contribution of the manuscripts makes them unique instruments of knowledge that we must guard and know. Most of the manuscripts of Europe and America are written with iron gall inks, documented from 4th century [1] to 19th century [2]; and already since the 17th century we have news of the problems of conservation that generated because the same scribes echoed the convenience or not of its use [3].

The Valencian archives conserved numerous documentary collection from the period after the Conquest, but those of the stage between 1450 and 1600 stand out by the deficient state of conservation.

For this reason it has been tried to go in depth into the characterization of the components of these inks in relation to their preservation. Given the high iron content of these inks, a systematic study of 989 microsamples has been carried out. The iron concentration ratio results obtained have been evaluated - since the samples are not homogeneous and the proportion of ink in the paper could modify and the filament current values could also be different - depending on the dates and the archives which to the microsamples belong, with the semiquantitative results offered by SEM / EDX analysis.

A statistical study has been carried out using an ANOVA analysis of iron concentration as a function of the archive. Ten homogeneous groups are identified but do not have any significant geographical relationship. On the other hand, the concentration of iron is analyzed according to the date in which there is an increasing trend of the means between the thirteenth and seventeenth centuries. These values can be related to the incorporation in the preparation of recipes for new organic and inorganic ingredients, as well as the difference in preparation and concentration of iron sulphate according to the solvent used. Significant is the evidence that we note that the highest extremes of iron concentration are witnessed between the 1450 and 1550 range, which coincide with the most deteriorated documents.
The integrated study of historical sources and elementary analyzes help to recognize both the materials and the state of conservation of the same, which facilitates the process of conservation and restoration.

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Applicability of micro-reflection-FTIR-mapping for the investigation of medieval manuscripts – a case study

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A Greek manuscript of the Austrian National Library (13th century) was studied by applying micro-reflection-FTIR analyses. The manuscript consisted of a single folio folded in the middle, by which only one side was accessible for analysis. Brown-black and red inks were used to execute the script and moreover, a fairly well readable underlying brown text showed that the writing support was reused (palimpsest). The main aim of the analyses was to assess the applicability of micro-reflection-FTIR for mapping of materials on the surface of the manuscript, and the potential of this method to improve the legibility of badly preserved texts. The analyses were performed using a FTIR-microscope with a 8x objective and MCT-detector in the spectral range between 7000 and 450 cm^{-1}. A motorized stage enabled automatic point by point scanning of the areas of interest and the microscope camera provided an autofocus function. Measurement points were set next to each other without overlap. The spectra obtained were evaluated in various representations, such as reflection or absorption index. In addition, energy dispersive XRF with a spot diameter of 1 mm was utilized to obtain elemental information of the analyzed areas for improved evaluation of the FTIR-spectra.

The Results showed that the unevenness and other irregularities of the surface strongly complicate the analyses on the microscopic level. Moreover, the autofocus frequently failed due to lack of contrast. Consequently, only small areas on the same focus level were analyzed (Fig. 1). This finding also limits a possible use of FPA-detectors, which would allow for shorter measuring times. Provided adequate focusing, a satisfying spectral quality was obtained with an aperture of about 100 x 100 μm^2, although lower levels of noise were achieved with larger apertures. The set-up allowed the identification of variable amounts of chalk and silicates on the parchment support, partially in combination with lime soaps, whereas the detection of ink components (gallates, sulfates or gum) in the brown-black and the underlying text failed. The spectra from inked areas mainly showed a variable contribution of the support and additional contents of calcium oxalates, which indicated fungal degradation. Furthermore, the chemical maps revealed a strong inhomogeneity of areas with similar visual appearance, even in case of adjacent measurement points and hence, an improved visualization of characters could not be achieved.

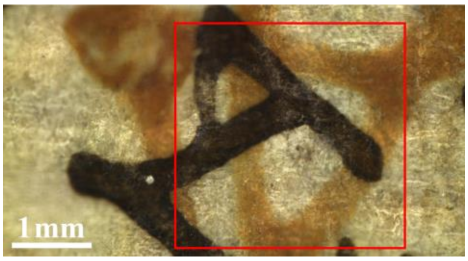

Figure 1. Detail from a Greek manuscript - image from the FTIR-microscope camera showing a scanned area (red). Please note the areas out of focus on the left side.

A multi-analytical characterization of French paper negatives: how to see through many processes?

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Photographic negative images on paper are certainly the earliest types of photographs ever produced, giving access to multiple prints of a same image using a unique matrix. As early as 1841 in France, many variants of the paper negatives processes have been developed by skilled chemists and photographers covering a wide spectrum of practical and aesthetic concerns. Nowadays, due to their inherent historical and esthetical values, those negatives are getting an increasing interest from the art and museum community. However their materiality has been less studied than positive images despite a large variety of processes and post-treatments involving many different chemicals and organic coatings; limiting our possibilities of identification, attribution or even preservation.

The aim of this work was to develop a methodology to better assess the way those images were produced based on physical or chemical characteristics. A non-invasive approach combining optical, vibrational and X-Ray spectroscopies is implemented on a collection of 50 historical images between 1841 and 1860 from French collections. Working with non-invasive reflectance FTIR on such paper prints shows great potentiality in revealing the presence of organic coatings such as gelatin or wax. Besides, a survey is carried out on these negatives to provide a series of relevant dimensional and morphological data (dimensions, weight, paper texture, etc). The power of multivariate analysis is demonstrated first on each spectroscopic data set, and then using methods that combine data of different dimensions. With this effective statistical approach, it is possible to correlate the physical, chemical and dimensional characteristics to particular photographic practices, and highlight relationships between different makers.

In situ spectrofluorimetric analysis of red & blue colours on 19th century Japanese engravings (Torralba collection, Zaragoza Museum)

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The study of fragile objects kept in museums requires mobile devices, short time of analysis and a minimal of disturbance to preserve the works of art. *In situ* spectrofluorimetric studies are mostly developed for organic pigments identification. The LED microspectrofluorimeter (LEDμSF) is a mobile device dedicated to in situ measurements that uses UV-light emission diodes (LED) excitation sources. It has proven to be an effective device for the study of binders, pigments and dyes in fragile paintings as some of these materials can be identified from their UV-fluorescence emission. The interpretation of the *in situ* fluorescence emission spectra can be rather difficult because of the variety of pigment mixtures, natural aging of colorants and fluorescence of the support (paper) that can lead to spectral changes or band shifts. One solution to interpret the data is to apply mathematical treatments to distinguish the pigments in case of mixture.

The colours of five Japanese engravings (woodblock prints with pigments) from the Torralba collection in the Zaragoza Museum were studied by the combination of hyperspectral imaging in the visible range (HSI), fibre optic reflectance spectroscopy in the near infrared range (FORS-NIR), colorimetry and ultraviolet fluorescence emission. This paper focuses on the red & blue colours analysis obtained using the LEDμSF on 5 engravings by Koryusai, Utamaro and Eisen (18th-19th). In the Japanese Prints, red, blue and purple colours were mostly used to illustrate various facts of the city of Edo (Tokyo) and scenes of everyday life (famous courtesans, kabuki theater, sumo, nature...). A lot of inorganic and organic red (vermilion, cochineal...) and blue (indigo...) pigments were used alone or as a mixture to obtain, for example, a purple colour. The fluorimetric spectra obtained *in situ* were compared with those obtained in laboratory on model samples. Red, blue and mixtures were studied to build a database of fluorescence emission spectra.

Printing materials and technologies in the 15th-17th century book production: an underestimated research field

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This research presents the results of a broad campaign of non-invasive investigations of inks and papers of a selected corpus of sixty books conserved in the Ateneo Veneto (Venice), instituted in the 1838. The books were printed in different European cities (e.g. Venice, Cologne, Basel) between the 15th and the 17th centuries. They are all related to scientific disciplines such as mathematics, astronomy, medicine, etc. like the *"De reuolutionibus orbium coelestium"* of Nicolaus Copernicus, printed in Basel in 1566 and the *"Exercitationes anatomicae, de motu cordis & sanguinis circulatione"* by William Harvey printed in Rotterdam in 1660.

Scope of this work is to study the printing technologies and evolution between the three centuries in order to highlight potential differences over the production areas, and potentially to identify chemical fingerprints.

Taking into account the historical value of the books, a specific protocol based on the application of non-invasive analysis were preferred. Multiple preliminary imaging analysis (visible, infrared and UV), X-Ray Fluorescence (XRF) measurements and Fourier Transformed Infrared Spectroscopy in Attenuated Total Reflectance (FTIR-ATR) of both papers and inks of all books were collected in order to highlight potential differences or similarities within different production areas and centuries. Next to the over mentioned techniques, colorimetric and pH contact analysis were also performed on the papers.

Thanks to the peculiar conservation history of these books, subjected to the same environmental conditions for more than two centuries in Venetian convents and subsequently for two other centuries up to now in the Ateneo Veneto, the possible correlation within the collected data, excluding potential interference related for example to different conservation states and/or degradation processes, was also taken into consideration.

FTIR-ATR analysis of the papers showed similar results for all the analyzed books. FTIR-ATR, imaging and XRF analysis highlighted the carbon-based nature of the inks with the presence of minio and cinnabar inks for some books. The XRF investigations showed moreover the presence of heavy elements like K, Ca, Mn, Fe, Cu, Zn and Pb. A detailed statistical analysis of the presence of these elements and their relative quantities performed using a mix of simple and multinomial logistic regressions and PCA, allows us to identify potential fingerprints of national manufactures and further macro as well as micro trends in the corpus.

The use of polyamidoamines for the deacidification of iron-gall inked papers

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Cellulose, the main constituent of paper, can be subjected to progressive acidification, hydrolysis and oxidation causing structural weakening of paper. In addition, enhancement of degradation processes due to acidity occurs in the presence of iron-gall ink, as transition metals can catalyze cellulose oxidation through Fenton reaction depending on pH values [1,2].

In this research, polyamidoamines functionalized with alcoholic groups (PAAOH's) in the native form or neutralized with boric acid [3] have been used for conservative treatment of iron-gall inked model paper. The treatments were performed by immersion of paper samples, brushing or by agar gel vehiculation. Deacidification effects induced by PAAOH's at different concentrations were evaluated by pH measurements on ink-free areas, on ink spots and around the edge of the spots and mass gain determinations of paper samples were carried out.

Besides deacidifying effect, PAAOH's showed a protective action towards iron-gall ink spots against water smearing and thermo-hygrometric ageing as suggested by FTIR, Raman investigation and colorimetric analyses.

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Interdisciplinary approach for cleaning graphic artworks: the case study of Diana Scultori engraving

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An innovative cleaning method was used for restoring an engraving by Diana Scultori (1547-1612), titled "Le Nozze di Psiche". The artwork, engraved in 1575 and printed in 1613, was affected by a structural and chromatic deterioration due to a strong oxidative degradation. Such deterioration was probably accelerated by the adhesive used for a previous lining intervention. The artwork was cleaned with Gellan gel and chemically stabilized with an alcohol solution of Borane Tert butyl ammine complex (TBAB) [1]. Preliminary analysis showed that the lining of "le Nozze di Psiche" was glued using a mixture of starch paste and animal glue. Thus, for the removal of the lining, enzymatic hydrogels were used. In particular, two Gellan gels loaded with different enzymes were applied consecutively: the first gel was loaded with *alpha-amylase* (*hydrolase*) to remove starch paste and the second with *Proteinase K* (*protease)* to remove animal glue. Monitoring of the cleaning process of "Le Nozze di Psiche" was performed by means of a non invasive cleaning and diagnostic tool, based on Gellan gel combined with an electrochemical sensor. This system is suitable to verify *in sit* ,in a real time and in a simple way the paper degradation progress, and the efficiency of the cleaning treatment [2, 3]. Using this diagnostic tool~~,~~ it has been possible to know when the cleaning process was completed, avoiding lengthy and unnecessary cleaning material applications. The effectiveness of cleaning with Gellan gel and chemical stabilization was assessed quantitatively by using non-invasive reflectance spectroscopy. This approach is based on an improved version of the Kubelka-Munk theory for recovering the absorption coefficient of cellulose fibers from reflectance measurements. Experimental absorptions were fitted to theoretical absorption spectra obtained by ab-initio computational simulations of oxidized groups acting as chromophores [4, 5]. Results indicate a large decrease of their concentration following the cleaning with Gellan gel and a minor one's following the chemical stabilization by TBAB.

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Combined macroscopic XRF and FTIR mapping of a 14th century illuminated manuscript fragment

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Macro X-ray fluorescence scanning (MA-XRF) is gradually becoming an established technique for the noninvasive analytical investigation of painted surfaces [1]. The elemental maps it provides allow to visualize the distribution of many of the inorganic paint components present at and/or below the surface [2]. In addition to oil and tempera paintings from different historical periods [1-3] and to stained glass windows [4], recently also (fragments of) illuminated manuscripts have been studied [5].

However, MA-XRF also has its limitations: since XRF yields no information on the organic fraction of the paint (binding media, organic colourants, …), it is advisable to combine MA-XRF with other point-based or image-based spectroscopic methods that provide more specific information on these compounds.

In the present work, a combination of macroscopic scanning XRF, reflection mode FTIR [5] and point-specific FTIR measurements were employed for the study of a fragment from an illuminated Gradual made at Santa Maria degli Angeli (Florence, Italy, 1370s), currently at the Fitzwilliam Museum in Cambridge, UK (MS 5-1979). The distribution of artists' materials including azurite, ultramarine, lead tin yellow, mosaic gold, gold leaf, lead white, vermilion, green earth, gypsum and minium could be determined, and information on some of the binding media employed was also obtained. At least two different binding media were identified, including egg yolk, which appears to be associated with minium and vermilion.

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Highly retentive hydrogels for paper cleaning

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Wet cleaning is usually performed during the restoration of paper artworks. The traditional procedure, which implies the immersion of paper in water bath, may lead to several drawbacks, including paper fibers swelling and dissolution of water-soluble original components. Moreover, pastes and glues are usually found in old paper artworks, and their removal is necessary not only for aesthetic reasons but because these components accelerate ageing processes. Recently, the use of hydrogels that allow an effective cleaning action by absorbing degradation products, inducing, at the same time, a very reduced water uptake by paper, has been proposed [1-2]. In this work, the usage of innovative highly retentive semi-IPN p(HEMA)/PVP gels for the cleaning of paper artworks is presented. These gels have been recently developed within the EU-funded NANOFORART project [3-4]. The semi-interpenetrated network takes advantages from both the mechanical stability of the p(HEMA) and the high hydrophilicity of PVP. These hydrogels are soft, transparent and easily handled without leaving residues. Furthermore, they are stable, not perishable and can be stored in water for months. Due to their properties, these gels have been tested for a residue-free and controlled cleaning intervention on water-sensitive works of art. In this work we report the results obtained by applying the proposed gels for the cleaning of the "*Breviarium Romanum ad usum Fratum Minorum*", a breviary of 18th century. Moreover, gels capability of loading the hydrolytic enzymes needed for a selective removal of old glue (starch paste and animal glue) has been studied. To assess the effectiveness and safety of the proposed cleaning method, we have employed a multi-technique approach, using high-performance liquid chromatography (HPLC), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and pH measurements.

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Direct fluorimetric characterization of dyes in ancient purple codices

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Purple codices are manuscripts written in silver and golden inks on purple-coloured parchments produced from the Late Antiquity to the Middle Ages to be owned by Kings or Emperors. Only a few examples of these amazing works of art still survive in libraries or archives. The identification of the purple dyes employed to colour purple codices is an intriguing task, as sampling is seldom permitted on these precious manuscripts and thus scientists should rely only on *in situ* analytical techniques. Nevertheless, non-invasive procedures show both strong and weak points. In particular, when natural dyes are considered, the obtained information may in some cases be unsatisfactory in order to achieve a thorough characterisation of the dyes [1-3]. For this reason, micro-invasive techniques are still widely employed when the presence of natural dyes is hypothesised in an artwork [4-5].

The exceptional availability of a small sample from the 6th century *Codex Brixianus*, conserved at Biblioteca Civica Queriniana (Brescia, Italy), allowed us to perform an in-depth fluorimetric survey of the purple parchment of this artwork. This manuscript has been previously investigated by means of non-invasive techniques (portable X-Ray Fluorescence spectrometry, UV-visible diffuse reflectance spectrophotometry with optic fibers and portable fluorimetry) which suggested that orchil or folium are most probably present in the parchment [6].

In this work, *in situ* fluorimetric measurements widened the previous analyses on the manuscript and suggested the contextual presence of both folium and orchil in some pages. In addition, emission fluorescence and luminescence lifetime measurements were performed on the sample from *Codex Brixianus* and on a set of reference parchments dyed with folium, orchil or a mixture of these two dyes. These measurements confirmed and narrowed the results obtained with *in situ* fluorimetry, thus opening the discussion about the peculiar manufacturing technique of this purple codex.

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Shades of blue: non-invasive spectroscopic investigations of blue paints on Mesoamerican Pre-Hispanic codices

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Mesoamerican codices represent the cultural legacy of pre-Hispanic indigenous people who recorded historical, religious, calendrical, and astronomical information using colorful images and logophonetic writing [1]. Only a small part of the Mesoamerican library holdings survived the Spanish conquest and the ravages of time. In recent years, non-invasive *in situ* spectroscopic investigations have been applied to study Mesoamerican pre-Hispanic codices revealing valuable information about the materials composition and painting technique while preserving their physical integrity [1]. In particular, nine of the thirteen extant codices and four early colonial codices were investigated by the mobile laboratory MOLAB combining UV-vis-NIR reflectance and fluorescence, mid-FTIR, X-ray fluorescence and Raman spectroscopy.

The present work is focused on the study of the UV-vis spectral properties of Mesoamerican blue dyes/pigments aimed at their non invasive in situ identification on codices. Specifically, a detailed study of the photophysical properties of indigo and Maya blue, the well-known organic-inorganic hybrid pigment [2], will be presented discussing the possibility to distinguish different types of Maya blue obtained by heating indigo and clay (either palygorskite or sepiolite) from the simple mixture. The influence of the synthesis parameters (indigo/clay weight ratios and heating temperatures) on the resulting UV-vis spectra will be also addressed comparing data from specifically conceived paint models and real cases.

Moreover, the experimental evidence of the use of a different blue paint, seemingly prone to fading and chemically related to commelinin, a metalloanthocyanidin extracted from the flowers of *Commelina communis* belonging to Commelinaceae family [3], will be discussed presenting the comparison of data from real codices and reference samples artificially aged.

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Quantitative diagnostics of ancient paper using THz time-domain spectroscopy

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An innovative method to quantitatively assess the state of degradation of paper in a non-destructive way has been developed by using THz time–domain spectroscopy (THz–TDS). The method relies on the observation that the hydrolytic and oxidative degradation of cellulose in paper is accompanied with rearrangement of the hydrogen bonds (*H*–bond) network of cellulose polymers. This gives clear fingerprints in the THz spectral profiles.

THz–TDS is a suitable approach to study low–energy vibrational properties of biological materials in a non-destructive way. The THz photon energy range (about 1–40 meV) is particularly suitable to probe the *H*-bonds between molecules. However, the quantitative assessment of the state of preservation of artworks poses significant challenges, in particular when measurements on low refractive index and thin samples, such as ancient documents and drawings, must be carried out [1].

In the present study, we have successfully solved this problem obtaining a precise determination of the absorption by cellulose fibers in the 0.2–3.5 THz (7-117cm^{-1}) range in single freely standing paper sheets. This has been achieved by developing a new procedure to remove from the experimental signals the spurious interference effects generated by the Fabry–Pérot resonances in the sheet. By using this approach, the THz absorption coefficient of cellulose fibers in ancient and modern samples artificially aged has been obtained.

The THz absorption spectra are explained in terms of absorption peaks of the cellulose crystalline phase superimposed to a background contribution due to a disordered *H*-bonds network [2]. The complex evolution of the spectra as a function of natural and artificial aging is explained with a reduction up to 30% of the *H*-bond density in the cellulose polymer networks and a parallel increasing of the sample crystallinity evident in the peaks at about 2.1 and 3.1 THz. The comparison with density functional theory *ab-initio* calculations suggests that the observed THz spectral changes could be related not only to the recrystallization of amorphous regions, but also to the progressive degradation of the external surfaces of crystalline domains. These results demonstrate a significant potential in the non-destructive analysis of the structural modifications of cellulose and paper artifacts by aging, resulting, at a macroscopic scale, in a progressive weakening of the mechanical properties of paper [3].

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What Vis-NIR reflectance spectroscopy can reveal about 15th century illuminated manuscripts: the *Corale 43* by Beato Angelico at the Biblioteca Medicea Laurenziana in Florence (Italy)

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Ultraviolet (UV), visible (Vis) and near infrared (NIR) fiber optic reflectance spectroscopy (FORS) is a portable, non-invasive, quick and versatile investigative technique for the identification of artists' materials. Since the early 2000s, the heritage communities have showed interest in this emerging technique, which has since been applied to a considerable number of works on paper and parchment in several museums and libraries in Florence and elsewhere [1-3]. The non-invasive nature of FORS is of paramount importance for the analysis of delicate and rare artefacts, such as illuminations on parchment, which mostly cannot be sampled.

FORS was therefore selected from the available in situ non-invasive techniques and applied to the identification of the materials used by Beato Angelico, his collaborators and followers in a number of illuminated manuscripts. Guido di Pietro, better known as Beato Angelico or Fra Giovanni da Fiesole (c. 1400-1455), is considered one of the most prominent artists of the 15th century in Italy; he was a versatile artist who excelled in creating illuminations, frescos, as well as panel paintings

This work will describe the main results of a multidisciplinary research project, which included a close collaboration between curators and scientists, on the illuminated book *Corale 43* (51 cm x 37.2 cm) attributed to Angelico. *Corale 43* was made for the convent of San Domenico in Fiesole in the 15th century and, after the Napoleonic suppression of religious orders at the beginning of the 19th century, it was moved to the Biblioteca Medicea Laurenziana in Florence. This study will report, for the first time, on the technical investigations undertaken on the manuscript. In the attempt to place the results within the wider context of the production of illuminations in the 15th century, the technical examination will be compared with other illuminated manuscripts from the same artist, from collaborators, as well as followers.

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Quantitative Monitoring of Works Of Art On Paper With Spectral Imaging

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When using Spectral Imaging (SI) for monitoring ageing processes in works of art on paper, the experimental and analytical methods differ greatly from those used for the more common applications of SI, such as the identification of writing media or the visualization of hidden textual information. For monitoring applications, the contrast-enhancing analysis of a single SI measurement is not sufficient. It is necessary to compare SI measurements that are performed on exactly the same area of a document multiple times in the course of the monitoring period, which may extend from a few weeks to many years.

To date, very few attempts have been reported in the literature to experimentally test the actual capacity of SI systems for detecting, identifying and quantifying low intensity ageing processes in cultural heritage artifacts on the short and long term. The aim of this study was to investigate experimental approaches for evaluating the suitability of SI instruments for monitoring applications and to develop standard procedures. In the course of a research master project at the Institute for Sustainable Heritage (UCL-London), experiments were carried out using the hyperspectral imaging system "SEPIA" of the *Nationaal Archief* (National Archives of The Netherlands), which operates in the VIS/NIR wavelength range from 365 to 1100 nm.

For this particular SI instrument, the sensitivity to detect changes and the impact of the repeated measurements on the monitored samples were investigated. For the experiments, a set of blue wool standard (BWS) ISO standard materials was used as well as samples from discarded original documents made of materials that are very typical in European archives. Artificial light-aging was applied (5 steps, 5 intensities) and the same samples were measured also with a spectrophotometer (colorimeter) and a fiber-optic spectrometer for comparison.

The impact of repeated measurements with the "SEPIA" instrument was found to be minimal even for the most light-sensitive BWS grade. After 41 measurement cycles, corresponding to a monitoring period of 20 years according to the exhibition practice at the *Nationaal Archief*, the $\Delta E2000$ value was only 0.5 ($\Delta E2000=0.7$ corresponds to a 30% probability that a colour change is visible under ideal viewing conditions [2]). The sensitivity of the SI instrument to detect spectral changes of light-exposed objects is wavelength-dependent, but in general very high. For example, it was possible to detect reflectance changes of lignin-containing paper after an exposure period of only 5 hours at 312 lux (equivalent to 4 days in the *Nationaal Archief* exhibition).

In a current project, the developed methods are transferred to the evaluation of the monitoring capabilities of other SI instruments at various institutions in Europe. For this research, a new set of samples is used, including discarded original papers of the Rijksmuseum. This research project is made possible by the Migelien Gerritzen Fund/Rijksmuseum Fund.

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Spectroscopic methods for mapping and dating restoration phases on two Egyptian sarcophagi (XXI dynasty)

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The restauration phases of the XXI dynasty sarcophagi are hidden behind their unique conservation history. Two wooden anthropoid sarcophagi (both composed by coffin and cover) and one death mask were studied; they belonged to a Theban priests and were discovered in 1891 in the Second Cache of Deir el-Bahari. Since 1894 they are held by the Musées Royaux d'Art et D'Historie of Bruxelles. The present work is aimed to cast light on the different interventions through the characterization of painting materials of five pieces whose final application was a conservative restoration by Istituto Europeo del Restauro in 2015.

After a preliminary phase of analysis by imaging techniques such as Infrared Reflectography and Fluorescence induced by Ultra Violet light, the pigments and binders were examined exploiting the synergy between four complementary non-invasive techniques. EDXRF (Energy Dispersive X-ray Fluorescence), FORS (Fibre Optics Reflectance Spectroscopy), FTIR (Fourier Transform Infrared Spectroscopy) and micro-Raman spectroscopy were applied in situ on the internal and external decorations of the five pieces. More than one hundred points were analysed in total and the different penetration depth of the applied analyses allowed to infer a possible stratigraphy.

Based on imaging techniques the painted surfaces showed areas with different features: dark areas with no UV fluorescence and low reflectance in IR, bright UV fluorescence and high IR reflectance (wavelength >700 nm) and low-intensity UV fluorescence with no difference in infrared reflectance. Such zones can be linked to the presence or absence of marker chemical elements (for instance Ba or Ti) or compounds that give hints about the presence and the period of the restorations. In these areas, an overlapping of a modern layer on the ancient and original one is the most probable current status of the pictorial stratigraphy.

Original identified pigments include Egyptian blue, copper based green, and Red Ochre on an underlying Orpiment yellow layer. In the areas put into evidence by imaging techniques and considered as already restored, we find Azurite, Prussian blue, Egyptian Blue, Vermillion, Red Ochre, Chrome Red, Chrome Green, copper based green, Zinc Yellow. The identification of more than one non-original blue, red and green pigments confirms the presence of successive different intervention. The historical knowledge of pigments permits to gather details on the conservative history of the sarcophagi. A layer composed of a natural resin was also detected, and then the resin could be more precisely identified as mastic by laboratory analyses.

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An Insight Into The Complexity Of Agar Gels

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Gels are commonly present in our every-day life and in particular they have gained an important role as a cleaning tool in the field of conservation of Cultural Heritage [1-2]. The main advantage of using gels consists in a confined release of the liquid phase minimizing the aggressiveness of water and solvents and reducing their diffusion into the artwork bulk. An increasing number of gel systems have been introduced in the conservation community, such as rhesponsive, peelable and biodegradable gels [3-5]. The literature highlights the important role of a polysaccharidic gel, the so-called Agar gel [6-7].

Agar is a phytocolloid extracted from red seaweeds of the class Rhodophyceae and in particular in Gracilariales and Gelidiales order since ancient times. Its main components are agarose and agaropectine: the first one is a linear polymer and it forms the gelling fraction, the second one is an heterogeneous agarose deeply modified with acidic side-groups (sulphate/pyruvate) that reduce the gelling properties. Experiences collected up to now from the restorers demonstrate agar ability to satisfy the fundamental requirements of a correct cleaning method, in terms of effectiveness, selectivity and respect of the surface to be cleaned. Nevertheless, a lot of issues concerning the cleaning mechanism are still opened.

This research focuses on the investigation of real cleaning mechanisms starting from the in depth study of different raw materials in powdery and gel form by a multi-analytical approach. Beside a chemical characterization with vibrational spectroscopies and chromatography to identify possible compositional differences, an insight into the micro-structural complexity of gels is fundamental to understand the cleaning mechanism and the transport phenomena of liquid phase and soiling. With this goal, scanning electron microscopy, thermogravimetric analysis and NMR relaxometry have been used to identify the microstructure and the water state in agar gels at different concentrations, whereas mechanical properties as a function of concentrations and heating processes have been investigated by rheological measurements. From the analysis of the different data it appears that it is quite hard to discriminate the different agar powders by vibrational spectroscopies; on the contrary, chromatography underlines compositional differences among raw materials. About agar in the gel form, analyses carried out up to now demonstrate suitable and significant differences in the overall water content and gel strength.

Future work will use these studies to probe agar gels on unsolved conservation problems.

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Evaluating the exploitability of several Essential Oils constituents as a new biological treatment against Cultural Heritage biodeterioration

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Biological colonization represents one of the most dangerous degradation processes jeopardizing Cultural Heritage. Several kinds of micro organisms, such as algae, bacteria, lichens and moods are capable of colonizing materials of cultural interest thereby seriously endangering their conservation [1]. In this light, this work was focused on the evaluation of the possible use of biological aromatic compounds as novel conservation treatment against the fungal colonization of Cultural Heritage materials.

Thus, the antifungal activity of 10 selected Essential Oil (EO) constituents have been tested against a wild strain of *Aspergillus niger*. The fungal strain was collected from the biological patina jeopardizing a mural painting conserved in the Archaeological site of Pompeii (Ariadne House, Regio VII 4.31/51).

The biocide assays, carried out by disc diffusion method, allowed identifying thymol, eugenol and cinnamaldehyde as the most effective antifungal agents.

However, one of the reasons behind the limited use of EOs is the lack of knowledge concerning the possible interaction of their constituent with the environment. For this reason, thymol, eugenol and cinnamaldehyde were exposed to different lighting condition aiming at identify the possible side-effect entailed by photo oxidation processes. After aging, all samples were characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography–Mass Spectrometry (GC-MS) techniques and used to carry out further antifungal assays.

The results proved that, after sun and UV light exposition, the photo oxidation processes suffered by cynnamaldehyde samples had a critical repercussion on their antifungal activity. On the contrary, composition and properties of eugenol and thymol samples were not affected by aging.

To conclude, this study confirms the possible exploitability of pure eugenol and thymol as alternative biological products against the fungal colonization of Cultural Heritage materials.

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Testing of new mortars for the conservation of *frescoes* in the wooden church in Amărăşti, Romania

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The wooden churches with *al fresco* painting constitute a unique Romanian heritage dating back to the 18th and the 19th centuries. The unicity comes from the painting technique of applying the *fresco* straight onto the wooden beams in the church. The fact that wooden surfaces are incompatible with *frescoes* combined with the fact that natural weathering of the site has been aggravated by a complete lack of maintenance have led to an advanced state of deterioration of the painting. This paper presents diagnosing of *fresco* paintings and *in situ* applying of restoration mortars similar to the original mortars in order to find proper conservation and restoration methods for such historic monuments. *In situ* analysis of the *fresco* painting was carried out by using image acquisition with a camera and a portable microscope. Samples were taken for carrying out analyses by optical microscopy, X-ray diffraction (XRD), scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM–EDS), Fourier infrared spectroscopy (FTIR) and thermogravimetric analysis (TG–ATD). The investigation showed a lime-rich mortar containing a mineral aggregate (river sand) and a vegetal aggregate (hemp tow). The original pigments have been identified to be specific to *frescoes*. Gypsum-containing efflorescence has also been found. The investigation has also revealed various biological contamination forms. The restoration mortars were first tested in the laboratory [1] and then applied *in situ* on small areas in the altar apse of the wooden church in Amărăşti, Romania (fig.1). In order to see how the restoration mortars stand the test of time, they were checked five and ten months on. The results proved that the restoration mortars to have maintained adherence to the wooden surface without any secondary effects such as biologic contamination, saline efflorescence, or colour change next to the restoration work.

Figure 1. In situ application of the restoration mortars

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A multidisciplinary investigation on a pair of leonardesque canal gates

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Leonardo's Atlantic Code depicted a detailed drawing for a new wooden canal lock to control the water flow in Milan canal system. Museo Nazionale della Scienza e della Tecnologia "Leonardo da Vinci" in Milan has been conserving for fifty years two pairs of canal gates in its depository, until a complete and multidisciplinary study was launched to deeply examine one of them. Both historical and scientific research teams joined their efforts. While historical research has reconstructed the provenience of the gates until their arrival to the Museum, the scientific analyses were a new opportunity to help the reconstruction and the characterization of the canal gates' history, enlightening the construction technique, the structural modifications over time and the conservation conditions.

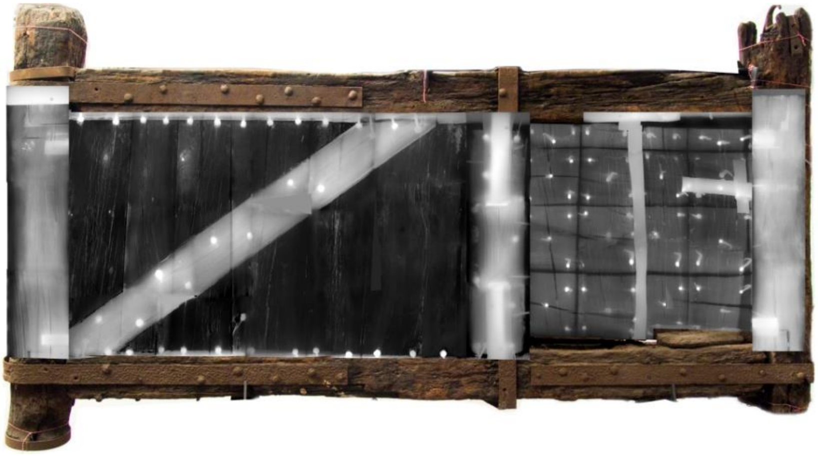

Figure 1. X-Ray image of the gate as a result of a stitching of 37 X-Ray images.

The multidisciplinary investigations involved radiographic analyses, 14C dating and the characterization of the wood species present in the gate and the degradation of this wood.

Through the radiographic analyses (including EDXRF ones) it was possible to show the structure of the gate, the joints and the position of the metal components. Eighteen micro-samples were collected on selected areas of the gates. Each sample was divided in two halves to allow performing both the radiocarbon dating and the degradation study on the same sample. After the chemical preparation only eight samples were eligible to undergo 14C dating with AMS. They provided interesting results: artefacts dating results span over four centuries. DNA barcoding analyses allowed identifying the wood species as Norway spruce and common beech; the degradation of the wood was studied measuring the amount of lignin and holocellulose and the distribution of their molecular weights as well as the study of inorganic elements inside the cells.

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In-situ micro XRF investigation of four Mycenaean gold signet rings from the grave of the Griffin Warrior at the Palace of Nestor in Pylos

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An in-situ micro-XRF analytical campaign was conducted in March 2016 at the archaeological museum of Chora in Pylos, the goal being a non-destructive examination of recently excavated artefacts from the grave of the Griffin Warrior. The grave of the Griffin Warrior was discovered and excavated in May 2015 by the team of the University of Cincinnati under the aegis of the American School of Classical Studies at Athens [1]. Hundreds of grave goods made of gold, silver, bronze, ivory, and semi-precious stones were excavated. Among the gold artifacts four signet rings were found near each other near the rib cage of the Griffin Warrior; all are decorated with Minoan ritual scenes [2].

Scanning micro-XRF analysis was carried out for the first time on signet rings by a customized model of the ARTAX portable micro-XRF spectrometer (Bruker Nano GmbH). The spectrometer offers a non-contact and non-invasive elemental analysis of small areas (typical dimension of the spot analysis is 0.064 mm for Cu-K). For the determination of the composition of the gold rings an in-house software package was used [3]; it was validated by four reference gold alloys with an Au content in the range 58 - 95% w/w.

The analytical investigation aimed to determine the composition of the gold alloys from which the four signet rings were made and to identify soldering techniques. For each ring, the top, bottom and side of the bezel was analyzed, as well as the outer surface of the band of the rings. In addition, micro-XRF scans were also performed within the engraved decorative regions on bezel of the rings, in order to detect possible differences in the composition of alloys owing to surface treatment. The results are discussed and compared with available data from the literature [4].

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Combined μ-XRF and μ-PIXE/μ-EBS analysis of ancient copper coins

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In ancient coins, the corroded surface is usually a slowly grown inhomogeneous and multielemental layer with a thickness that ranges from a few micrometers to the full coin thickness (in extreme cases). Its study provides important information about the environmental conditions that triggered corrosion and which procedures are more efficient to restore or stabilize the metallic surface. The numismatic and historical value of ancient coins usually demands a non-destructive approach for this study. This work presents the results obtained by the combination of μ-XRF (X-Ray Fluorescence) and μ-PIXE/μ-EBS (Particle Induced X-ray Emission/Elastic Backscattering Spectrometry) analysis for two ancient Portuguese copper coins: a XV Century Real Preto and a XVI Century 2 Reais. μ-XRF probed the coins surface without incrusted dust (no Fe detected) from which the bulk elemental composition was retrieved. μ-PIXE and μ-EBS spectra were obtained simultaneously and analyzed in a self-consistent manner in regions with different patterns of surface alteration. This approach allowed the determination of complex elemental depth profiles, as exemplified in fig. 1 for the 2 Reais coin: an iron incrustation that extends as deep as ≈ 36×10^{18} at/cm^2 (≈ 4.6 μm), showing a maximum concentration at a depth of ≈ 20×10^{18} at/cm^2 (≈ 2.6 μm). This depth also defines the extension of the corroded layer, due to oxidation from the surface.

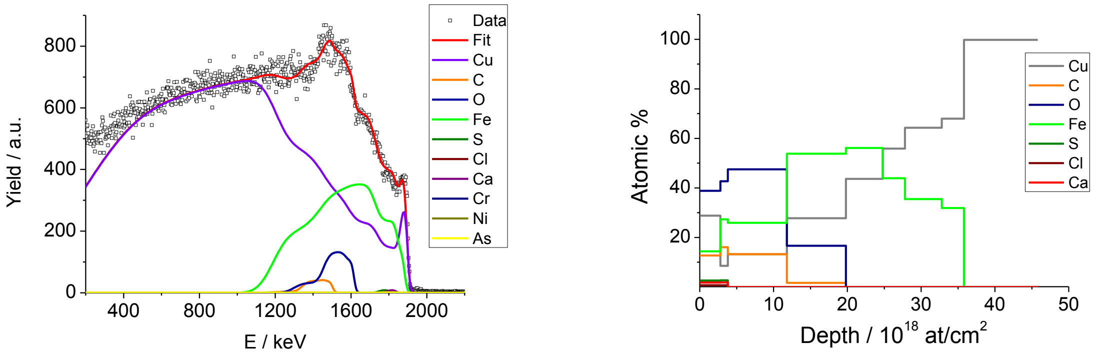

Figure 1. (a) μ-EBS spectrum taken in a location (3×4 μm^2) where Fe was clearly identified. Spectrum fitted with DataFurnace [1]. Coin: 2 Reais. Beam energy = 2.0 MeV. (b) Elemental depth profile obtained from the μ-EBS spectrum fit. Depth distributions for As, Ni and Cr are not plotted.

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Chemical analysis of the Pharaonic Period bronze mirrors stored in the Museo Egizio and study of the degradation phenomena. A completely non-invasive approach

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The mirror, mostly feminine object, seems to have been constantly used in ancient Egypt. From the Sixth Dynasty (2350–2250 BC) until Greek-Roman times, it accompanies the deceased in their houses of eternity. Mirrors were part of the luxury items reserved for the affluent classes. Associated to the goddess Hathor and similar to the Sun with their circular or elliptical shapes, for the ancient Egyptians mirrors could symbolize the resurrection in the afterlife. This may explain why mirrors were not only part of the grave goods of the deceased, but they were also wrapped with the mummy, unlike other objects in the tomb [1]. The mirrors here discussed are all stored in the Museo Egizio of Torino and they were analysed to obtain information about their composition and the degradation phenomena [2].

This project followed a mainly non-invasive approach able to obtain information without altering and/or sampling the objects. The aim was the characterization of the chemical composition of the whole Egyptian mirrors collection and their compatibility with the historical information. The applied non-invasive methodology was supported by a parallel laboratory study on the influence of degradation phenomena on the p-XRF analysis of a copper alloy with a composition similar to the analysed New Kingdom's mirrors (1550–1060 BC) [3].

The optimization of the surrounding set-up conditions and the analytical algorithms in the context of a portable and non-invasive approach, allowed determining the Bronze alloys evolution in the metallurgical technology of the ancient Egypt, exclusively working with data from in-situ measurements performed within the museum galleries.

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Metallurgy of the earliest lost-wax cast

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In the field of semiconductor Science, photoluminescence spectroscopy is a well-established technique and energy bands [2]. However, in the field of ancient materials, very scarce works have been undertaken to impart luminescence-based technique capabilities to retrieve quantitative information on the composition or structural specificities of materials at the microscale, since the pioneering work in the early 20th century established UV photoluminescence photography to study works of arts of museum collections. Since few years, synchrotron photoluminescence imaging has emerged as a promising method to study heterogeneous materials, composed of inorganic and organic compounds as those in ancient material sciences [3,4]. Recent developments have allowed to tackle the study of semiconductor phases within archaeological and cultural heritage samples. Particular effort have been undertaken to increase the spatial dynamics and the spectral dynamics in emission and excitation to collect low-signal emission at the sub-microscale from heterogeneous systems and in particular on archaeological artefacts.

In particular, within the study of a 6,000-year-old amulet from Mehrgarh (Baluchistan, Pakistan) identified as the oldest known artefact made by lost-wax casting, we demonstrate that our novel approach allows accessing the spatial distribution of crystal defect fluctuations at the crystallite level across centimeter-wide fields of view. Such capabilities allow revealing the coexistence of two hitherto indistinguishable non-stoichiometric cuprous oxide phases. Such results were the missing brick to access key information on the early step of this fundamental invention, still in use nowadays for precision casting [5]. We therefore demonstrate the exceptional potential of high spatial dynamics-photoluminescence imaging to study nano- and poly-crystalline materials for applications within a variety of fields, ranging from quality control in semiconductor solid-state physics to geophysics, archaeology, cultural heritage and environmental sciences.

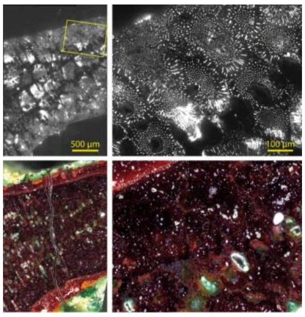

Figure 1. Photoluminescence Image. High spatial dynamics photoluminescence (PL, top) and optical microscopy (bottom) images of an area of a portion of one spoke of the amulet. The PL images reveal a rod-like structure of the eutectic which was not visible using other techniques. With this information, the method of manufacturing of the ornament can finally be explained.

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Effectiveness of optical micro-profilometry for monitoring the surface morphology in metals and pictorial layers under aging process

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The collection and the integration of multi-modal information allow a comprehensive diagnostics of the artwork that includes the monitoring of surface, sub-surface, and material properties. For an advanced diagnostic of real artworks, which are complex multi-material objects subjected to different environmental factors, laboratory measurements of mock-ups in controlled conditions, together with data processing to extract the appropriate material features and the definition of material-specific ageing models represent a fundamental phase. This is one of the main aim of the Scan4Reco European project [1] within the Horizon 2020 framework.

Among the diagnostic techniques, micro-profilometry provides the quantitative measurement of the surface texture and roughness at micron scale, which is mandatory to obtain information about the material changes over time in terms of its surface behaviour. Besides the metrological parameters several material features are detected. The surface cracks and the craquelure can be easily mapped, and some information regarding the material can hence be extrapolated from the analysis of these patterns. Scratches and surface defects can be documented using different algorithms to allow monitoring the conservation state or to test cleaning procedures.

In this work, we employ a scanning profilometer based on conoscopic holography to measure a set of reference samples of different materials (bronze, silver, pictorial layers) during artificial aging process in order to monitor the behavior of the surface morphology under controlled condition. The optimal measurement procedure, the surface data obtained, and the methods for the features extraction are evaluated to provide a valid diagnostic protocol.

The implemented micro-profilometry setup allows extending the surface measurement to large area together with keeping high resolution (sub-micron), thus providing excellent data for analysis purpose. The use of high-sensitive micro-profilometry, optimal measurement protocols, and advanced data processing, together with well-prepared mock-ups and aging schemes, allow a comprehensive study of the degradation mechanism.

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None invasive Synchrotron based X-ray Diffraction investigations of Archaeological Bronze and Gold

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For many archaeological metal objects the production techniques are known or at least suspected. Nowadays information about the grain structure, crystallographic orientation and the strain can help to monitor or identify different production pathways and can be obtained none destructively. These information may provide also provide new insight trying to understand knowledge transfer patterns of times before written documents, when collected from well attributed objects. On the other hand insight into the production method of an object can help to evaluate the potential origin or authenticity of poorly documented finds.

We show case studies with mainly Synchrotron radiation X-ray diffraction methods for characterizing bronze and gold objects upon treatment methods, as historically relevant forging and tempering, as well as modern drawing and rolling. To allow destructive reference tests without damaging any historic objects and to provide reliable reference data for clearly defined production states, we replicated several objects in various states. Measurements were performed at Beamlines L, HARWI and G3 of DORIS III, as well as P02 and P07 of PETRA III at the Deutsches Elektronen-Speicherring (DESY) in Hamburg, Germany.

Analyzing bronze age axes we could already make use of information these methods can provide [1] and as an unintended side effect expose a 160 year old forgery [2], thus redating the hoard find from 1500 B.C. to 1850 A.D. - so the find remains historic, but not quite as historic as believed.

In the progress of the authenticity validation of several bronze age gold discs, we could transfer the methodology to a significant part and provide new insight for the still ongoing inspections. We could clearly show that the objects in question had been produced with traditional hammering technique and thus could exclude the option of rolled sheet metal as starting material – hence these discs may really be as old as hoped for.

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Armourers’ marks and their detection

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High-quality armour made during the Middle Ages, such as the products of 15th century Milan, which were exported in some quantity, was frequently marked by the craftsmen who made pieces of plate armour, as well as by the “traversator” who assembled the suit[1]. These marks can identify both the craftsman and the city and, sometimes also, the arsenal where it might have been stored. These marks were stamped on the finished plates but frequent use and polishing has worn away the top layer of steel and, in many cases, only traces of the marks are now visible. However, if these marks had been struck in cold metal, there should still be layers of strained grains below the outermost polished layer. Forensic scientists usually etch metal artefacts such as gunbarrels in order to reveal hidden serial numbers by using strong acids to dissolve away the polished layers. This approach is, of course, ruled out for museum objects. We believed that advanced neutron imaging techniques would provide a non-invasive alternative. In this experiment we have performed radiographic experiments exploiting polychromatic phase-contrast imaging; a method for contrast enhancement in transmitted neutron beams by measuring a sample made with a homogeneous material but exhibiting a different microstructure induced by mechanical actions. We were able to reveal the armourers’ marks now obscured by polishing. Five helmets from the European Armoury of the Wallace Collection were examined, with very promising results. One example is shown here:

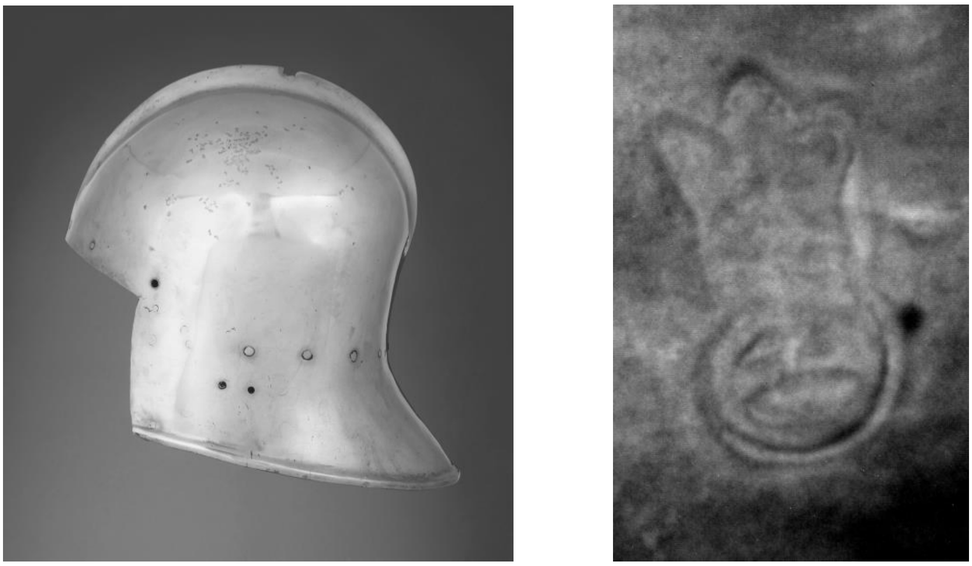

Figure 1. (left) A 15th-century Flemish helmet from the composite armour Catalogue no. A20; bears an almost erased mark [2]; (right) The radiograph shows the details of this mark which may now be attributed to the armourer Martin Rondel of Brussels.

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7. ABSTRACTS: ROUND TABLE

European Research Infrastructure for Heritage Science (E-RIHS)

The Round table organized in the framework of Technart 2017 will present the future European Research Infrastructure for Heritage Science (E-RIHS). E-RIHS will support research on heritage interpretation, preservation, documentation and management. It will comprise: E-RIHS Headquarters and National Hubs, fixed and mobile national infrastructures of recognized excellence, physically accessible collections/archives and virtually accessible heritage data. Both cultural and natural heritage are addressed: collections, buildings, archaeological sites, digital and intangible heritage. E-RIHS will provide state-of-the-art tools and services to cross-disciplinary research communities advancing understanding and preservation of global heritage. It will provide access to a wide range of cutting-edge scientific infrastructures, methodologies, data and tools, training in the use of these tools, public engagement, access to repositories for standardized data storage, analysis and interpretation. E-RIHS will enable the community to advance heritage science and global access to the distributed infrastructures in a coordinated and streamlined way.

Sorin Hermon, *The Cyprus Institute, Cyprus. "Overview of the preparatory phase of E-RIHS".*

Marta Castillejo, ***Instituto de Química Física Rocasolano, CSIC, Spain.*** *"The Spanish hub within E-RIHS".*

Bruno Brunetti, *CNR-ISTM and SMAArt, Perugia, Italy,"Access to Mobile Laboratory for in-situ diagnosis (MOLAB)"*

Quentin Lemasson, *C2RMF-**Centre de Recherche et de Restauration des Musées de France, AGLAE, France,** "Access to Large Scale Facilities (FIXLAB)"*

María Martín Gil, ***Instituto del Patrimonio Cultural de España (IPCE), Spain, "Access to scientific Archives for*** *Heritage Science (ARCHLAB)"*

8. ABSTRACTS: POSTERS

On the modification of photoluminescence properties of zinc white induced by carboxylate formation

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At the end of eighteenth century, zinc white became the top white pigment in substitution of lead white. Despite its wide diffusion, zinc white paintings showed to be subject to fast degradation processes, especially when mixed with organic binders. Recently, metal soap formation has been identified as frequent explanation of degradation in modern painting layers [1]. During the ageing of the paint, these aggregates are naturally formed due to the interactions between the fatty acids of organic binder with metal ions of pigment, altering the paint chemical and physical properties [2].

In this contest, we have performed a systematic study on the photo-physical properties of zinc white-based painting layers by means of time-resolved photoluminescence (TRPL) spectroscopy. The technique has allowed the detection of important changes in trap state photoluminescence emissions when zinc white is mixed with binders. The enhancement of emission in the blue region (BL) combined with a change of the decay kinetic of the well-known green emission (GL) are the most remarkable outcomes [Fig.1]. FTIR spectroscopy analysis on samples mixed with lipid binder suggests a significant correlation between the formation of zinc carboxylates (~1590 cm^{-1}) and the decrease of GL lifetime. This result may be related to zinc ions migration in binder matrix, as reported in recent studies on zinc soaps formation [3]. Indeed, the creation of novel zinc vacancies can affect the PL properties of the semiconductor pigment.

Generally, this work demonstrates that the analysis of trap state PL emissions is a powerful method to detect structural defects inferred by degradation phenomena in painting layers, with promising results in the field of Cultural Heritage conservation.

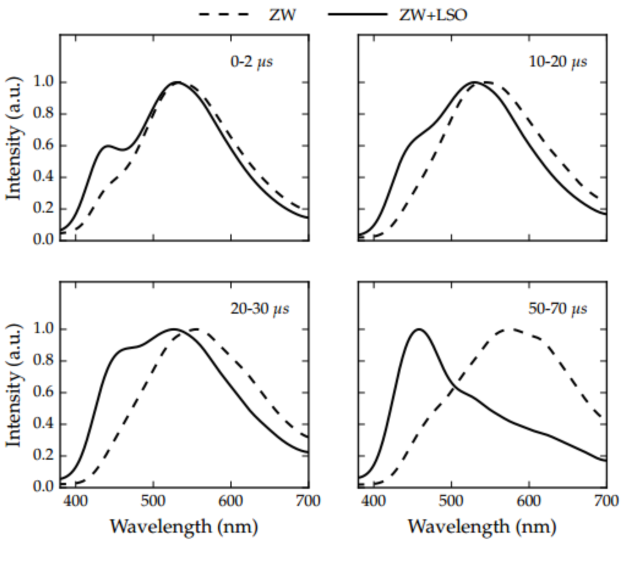

Figure 1. Time gated PL spectra of zinc white powder sample (ZW, dashed line) and the same powder mixed with linseed oil (ZW+LSO, black line). Gated PL spectra are taken in different spectral windows explicated in labels. The enhancement of BL and the change in GL lifetime is clearly recognizable through this analysis.

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Profiling of free fatty acids and acylglicerols in oil paint by a novel HPLC-ESI-Q-ToF method

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The appearance, stability, degradation and response to conservation treatments of oil paint are strongly dependent on the molecular composition of the lipids that compose them. The profiling of free fatty acids, along with triacylglycerols and intermediate hydrolysis products and possible oxidation materials is thus a valuable information for those dealing with the characterisation of the reactions occurring in paints during ageing.

The profiling and semi-quantitative analysis of di- and triacylglycerols is commonly performed by HPLC analysis, entailing the separation of the analytes on a reverse phase (RP) analytical column, interfaced with UV spectrophotometric, evaporative light scattering detection, charged aerosol detector (CAD) or MS detection [1, 2]. Nonetheless, the simultaneous detection of fatty acids and triacylglycerides has seldom been performed, and only in conditions entailing the use of complex elution mixtures and often more than one chromatographic column in series, leading to high back-pressures in the chromatographic system and very long analysis time. The detection of fatty acids by HPLC is generally performed after suitable derivatization reactions, to increase their retention times on RP columns, and to allow their detection by spectrophotometric detectors. These derivatization reactions mostly entail transesterification, and can thus be applied to the free fatty acids extracted from the samples, or after saponification and subsequent acidification and extraction in organic solvents. As a consequence, this strategy is not applicable for profiling of free fatty acids, mono-, di- and tri-glycerides in the same sample.

In this paper, in the frame of the collaborative European JPI project C-MOP (Cleaning Modern Oil Paint), we optimised the derivatization of long chain fatty acids (from 12 to 20 carbon atoms) in oil samples with 2-hydrazinoquinoline, which has been experimented for the derivatisation of short chain organic acids (up to 4 carbon atoms) [3]. This reaction does not entail transesterification, thus allowing us to separate and successfully quantify the free fatty acids in the presence of mono-, di- and triacylglycerols. This new analytical method allowed us to obtain the full lipid profile of fresh oils and modern oil reference paint layers (both naturally and artificially aged) within a relatively short chromatographic run (less than 40 min) and low backpressure (less than 110 bar), allowing, at the same time, the identification of the lipid binder, based on the TAG profiling [4], as well as the evaluation of the degree of hydrolysis of the paint.

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Identifying the origin of pink pigmentation on mural paintings in churches from Romania

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Pink pigmentation of mural paintings in historical monuments from Romania was identified mostly in churches with poor state of conservation. The pink pigmented areas are located on the lower part of the wet walls which are rich in salt. Little attention has been paid to origin of pink pigmentation because it was attributed to chemical reactions.

The aim of the present research is to characterize the pink pigmentation and to find analytical techniques for its the accurate identification. To reach this goal was performed investigation based on Raman and FTIR spectroscopy, XRF spectrometry, optical microscopy, and scanning electron microscopy with X-ray microanalysis. Microbiological techniques had been also used for isolation of carotenoid producing bacteria, inoculation of experimental models of mortars in order to reproduce pink pigmentation in laboratory as well as to be used for identification of pink pigmentation using above analytical techniques.

The results showed that pink pigmentation has microbial origin, mainly bacterial. Carotenoids pigments had been identified by Raman and FTIR spectroscopy on the original and infilling mortars as well as on pictorial layer samples, but not by XRF spectrometry most probably due to their organic origins.

Optical microscopy and scanning electron microscopy with X-ray microanalysis are good tools for identification of bacteria on the infilling samples and on the experimental models where pink pigmentation had been reproduce in laboratory conditions. Salts had been identified around bacterial biofilm (SEM-EDS).

Observation by optical microscopy of cross-sections of the infilling mortar samples as well as of the contaminated experimental models revealed pink efflorescences colonized by bacteria, extended pink biofilm and pink colonies of bacteria.

In conclusion, our results established bacterial origin of pink pigmentation and pointed analytical techniques for its identification. In addition, FTIR spectroscopy can be used *in situ* for mapping of pink biopigmentation.

Acknowledgements: This research has been carried out with financial support of the National Research Program ***Parteneriate în domenii prioritare*** – *PNII*, MEN – UEFISCDI, project no.PN-II-PT-PCCA-2013-4-0660.

Analysis of materials applied in the Banner of Sanlúcar de Barrameda

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The Banner of Sanlúcar de Barrameda (Spain) was made in the second half of the 17th century and used in the most solemn occasions, as the coronation of monarchs or religious festivities. On the red base of the textile in crimson damask a central shield represents the weapons of Carlos II on a golden background. Due to its antiquity and use, his conservation state was very deteriorated, which is why it was sent to the Instituto Andaluz de Patrimonio Histórico (IAPH) in order to be restored and properly conserved once returned to the Town Hall of Sanlúcar.

Before and during its restoration, analyses have been carried out to characterize materials applied and artistic techniques used. First, UV images have been carried out to observe later interventions. Next, small samples from the painted shield have been carefully extracted and once prepared as cross-sections, observed under optical microscope (OM) and analysed with Scanning electron microscopy with Energy dispersive X-ray technique (SEM-EDX). Also the non-destructive X-Ray Fluorescence (XRF) was applied to analyse materials in the areas where no samples could have been taken. [1]

The UV images showed many retouched areas and also several textile patches were revealed, added through time in order to cover and repair the broken areas of the textile. SEM-EDX and XRF results identified pigments and the preparation used. The authors applied a gypsum preparation (characterised by Ca peaks), on top of which red bole (Fe) and gold (Au) were applied. The presence of silver (Ag) found only in some points is probably result of the textile contamination by the banner's stick, around which the banner is rolled up. The pigments applied are lead white (Pb), yellow ochre (Fe) lead-tin yellow (Pb, Sn), red ochre (Fe), vermilion (Hg), minium (Pb), blue smalt (Co, Ni, As), azurite (Cu) and umber (Mn, Fe). The presence of Naples yellow (Pb, Sb) on one of the added patches is obviously a later intervention.

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Characterization of the Inkaterra rock shelter paintings exposed to tropical climate (Machupicchu, Perú)

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During many centuries rock art has been a form of expression of human being. This practice is part of the spiritual expression of ancient cultures, which represented and today continue representing their magic-religious concepts and daily acts. The historical and cultural value of rock paintings is very high, and should be valued as a part of the cultural heritage. Example of this are the Inkaterra rock shelter paintings, which are placed in one of the most impressive and unknown natural setting, located in the town of Aguas Calientes, belonging to the lands of the Hotel Machupicchu Pueblo, forming part of Machupicchu Archaeological Park (Peru).

In the rock substrate of the shelter, rich in albite ($NaAlSi_3O_8$), circular and geometric pictographs in three different colors (black, red and orange) can be distinguished (see Figure 1). In this area the humidity level is very high (70-90%), favouring the growth of biological colonizers, to such an extent that sometimes specific biofilms can be mistaken with pigments used to create specific decorations.

In this work, thanks to the use of micro-Raman spectroscopy, X-ray Diffraction (XRD) and Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDS), the molecular and elemental composition of the rock substrate and the one of the different pigments (iron oxides, organic compounds, etc.) used to create the pictographs visible on the Inkaterra rock shelter was studied.

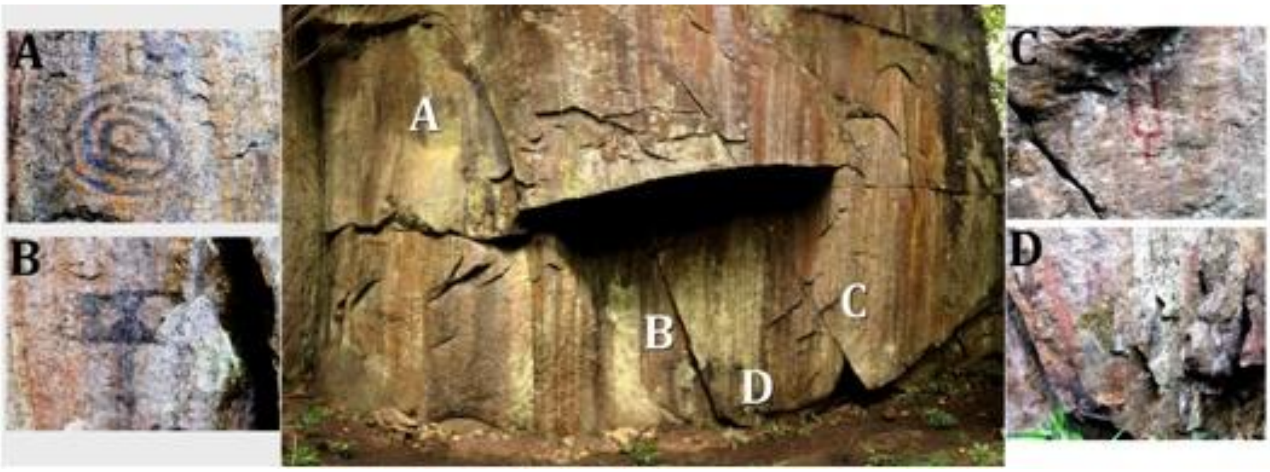

Figure 1. Inkaterra cave shelter general view and some details of the (A) black and orange circular pictograph, (B) black geometric pictograph, and (C) (D) red geometric pictographs.

Data integration schemes from UV imaging analysis for mapping and dating restorations on two Egyptian sarcophagi

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The use of analytical techniques without sampling can face with insurmountable limits when applied to artworks exposed to intensive restorations in the past. The present work is aimed to cast light on two wood sarcophagi of XXI dynasty, subjected to a complex restoration history since their discovery (1891) and since the assignment (1894) to the ***Musées Royaux d'Art et D'Historie of*** *Bruxelles*. Before any analytical investigation on the painting materials of the several layers found during the preliminary phases of restoration carried on by *Istituto Europeo del Restauro* in 2015, an intensive multispectral investigation has been performed. Imaging techniques, such as multi-band Infrared Reflectography (RIR) and visible Fluorescence induced by ultra violet light (FUV), allowed to distinguish areas with different kind, and probably age, of intervention thanks to both different surface fluorescence and near infrared reflectance of some pigments. Morphological study of the areas pointed out by means of RIR and FUV was essential to understand history of the sarcophagi before any analytical techniques (elementary, optical or vibrational) could be applied. This work deals with the problems occurring in reconstructing a map of fluorescence, depending on both the use of non-original pigments and the modern binders or protective varnish. In both cases, the luminance of some areas obtained under different condition of light (visible, infrared and UV) in digital images has to be compared and considered in order to obtain reliable results for the whole surface of the two sarcophagi (coffins and covers).

Due to different angles between lamps and sarcophagi pictorial surfaces, the signal of luminance recorded by the camera in the different spectral bands cannot be quantitatively associated univocally to a certain kind of pigment or binder. To overcome this problem and to obtain a map with a clear relationship between fluorescence and diagnostic information, an algorithm, working with local equalization of UV fluorescence and a mask selection, was realized. It works through the comparison between each pixel luminance in visible region of spectrum and in UV fluorescence. Based on UV induced fluorescence and visible luminance data, the surface has been divided into three areas free from any influence of shooting and lighting conditions with different features: no UV fluorescence, bright fluorescence, intermediate fluorescence. Finally, data were compared with those obtained by RIR.

In the subsequent analyses with punctual spectroscopic techniques (XRF, FORS, FTIR and Raman), such zones were linked to the presence or absence of chemical elements marker that give hints about the presence and the period of the restorations, namely late XIX cent. and middle of XX cent.

Development of a simple method for the identification of proteinaceous binders in easel paintings

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Easel paintings emerged in the Middle Ages and since then have been one of the most important art expressions, constituting today relevant Cultural Heritage assets with important historic and cultural value. Due to the high importance in the preservation of these artworks, the correct identification of proteinaceous binders is a crucial step for a better understanding of the techniques used by the artist, and to provide relevant information for conservation and restoration processes [1]. Easel paintings contain proteinaceous binders which are commonly produced from egg, milk or animal skin and bones but unfortunately the detection of the different protein materials in these complexes matrices is a difficult task. In this work a new fluorescent labelling methodology is developed using coumarin derivative chromophore (4-sulfotetrafluorophenyl coumarin ester) in order to increase the detection signals of proteins. Firstly, we have developed and optimized a simple method with high sensibility using commercial proteins such as BSA (A2153), ovalbumin (A5378), casein (C3400) and collagen (C9879) (all from Sigma-Aldrich). This method is efficient in showing the characteristic profiles of each commercial proteins tested with the advantages of higher sensitivity and less time required for the electrophoretic detection. The optimized method was also used to test proteins extracted from hen's egg yolk and white, bovine milk and animal skin. The electrophoretic profile showed similar characteristic band profiles between the extracted and the commercial proteins.

To fulfill the aim in minimizing the amount of samples required and to try to mimic the real conditions, we performed paint mockups of easel paintings. For that, we mixed the proteins extracted from hen's egg yolk and white, bovine milk, animal skin with pigments like lead white, yellow ocre and bone black. The proteinaceous content was extracted from paint microsamples, using a previously optimized protocol [2] and the extracted proteins were used to bind with coumarin derivative chromophore which allowed to identify and distinguish the different protein binders used in each paint model. These results evidence the enormous potential to apply this optimized methodology as an effective and useful analytical tool in the identification of protein binders in samples obtained from easel paintings.

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Scientific study for the evaluation of intervention methodologies in polychrome stone treatments

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The present abstract proposes a research project focused on the scientific evaluation of the risk and effectiveness of restoration treatments such as cleaning and stabilization of pictorial layers in stone cultural heritage. It is important to systematize the processes of study of the interventions, elaborating a protocol that allows to optimize the selective elimination of the materials to be removed, to fix or to repair the disintegrated layers. The assessment of the effectiveness of the work and the risk will focus on the determination of the action of the systems used, the permanence of residues and possible changes in color, texture and compactness that may occur. In this way, an integral, objective and scientific evaluation of the risk that each proposed treatment can represent for the particular conditions of each work, allowing to propose in an objective and reliable way optimal systems of intervention.

These studies focus on:

1. EVALUATION OF CLEANING SYSTEMS

Analysis of the risk of polychrome leaching by cleaning with solvents and gel systems and the analysis of possible residues after the application of physical-chemical cleaning systems. The study is completed with the evaluation of laser cleaning systems.

For the evaluation of solvent cleaning the study focuses on analysis of cotton swabs moistened with the solvents to be evaluated. In this case the risk of solubilization of the polychrome layer is evaluated. For the evaluation of cleaning with gelled systems, the risk of solubilization of polychrome layer and possible residues that could leave cleaning systems is evaluated. Analytical techniques used to perform the analyzes include gas chromatography-mass spectrometry (GC-MS and Py-GC-MS). For the evaluation of the laser cleaning tests, the materials released as a result of the laser ablation were analyzed, as well as the textural and compositional characterization of the cleaned surface by SEM and EDX analysis.

2. EVALUATION OF STABILIZATION SYSTEMS OF POLYROMY LAYERS

A first phase of the study is developed through the test of sample films of the polymers before and after their accelerated aging in controlled conditions of temperature and humidity in climatic chamber. The test is performed with a control of optical changes, chemical stability (reactivity, pH control, etc.) and mechanical (stress-deformation, adhesion and cohesion level). After the test of the polymers, the results allow to establish which are the most appropriate materials, based on chemical stability and mechanical behavior, to continue with a second phase of study focused on the testing of polymers in polychrome test specimens and in pilot areas in situ. Among the analytical techniques used are FTIR, GC-MS, stratigraphic and superficial study with stereoscopic microscopy, optical microscopy and SEM-EDX.

The effect of different silver nanoparticle substrates on SERS spectra of selected synthetic organic pigments

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Surface-Enhanced Raman spectroscopy (SERS) has been demonstrated to be a very powerful and minimally invasive tool for the ultrasensitive and (highly) selective detection of organic molecules. The advantage of SERS with respect to classical Raman spectroscopy is the capacity to achieve an amplification of the Raman scattering as well as a quenching of fluorescence signals by the absorption of the dyestuff/pigment on specifically prepared metal nanostructures [1]. The knowledge about the presence of synthetic organic colorants on an artwork is extremely valuable not only to address queries about the historical context and chronology of the work as well as the studio practice of a specific artist, but also to identify non-original materials in order to reveal retouches or forgeries.

The present study focuses on the investigation of changes in the SERS spectra of a selection of dyes and organic pigments acquired using silver nanoparticle substrates synthetized by two different procedures:

As first step two different silver colloids were synthetized using sodium citrate (Lee-Meisel) [2] and hydrochloric hydroxylamine (Leopold-Lendl) [3], respectively, as reducing agent. Whereas Lee-Meisel silver colloids are used in most SERS applications in Cultural Heritage science at the moment, the Leopold-Lendl colloids have not yet been subject to exhaustive performance tests in the field. The morphology and plasmon resonance of the single nanoparticles were characterized by means of UV-Vis absorption spectroscopy and scanning electron microscopy, revealing important differences in terms of stability and reproducibility. A selection of 20 synthetic organic dyes and pigments, belonging to different chemical classes, were analysed using both silver colloids. The analysis was carried out using a Raman Microscope XPlora (Horiba Scientific) equipped with three diode lasers (532nm, 638 nm and 785 nm). The SERS measurements were performed depositing a drop of 5µL colloid directly on the colorant sample in the form of bulk powder or solutions at four different concentrations ($10^{-2} - 10^{-4}$ M), respectively. The sensitivity of the colloids and the reproducibility of the different measurements, in terms of Raman shift and signal intensity, were evaluated. The enhancement of the Raman signal is influenced by the localized plasmon resonance on the silver nanoparticles as well as by chemical affinity and molecules orientation on the metal substrates [1]. SERS spectra of unknown compounds may present important changes depending on the type of interaction between the silver nanoparticles and the colorant under specific chemical conditions. Thus, SERS spectra acquired using both colloids were compared and variations in relative intensity of the characteristic peaks were studied. SERS spectra of triarylcarbonium pigments acquired with both colloids are very similar and reproducible; otherwise some others such as Eosin (xanthene), Indigo carmine (Indigo) and Martius Yellow (Nitro) may present different spectral features that should be taken into account for the interpretation of unknown spectra.

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Investigation of Color Layers of Bohemian Panel Paintings by Confocal Micro-XRF

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Confocal micro X-ray fluorescence spectroscopy (confocal micro-XRF) has recently become a useful instrumental method for analyses of art and archaeological objects. Since 2005, when the first application of confocal micro-XRF on investigation of paint layers was published [1], several authors have demonstrated the advantages of this technique in pigment composition analyses. The confocal micro-XRF, unlike the conventional XRF, enables acquiring a depth-resolved elemental composition of measured samples. The confocal micro-XRF setup contains two X-ray optics. The first one in the excitation channel focuses the primary X-rays from the X-ray tube. The second lens (in front of the detector) collects the fluorescence X-rays. The two optics are placed in such a configuration that their focal points are overlapping. As a result, a small volume in space is created which represents the probing volume of the confocal micro-XRF setup. Depth-resolved information on elemental distribution can be obtained by scanning the sample with this volume perpendicularly to its surface (depth-profiling). Thus, it is possible to distinguish single layers in multilayered samples in a non-destructive way.

This work describes results of confocal micro-XRF analyses of paint layers of Bohemian panel paintings from the half of the 15th century that are part of the collections of the National Gallery in Prague. Two small paintings Lanna's Madonna (ca 1450, inv. no. O 494) and Lanna's Assumpta (ca 1450, inv. no. O 495) were chosen for this analysis because it was not possible to take samples from these artworks. All the measurements were performed using a table top confocal micro-XRF setup designed at the Czech Technical University in Prague. A depth-profiling was used for investigation of red and blue paint layers in order to compare the composition and structure of the used pigments. Obtained results were compared with findings from the material survey on the samples taken from the painting Assumpta from Deštná (ca 1450, inv. no. O 724) to verify their origin in the same workshop. Confocal micro-XRF provides satisfactory data to specify the art workshop.

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Automated integration of 3D Multispectral data from works of art using *Image Based Modeling* technique

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The advent of the new 3D Data capture Image-Based methodologies opens up new scenarios in favor of a more computationally oriented documentation and diagnostics of Cultural Heritage. Even though many case studies demonstrate a well-established practice to obtain valid 3D models of artworks for documentary purposes, on the diagnostic side the development of an integrated 3D Multispectral system is still in its experimental phase. With 3D models obtained by an integration of different surveying techniques, the learning rules applied to the knowledge of the single work of art are considerably multiplied: the 2D Multispectral digitization and the 3D modeling of easel paintings collect complementary information (both spectral and spatial). Therefore, the integration of the analysis of radiometric contents obtained using 2D multispectral images and the acquisition of 3D morphometric details of a painting in a single coordinate system can obviously enhance the potential insights into data analysis. In this way, digital models can become collectors of heterogeneous information – both quantitative and qualitative – for multi-temporal evaluation processes. With all this in mind, we brought together in a single solution all the instances above mentioned, using a specific variant of 3D Reality Based Modeling integrated with the Multispectral Imaging technique with the simple assumption of considering a multispectral image as an extension of Color Imaging.

We developed a novel 3D Multispectral modeling procedure that avoids the complex registration procedure that is typical of acquisition set-ups composed of separate devices each based on different physical principles. Applying the Structure from Motion (SfM) technique, the post-processing step for mapping the spectral information to a 3D shape becomes unnecessary as any previous knowledge of the calibration parameters of the devices used. We adopted a bundle of commercial, and open source software together with a Multispectral digital camera covering the Visible and Near Infrared (NIR) band from 400 nm up to 1050 nm. With this same method, it is also possible to get in output a single 3D model starting from a variety of input data such as: RGB images, UV Induced Fluorescence images, Thermal images, etc.

Our approach has been tested on a 14th century panel painting signed by Barnaba from Modena (preserved at the Museum of San Matteo in Pisa). The relative accuracies of the RGB and IR models obtained are here evaluated for revealing deformations at sub-millimeter level. Lastly, to verify the quality of the results and the reproducibility of the method, a quantitative evaluation approach for 3D models distance computing has been used, applying the same procedure to a 15th century panel painting preserved at the Regional Gallery of Palazzo Bellomo in Syracuse.

A preliminary XRF study of Bernardino Luini`s use of smalt in the *Storie della Passione di Cristo* in *Santa Maria degli Angeli* church in Lugano

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In medieval and early Renaissance wall paintings, blue was the color of the Madonna`s robe, the sky, and significant details in the scenes depicted. However, the use of traditional blue pigments such as azurite and ultramarine was often limited and/or problematic in wall paintings due to instability in certain environments or prohibitive expense [1]. For this reason, the entry of a new blue pigment into the artist`s palette was a significant milestone. Smalt is a blue cobalt-colored potash glass pigment that first came into use in 15th century Europe and was in frequent use in wall paintings by the mid-16th century [2, 3]. The fact that it could be used in a variety of ways, including in *affresco* applications made it an appealing and versatile material to many artists.

Bernardino Luini (c.1480-1532) was a painter from Lombardy who was active at the beginning of the 16th century in both Italy and what is today the Canton Ticino area of southern Switzerland. His work is characterized by a sensitive depiction of figures and interpretation of scenes, as well as the use of a variety of pigments [4, 5, 6]. One of his best-known works is the painting on the large partition wall in *Santa Maria degli Angeli* church in Lugano, Switzerland [7]. This paper describes an initial study of the pigments used in this masterpiece, the *Storie della Passione di Cristo* (1529), with a particular focus on the artist`s use of smalt.

The study was performed using a combination of several non-invasive investigative techniques: Spectral imaging (IRFC), hand-held X-Ray spectrometry (HH-XRF), and the hand-held digital microscope. These different techniques were used in order to identify areas where smalt was used, to establish an initial elemental characterization of the pigment, to construct a preliminary overview of the ways in which smalt was used, and to identify some other pigments defining Luini`s "palette" in this wall painting. This investigation represents one part of a broader comparative study currently underway of the use, composition, deterioration, and treatment of smalt in 16th century Canton Ticino wall paintings.

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Preparation of SERS substrates by gel encapsulation of Ag nanoparticles prepared by laser ablation

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SERS effectiveness, nanoparticle stability and the overlapping from interference species eventually existing in the medium are the parameters to be considered in the application of metal nanoparticles for surface-enhanced spectroscopic techniques [1]. Silver nanoparticles (Ag NPs) are usually prepared by chemical reduction, using sodium citrate and hydroxylamine hydrochloride as reducing agents. In both cases, by-products of the reduction process can negatively affect the adsorption of the molecule of interest [2]. Ag NPs prepared by laser ablation are free from interferences, although their time stability is quite poor. For this reason, the encapsulation of Ag NPs in an agar gel can help to overcome this drawback with the addition of an increase of the SERS effectiveness [3] in the analysis of organic dyes used in artworks.

In this work Ag NPs were fabricated by pulsed laser ablation of a Ag target in milli-Q water. Laser irradiation was carried out with nanosecond laser pulses using the fundamental (1064 nm), 2nd (532 nm) and 4th harmonic (266 nm) output of a Q-switched Nd:YAG laser (pulse duration 15 ns, repetition rate 10 Hz). Two irradiation times (25 and 50 minutes) and two laser fluences (3 and 6 times the Ag ablation threshold fluence, F_{th}) were considered. Thus, 12 different Ag NPs preparations were tested to study their SERS effectiveness using Diamond Green as probe molecule. Characterization of Ag NPs was carried out by UV-Vis spectroscopy and transmission electron microscopy (TEM). Then, encapsulation of the SERS substrates on agar gels was carried out by two methods: (a) preparation of pieces of agar gel and their immersion in the Ag NPs solution for 24 hours, and (b) preparation of pieces of agar gel dissolved in the Ag NPs solution. In both cases the agar-Ag NPs were put in contact with a Diamond Green solution for 24 hours before the measurement of SERS spectra. The enhancement factor obtained by each of the Ag NPs preparations, both in solution and encapsulated, were calculated in order to study their effectiveness as SERS substrates. Best results were obtained by Ag NPs prepared by irradiation at 1046 nm and at $6xF_{th}$ for 50 min.

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Multi-analytical Study of Antimony Based Yellow Pigments on Czech Paintings around 1900

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This study presents the results of the material analysis on the works of famous Czech painters Julius Mařák, Antonín Slavíček, Antonín Hudeček and Otakar Lebeda originating around 1900. The survey focused on plein air landscape paintings created using waterborne colors Syntonos produced in Germany from 1890s. The material survey included non-invasive X-ray fluorescence analysis (XRF). After that, samples from carefully chosen places were taken. From major part of samples cross-sections were prepared and pigments in particular color layers were analyzed using µ-Raman spectroscopy (µ-RS) and scanning electron microscopy with X-ray microanalysis (SEM-EDS). In the remaining samples binding media were analyzed using gas chromatography/mass spectrometry technique (GC/MS).

XRF results showed broad range of elements from inorganic pigments used by the painters (Zn, Pb, Hg, As, Cu, Cr, Fe, Co, Cd, Sb and Ba were identified on most of the spots measured). Proper assignment of the elements to particular pigments was enabled by µ-RS and confirmed with SEM-EDS. Naples yellow (usual composition $Pb_2Sb_2O_6(O,OH)$, mineral analogue bindheimite) was presumed to be in the paint layers due to the presence of antimony confirmed via XRF, but no Raman spectrum similar to spectra of standards of Naples yellow (Naples yellow, dark, Kremer pigments no. 43 125 and Naples yellow from Paris, Kremer pigments no. 43 130) was obtained. Spectra with a strong signal around 660 cm^{-1} were often obtained on yellowish spots instead. This Raman band was assigned to mineral rosiaite – trigonal lead antimony oxide $PbSb_2O_6$. Its synthetic analogues, usually with tin and silica, are known as rare yellow pigments. Different recipes were used for manufacturing antimony based yellow pigments. The structure of the final product was strongly dependent on the ingredients as well as on the conditions (temperature) during the manufacturing. Pigments containing higher amount of synthetic analogues to rosiaite (significant Raman band around 660 cm^{-1}) were identified on works of Italian painters from the 17th century or on the palette of Polish painter J. Matejko (1838-1893) [1, 2]. Our samples will be further analyzed via SEM-EDS to identify minor components in the antimony-based yellow pigment. Presence of other antimony compounds with different structure or composition will be investigated by means of µ-RS.

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Raman Spectroscopy for the Assessment of an Artwork's Authenticity

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Growing market with modern artworks of a high price leads to creation and selling of artwork counterfeits. Material analysis is an important part in the process of assessment of the authenticity. Knowledge of materials and techniques used by original authors is also necessary. Non-destructive and non-invasive analytical techniques are of great interest for the analysis of the artworks. Raman spectroscopy is one of the most promising technique for the analysis of paintings because it enables identification of most of the pigments as well as some organic binding media. Non-invasive Raman spectroscopy with fiber optics is convenient method when sampling is not possible.

Within the framework of the project *Comprehensive Instrumental Methods for the Assessment of an Artwork's Authenticity, a Material Database of the 20th century* (VI20172020050) database of Raman spectra of pigments used in the first half of the 20th century (including synthetic organic pigments) and modern binders will be made. Extenders and other additives will be studies as well. Changes in material composition of grounds (e.g. different mixtures of calcite, chalk, gypsum, zinc white and barium sulfate) on commercially prepared primed fabric supports will be documented.

Data from the database will be compared with results obtained from the analysis of the paintings of selected Czech modern painters (např. Otakar Kubín, Josef Šíma, Jan Zrzavý) from the collection of the National Gallery in Prague. Chosen artworks will be analyzed with non-invasive techniques (X-ray fluorescence, fiber optics Raman spectroscopy) but also samples will be taken and analyzed using optical microscopy, scanning electron microscopy with X-ray microanalysis, µ-Raman spectroscopy and infrared spectroscopy. Differences between measurement conditions for measurements on the surface of the paintings with fiber optics Raman spectroscopy and on the cross-sections with µ-Raman spectroscopy will be observed.

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Nannofossil record in the chalk ground layers of Medieval paintings – a tool for the sediment provenance identification

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Nannofossil analyses and their biostratigraphic and paleoenvironmental interpretations of chalk ground layers used on Bohemian panel paintings from the 14th to the 16th century from the collection of the National Gallery in Prague were made. The cross-sections of samples taken from the paintings were prepared and pigments in ground and paint layers were analyzed using micro-Raman spectroscopy (MRS) and scanning electron microscopy with X-ray microanalysis (SEM-EDS). Polarized light microscopy contributed to identification of calcareous nannofossils in the ground layer. The work was focused on nannofossil marker species, that offered informations about age and source of natural chalk.

Nannofossil spectra with genera *Lucianorhabdus* indicate shallow sea of normal salinity. High numbers of *Micula staurophora* and vice versa rare *Watznaueria barnesiae* and absence of species preferring warm waters give evidence for high latitudes, Boreal province. Presence of *Nephrolithus frequens* and *Cribrosphaerella daniae* gives further details about geological time, Upper Campanian and Maastrichtian. To sum up, the natural chalk was deposited in the shallow epicontinental sea of North European Platform before 78-65 Ma (= million years). Rare *Micula murus* found in chalk under silvering (Master of the Puchner Ark, 1482) indicates the influence from the Tethyan realm and may demonstrate region located more southwards.

The use of natural chalk is characteristic for the ground layers of the Bohemian Gothic painting [1, 2]. However, such fine sediments of that geological age is not available on the territory of Bohemia. Nannofossil record indicates that natural chalk used on the artworks came from different locations of the Northern Europe (eg. nowadays Northern Germany, Denmark) even within one workshop (eg. Master of the Tebo Altarpiece, around 1380). The chalk from the Western European region (eg. France, region Champagne) was used under the gilding and silvering while the chalk from the Northern Europe was used under color layers on the artworks of the Master of the Puchner Ark, the Master of the St George Altarpiece (active around 1470–1480) and the Master of the Rokycany Altarpice (around 1490–1500).

The source of fine chalk sediment considerably influences the property of the chalk thus playing an important role for the choice of the particular material for its use in the ground layers under gilding or under color layers painting even within one artwork or in one workshop. The practice of using the different sediments of natural chalk may be characteristic for the workshop practice.

Acknowledgements: This work has been financially supported by the project of the Ministry of Culture of the Czech Republic: Historical technologies and modern methods of research. The interpretative possibilities of the specialized methods of research of medieval artworks using innovative technologies (DF 13P010V010).

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Investigation of environmental effects on decay of alizarin in egg tempera paints

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Paintings of cultural heritage importance are often subjected to uncontrolled decay due to the environmental influences, which reflects in changes of physical properties and also in chemical composition. In this work, the relation between environmental effects and the state of organic paint layers (alizarin in egg tempera) was investigated by utilization of combination of different techniques. Samples of prepared paint layers were exposed to artificial aging in climate chambers under the influence of relative humidity (RH) and temperature (T), and light (mimicking the museum conditions). Surface-Enhanced Raman Spectroscopy (SERS), as a suitable technique for detection of organic dyes [1], was employed to enhance the inherent weak Raman scattering of alizarin and to overcome the fluorescence emission. SERS spectra were collected after the application of a drop of HPC-based photoreduced substrate [2] directly on the top of the paint layers. The results showed prominent differences in the response of alizarin in paint layers after the exposure to light in comparison to non-aged and/or T, RH-aged samples. The main spectral differences correspond to changes in skeletal vibrations, stretching vibrations of carbonyl group and to combinations of vibrations of CC, COH, CH and/or CO groups. [3] Consequently, stronger contributions of alizarin in anionic and neutral form after exposure to light were observed, which also indicate the changes of surface pH of the paints. The non-invasive reflection FTIR measurements [4] offered the possibility for investigation of chemical changes of the paints' surface. Especially after exposure to light, the main differences in the spectral features suggest the degradation of the proteinaceous binder. Furthermore, the formation of new signals within stretching modes of carbonyl band demonstrates the oxidation of the triglycerides in the aged egg. The degradation of the paints (namely changes in the appearance of the paints, oxidation and formation of more acidic species) was confirmed also by means of colorimetry, and the surface pH measurements.

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Microchemical investigation of nanocrystalline CdS

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Since the discovery of cadmium in 1819 by Stromeyer, a new class of inorganic pigments entered and definitely changed the artists' world. Cadmium pigments have been used since 1840, first as simple sulfides, then mixed to other materials as zinc oxide or in alloyed structures with selenium or zinc. The most relevant impressionism and post impressionism's masters included this class of pigments in their palette without any hesitation [1].

Unfortunately, significant damages of several areas in precious paintings has been observed and attributed to photodegradation mechanisms [2]. Particularly, at the earlier times, preparation of cadmium sulfide was not well established and hues ranging from bright yellow to orange were produced and defined as cadmium sulfide [3].

The aim of this project lies on the microchemical study of cadmium sulfide pigments, II-VI semicondutors with cubic or hexagonal crystal structure, synthesized using traditional methods in order to reproduce ancient preparations and then determine their physical properties. Cadmium sulfide was prepared by aqueous precipitation in presence of soluble cadmium salts ($CdSO_4$, $Cd(NO_3)_2$, $CdCl_2$) and inorganic sulfide precursors such as Na_2S, NaHS, and H_2S, determining the acidity of the reaction environment and nucleation and crystal growth kinetics. The as-synthesized samples were analyzed by micro-XRD, diffuse reflectance, Raman spectroscopy, scanning electron microscopy, X-ray energy dispersive spectroscopy and atomic resolution transmission electron microscopy. We observed polycrystalline powders with grain size of about 5 nm. Depending on the reaction conditions, the inflection point of the reflectance curve ranged from *ca* 525 to 560 nm. EDX analyses pointed out the presence of an oxide layer and stoichiometric defects. However, thermal annealing of samples under N_2 atmosphere leads to grain size growth and reduction of crystal lattice defects, while the band gap becomes closer to the bulk hexagonal band gap value, *e.i.* 2.42 eV.

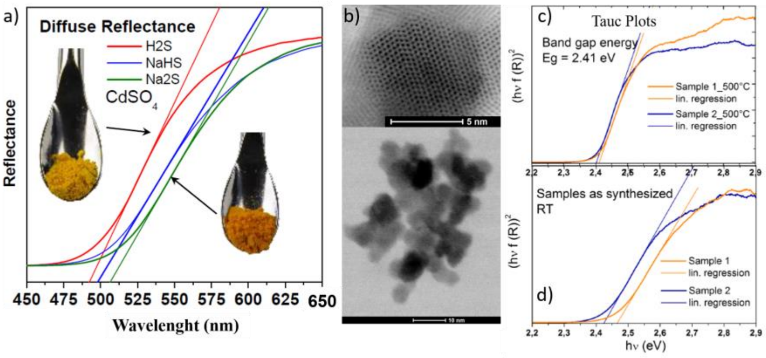

Figure 1. a) Diffuse reflectance of CdS pigments, b) HR TEM images, c) Tauc plots after annealing and d) as synthesized CdS powders.

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Analytical characterization of Jorge Afonso palette and painting techniques, the great master of Lisbon painting workshop

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In this work a study on a set of paintings from the most significant altarpiece assigned to Jorge Afonso (c. 1470-1540) painting workshop is presented. The last altarpiece of the master is composed by fourteen paintings made to the church of Convento de Jesus, in Setúbal, Portugal and is assigned to its workshop circa1517-19/1530, according to art-history and confirmed by dendrochronological analysis. Jorge Afonso was a royal painter of kings D.Manuel I and D. João III. His aesthetic and technical resources and materials stand out in the Portuguese panorama of the 16th century. In his workshop he employed as official painters the next most important generation of Portuguese painters: Garcia Fernandes, Gregório Lopes, Cristóvão de Figueiredo, Gaspar Vaz and, perhaps, Vasco Fernandes [1, 2].

The aim of this study is to determine the pigments and the ground layers used in Jorge Afonso workshop using complementary microscopy techniques. The cross-sections from the paintings were examined by optical microscopy analyzed by µ-X-ray diffraction, Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy, µ-Confocal Raman, High Performance Liquid Chromatography coupled to Diode-Array and Mass Spectrometry detectors. Pigments found in the characterized workshop palette were: lead white, ochre, malachite, vermilion and possibly cochineal, lead-tin yellow and ochre and azurite. Ground layers are made of *gesso grosso*, present calcium sulfate-anhydrite with small amounts of gypsum. The characterization of the palette and ground layers and the study of the overlapping of pigment layers will bring a new insight of the adopted painting techniques.

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Combined use of MA-XRF scanning and XRD for the noninvasive investigation of illuminated manuscripts

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The scientific investigation of illuminated manuscripts provides new insights into painting techniques, pigment signature, artistic process as well as to determine the conservation state of artworks and to identify conservative procedure occurred over the time. X-Ray based techniques are well established. Usually, they are noninvasive and implemented in portable setup. This paper discusses the combined use of MA-XRF scanning [1,2] and XRD [3] for the in situ analysis of illuminated manuscripts belonging to the collection of the Fitzwilliam Museum (Cambridge). Measurements were performed with instrumentation developed at the LANDIS laboratory of IBAM-CNR and LNS-INFN in Catania. Elemental distribution images have been obtained by a novel MA-XRF scanner based on an advanced real-time technology allowing a fast continuous scanning. XRD investigation was performed with a goniometric theta-theta set-up equipped with a Si-PIN and a polycapillary based X-ray source allowing an angular scanning with about 0.15° resolution.

A total of seven illuminated fragments have been investigated by MA-XRF with a measurement time limited to about 2 h per sample. MA-XRF elemental distribution images were obtained on the fly by the use of a least square fitting procedure applied in a live mode on the pixel spectra. XRD investigation was mainly addressed to better elucidate the nature of the green Cu-based pigments in the fragments. Analytical results allowed to assess differences and common patterns in painting techniques in samples of different dating and origin.

Figure 1. MA-XRF images of one of the investigated samples at the Fitzwilliam Museum.

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The Paston Treasure: a non-invasive elemental imaging by using a real-time MA-XRF technique

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The Paston Treasure (oil on canvas, 245x165 cm2, ca 1670) is a masterpiece of the British art history. Beyond the complexity of the pictorial composition depicting the wealth of the Paston family, the painting is fraught with metaphors and allegories that have attracted since long time the interest of art history scholars. In order to complement previous technical analyses, the artwork has been recently investigated at the Norwich Castle Museum and Art Gallery (Norwich, UK) with a non-invasive MA-XRF scanning, aimed to obtain new insights on pigment materials, state of conservation and artist creation process [1,2].

Measurements were carried out with a mobile XRF scanner recently developed at the LANDIS laboratory of INFN-LNS and IBAM-CNR in Catania (Italy) [2]. The instrument (named LANDIS-X) is based on a real-time technology enabling a fast continuous MA-XRF scanning of a 110x70 cm^2 area and a real-time elemental imaging based on a least square fitting procedure. The Paston Treasure was analyzed by capturing 6 sub-areas at a scanning speed of 50 mm/sec. Due to time constrains, a limited area in the bottom of the painting was investigated at 100 mm/sec speed. The chemical element distribution obtained with MA-XRF allowed elucidating the pigment palette of the Paston Treasure and to evidence lost details of the pictorial composition due to the darkening of pigments over the time. In addition, new information has emerged on the presence of a hidden woman below the visible surface allowing a new hypothesis on her identity and role in the painted scene.

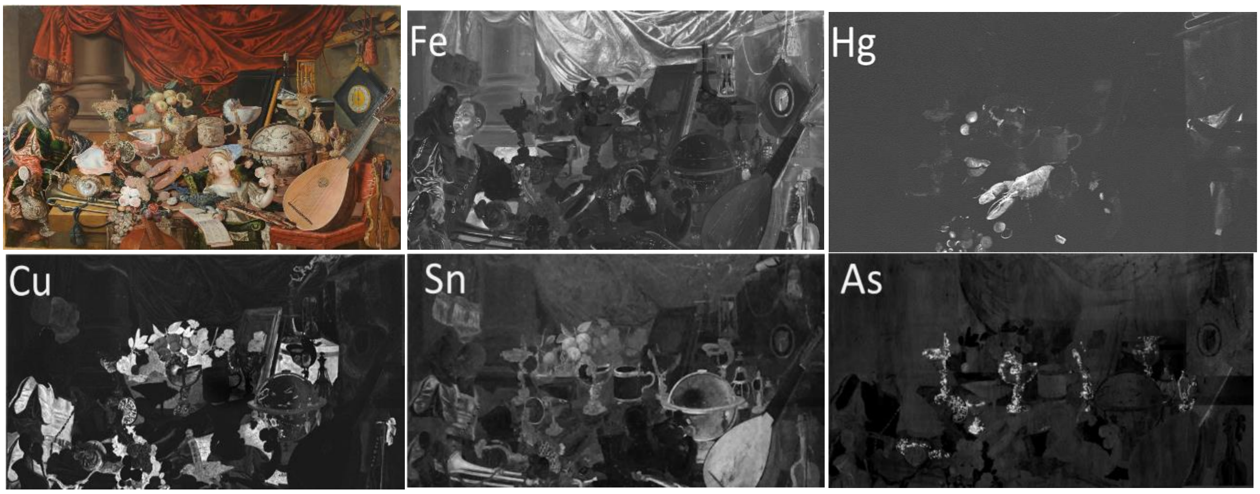

Figure 1. Some of the main elemental distribution images obtained with the MA-XRF scanning

[1] Alfeld, Matthias, et al. "A mobile instrument for in situ scanning macro-XRF investigation of historical paintings." Journal of Analytical Atomic Spectrometry 28.5, 2013, 760.

[2] F.P. Romano et al. "A mobile MA-XRF scanner for a (near) real-time elemental imaging of painted artworks.", presented at Denver X-ray Confrence, Chicago, August, 2016.

The Sicilian period of Old Masters of painting in 17th century: common patterns and differences investigated by a non-invasive MA-XRF scanning

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Despite painting in Sicily presents only a few examples of famous masters, the island has been a point of transit and meeting of great painters. Among these, Caravaggio is definitely the most significant case. His painting technique and composition influenced over many decades a number of Baroque painters from all over Europe. Some of these old masters have spent a period of their life in Sicily during the 17th century. This allowed them to follow tracks of Caravaggio and to continue to be inspired by his works according to the stylistic patterns nowadays identified in the movement named Caravaggism. Among these, Mathias Stomher, Jusepe de Ribera and Mattia Preti are some of the most significant examples.

This work presents the use at the Museo of Castello Ursino in Catania of a new MA-XRF scanning technique [1] for the noninvasive investigation of three masterpieces painted by the three old masters during their stay in Sicily. The instrument (named LANDIS-X) is based on a real-time technology enabling a fast continuous scanning of a 110×70 cm2 area and a real-time elemental imaging based on a least square fitting procedure. Elemental distribution images obtained by MA-XRF allowed comparative results on pigments used by the masters in their artworks. The use of *chiaroscuro* characterizing the pictorial composition of the three painters was better elucidated by determining the distribution of chemical element on the painted surface. Finally, evidences has emerged on presence of hidden paintings and *pentimenti* providing new insights on the creative process of the artists.

Figure 1.The Mocking of Christ (1640, oil on canvas 200x155 cm) by Matthias Stomer during the MA-XRF scanning; the scanning of the full panting lasted 8 h (left). The elemental distribution image of Pb evidencing a "pentimento" in the pictorial composition of the face of Christ (right).

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Multi-technique non-invasive investigation of visible and **hidden compositions of Titian's studio** *Ecce Homo*

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We report on a complex investigation of the painting of *Ecce Homo* attributed to Titian's studio and dating to ca. 1550 [1]. The study discusses the scientific data obtained by a multi-technique, non-invasive approach based on the integration of digital microscopy, UV-, IR-, X-ray imaging and micro-XRF spectroscopy. The complementarity of the applied methods and the process of their integration to answer specific art historical questions are demonstrated.

The *Ecce Homo* painting characterization included the analysis of the support, preparation techniques, pigment materials, state of conservation and painting stratigraphy. It was identified that (1) the areas of flesh tones have been recently cleaned from varnish; (2) the identified pigments of *Ecce Homo* include iron red, cinnabar, iron-manganese black, lead white, copper green, ultramarine, orpiment and a 0.3 mm thick preparation layer of gypsum; (3) the multiple retouched areas contain titanium white, zinc white, cadmium red/yellow, iron red, cinnabar and chromium green/brown.

X-radiography analysis allowed the detection of underlying composition, which appeared to be a nearly finished male portrait executed at a 180° angle to the visible composition of the *Ecce Homo*. The identification of the materials of the underpainting was crucial for the proper interpretation of the results of the visible painting analysis. We developed a non-invasive methodology integrating X-radiography, digital microscopy and micro-XRF for the analysis of the underlying composition. First, the examination of X-radiography images allowed the delineation of the elements of the underlying composition and the selection of the areas of interest, whose colour appearance and pigment composition needed to be studied. Second, maps of spots for micro-XRF analysis were created. The selected spots (at least three for each area of interest) were mapped on the X-radiography images and transferred onto the visible image in order to facilitate navigation, when performing the XRF analysis. The maps of elements indicative of certain pigments (Pb for lead white, Hg for cinnabar, Fe and Mn for ochres, Cu for copper green or blue) were obtained by evaluating the net areas of the characteristic peaks of XRF spectra. Important results were also obtained by digital microscopy applied on the *Ecce Homo* painting's cracks, which enabled the observation of the entire painting stratigraphy, starting from the canvas up to the uppermost layer. This test has also shown that the *Ecce Homo* was painted directly on the underlying portrait without an intermediate preparatory layer between the lower (earlier) and the upper (later) compositions.

The applied in the present study approach proved to be effective for the material analysis of paintings with hidden compositions and has an analytical potential to be used for comparative study of visible and underlying compositions in a completely non-invasive manner.

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Non-invasive multi-technique characterization of polychromed sculptures from Cyprus

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The present study describes a non-invasive multi-technique approach using portable equipment for the study of the polychromy. Nine limestone sculptures attributed to the Cypro-Archaic - end of the Hellenistic periods were examined *in-situ* in exhibition rooms of two museums in Cyprus by integrated use of digital microscopy, imaging under ultraviolet (UV) light, Visible-Induced Luminescence (VIL), micro-X-Ray Fluorescence spectroscopy (XRF) and Fiber Optics Reflectance Spectroscopy (FORS). The study discusses the precision of the pigment identification by aforementioned non-destructive technique also highlighting the advantages and problems of combined and separate use of portable XRF and FORS, raising the question of their complementarity and interchangeability for the purposes of pigment identification.

All the identified pigment compounds are consistent with the palette commonly used by artists in the East Mediterranean region during the studied period [1-6]: calcium containing white (calcium sulphate), iron red (hematite), iron yellow (goethite), iron green (green earth), copper green, Egyptian blue. The latter was applied in pure condition or in combination with iron green or copper green. Trace amounts of Egyptian blue, undetectable with the naked eye, were identified by means of VIL imaging; the meaning of this discovery is discussed in terms of artistic purposes. The results were compared with the analysis of local minerals for the purposes of provenance study [7].

The applied non-invasive methodology proved to be effective for the identification of general types of pigment compounds, enabling a preliminary characterization of polychromy and avoiding micro-sampling. These results raised important questions for employing methods of structural analysis, such as confirming or not the mixture of iron red and realgar (As lines in XRF spectrum); a local provenance of iron red and yellow pigments (Pb lines in XRF spectrum); the mineral composition of green earth; the chemical nature of copper green and the un-identified red pigment on lips, eyes and hair on two limestone heads (possibly a red organic dye).

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Potential of Micro-SORS for Cultural Heritage

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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 [1]. The technique combines conventional Spatially Offset Raman Spectroscopy [2] with microscopy concepts and represents a new imaging modality in Raman microscopy.

Two principal variants of the method were developed: i) 'Defocusing micro-SORS', exceptionally simple and usable with existing Raman microscopes without any modifications. The technique involves measurements performed at several defocusing distances from the 'imaged' position inducing the enlargement of both the collection and illumination points; ii) 'Full micro-SORS', a more effective variant mimicking classical macro-scale SORS effect on micro-scale using fully separated Raman collection and laser illumination zones. This variant requires adaptations to the configuration of existing Raman microscopes in order to be practised in its unrestricted form [3].

Here we present our latest results of micro-SORS experiments carried out with the aim to explore the applicability of the method in challenging situations including the recovering of sublayer signal in presence of a fluorescent compound and the non-invasive recovery and reconstructing of 2D images within overpainted sublayers [4]. Moreover, the recent developing of the first portable full micro-SORS prototype will also be illustrated unlocking fully the *non-invasive* and *non-destructive* potential of micro-SORS [5].

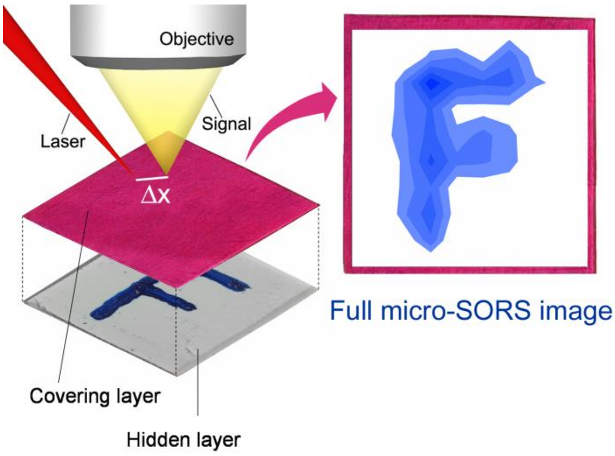

Figure 1. A scheme of 'full micro-SORS' variant applied to the reconstruction of hidden 2D painted images

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The role of mineral assemblages in oil paint films: a synergic study of chemical-mineral composition, pH and conductivity

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Oil polychromies on stone consist of oil paint mixtures applied on a natural aggregate of minerals. As an inorganic and reactive substrate as well as porous systems usually subjected to migration mechanisms of aqueous solutions and to ion leaching, stone substrates can promote specific reactions in oil paint films such as metal soap and other salt formation [1]. Very few stone sculptures conserve their original polychromy nowadays so the exceptional adhesion and cohesion presented by the polychromies of the case-studies here presented suggested that both the chemical-mineral composition and the porosity of the lithotypes chosen for the artists to be in contact with the oil paint films could be responsible for their unexpected durability.

In this study, the sandstone and the limestone employed for carving the *Tomb of Chancellor Villaespesa* in the Cathedral of Tudela (Spain) and the *Altarpiece of The Chapel of Los Corporales* in the Church of Santa María in Daroca (Spain) respectively are presented. Archival sources reported that they were extracted from *Pitillas* and *Villanueva de Huerva* stone quarries respectively at the beginning of the 15th century [2]. Microscopic observation, performed by Polarized Light Microscopy and SEM-EDX have been carried out to characterise these lithotypes; minero-petrographic characterization points out the structure, the porosity and the mineral composition of these stones and it lets to hypothesize their different behaviour in this context of study.

Mock-ups simulating different oil paint layers on *Pitillas* sandstone and *Villanueva* limestone have been prepared in this research in order to identify how porosity and mineral composition of the stone influence the chemical balances acquired in time by the oil paint film. Mock-ups with the same oil paint films on microscope glass, pinewood and some lithotypes have been made for comparison purpose.

As extensively reported in literature, due to oxidation and hydrolysis reactions, oil paint films increase their acidity and ionic strength in time [3]. Therefore pH and conductivity have been measured and monitorized in both the mock-ups and the case studies and our results point out that when oil paint films age in contact with the lithotypes here discussed they tend to become much less acid and almost neutral in time. The different behaviour between the paint film and the stone substrate in the presence of moisture can partially explain why the presence of some specific mineral assemblages in the substrate gives rise to new chemical balances at the interface oil paint film-inorganic substrate governing the stability of the entire painted system.

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Alteration phenomena occurring in modern oil paints: non-invasive and micro-invasive spectroscopic investigations on Cobalt Blue paint films

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This research aims to understand the alteration phenomena occurring in modern oil paints containing Cobalt Blue with a special attention to the interactions between the organic binder and the inorganic compounds present as pigments, additives, fillers, etc. The results here presented concern the non-invasive and micro-invasive characterization of several oil films before and after an accelerated ageing. Paints tube from Titan (Spain), Royal Talens (Netherlands), Winsor & Newton (United Kingdom) and Maimeri (Italy) were artificially aged by modifying the thermo-hygrometric conditions. The characterization was performed by means of external reflection infrared spectroscopy (ER-FTIR), Colorimetry, Visible Reflectance, μ-ATR (both on the surface and on the cross-section) O.M. and SEM-EDS.

The experimental work was divided in two steps. The former included a thorough characterization of each component of the tubes, *i.e.* binding media, pigment, fillers and other additives. The latter concerned the study of the paint films which underwent accelerated ageing under different relative humidity conditions (RH 30% and 90%) and in the presence and absence of daylight for 56 days. Experimental data had shown that the different RH conditions promote and/or accelerate the formation of metallic soaps. Additionally, depending on the chemical composition of additives and fillers, different paints oil tubes are subjected to different alteration phenomena. In particular, μ-ATR performed on cross section has allowed to understand the distribution of metal soaps across the paint layer, highlighting the presence of carboxylates close to the exposed surfaces.

Moreover, the present experimentation has assessed ER-FTIR as a valid non-invasive and contactless diagnostic technique to detect alteration products in modern paints.

Conservation of Contemporary Art: materials, technique and alteration phenomena on Alexis Harding artworks

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The present research deals with a preliminary study on two Alexis Harding canvas. The two artworks, belonging to a private collection, consist in glossy paints on aluminum and MDF panel, respectively. In both artworks, the glossy paint is poured on the support, producing a fluid movement on the paint itself. The two artworks, produced in 2003 and in 2008, were exposed in a private house and kept in proper conditions. The first one, *Quartet*, consist in a yellow and black glossy paint in a flowing movement from the top to the bottom of the canvas. The fluidity is highlighted by a gliding of the paint layer outside the bottom of the canvas itself. *Quartet* shows a evident alteration, consisting in substantial collapse of the paint layer on the bottom of the canvas. The second canvas, *Broken Line*, is also painted in yellow and black, but with a different *modus operandi*. The movement is more fluid, the surface' sagging is less evident and the canvas does not show any evident alterations.

The preliminary results here presented concern the study of the materials used by the artist and on the identification of the alteration phenomena. Both the paints were firstly investigated by means of external reflection infrared spectroscopy (ER-FTIR), in order to identify the materials and highlight, where present, possible chemical modifications induced by alteration processes. ER-FTIR has shown the presence of intense and complex C=O signals, suggesting the presence of alkyd paints probably mixed with a lipidic medium, and an inorganic ($CO_3^{=}$) filler. Concerning the *Quartet*, no evident differences in chemical features were detected between the non-altered and the altered surface. That being so, a micro-sampling campaign was performed to study in detail the nature of the alteration and to describe the alteration processes. μ-ATR confirms the presence of an alkyd paint (alkyd yellow paint by W&N). Further μ-ATR investigations on the cross-section will be presented, in order to understand the sequence of the material used by Harding. The absence of evident chemical modifications of the polymeric paint allow to hypothesize a physical transformation induced by the environmental conditions. In order to investigate on these possible transformations, thermal analysis was also performed.

In situ non-invasive characterization of the Pompeian pigments palette composition

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Pigments are one of the most important archaeological records recovered from the burial of the archaeological site of Pompeii (Italy). Their analysis and characterization is an important task from the historical, archaeological and chemical point of view. However, scientific researches of these archaeological samples are often very limited by sampling restrictions. Therefore, the use of non-invasive techniques to conduct the analysis of archaeological pigments is usually mandatory. Moreover, considering that most of the times there is not the possibility of taking any sample, an in situ study using portable/handheld instruments is the only possibility to undertake this kind of studies.

In this work, a wide collection of original raw pigments (red, yellow, blue, green and pink) recovered from the archaeological site of Pompeii and preserved in their original bowls in the Naples National Archaeological Museum (MANN) and in the Applied Research Laboratory of the archaeological site of Pompeii was analyzed. An in situ non-invasive analytical methodology was applied in order to accomplish the full characterization (elemental and molecular) of these raw pigments. For the molecular analysis, two portable Raman spectrometers (785 and 532 nm excitation lasers) were used. The elemental characterization was conducted by means of a hand-held energy dispersive X-ray fluorescence spectrometer.

Red and yellow colors were the main ones used to create Pompeian wall paintings. Among red pigments, they were obtained from two sources. On the one hand, from iron-rich earths [red ochre or hematite (α-Fe_2O_3)]. On the other hand, from minerals which were crushed in order to obtain fine powders, such as the case of the brilliant red pigment cinnabar (HgS). Apart from red ochre, yellow ochre [goethite (α-FeOOH)] was identified in the analyzed yellow pigment. The analyzed green color pigment was composed mainly by malachite ($Cu_2CO_3(OH)_2$). The seven blue pigments analyzed belong to Pompeian blue ($CaCuSi_4O_{10}$) in all cases. Pink colored ones were lake pigments, in where madder lake (mainly alizarin and purpurin) was used as colorant to dye their inorganic mordant. In the case of blue and pink pigments, since the number of samples was higher than for the rest of the colors, a Principal Component Analysis (PCA) was performed in order to observe similarities/differences in the elemental composition among samples of the same color.

Investigation of markers related to the degradation of binding media in wall paintings

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Wall paintings represent one of the oldest art expression, which thanks to the durability of its substrate offers us today a well preserved testimony of different archeological content and context worldwide. Lime-based wall paintings covers a very long-standing uninterrupted tradition, through which we can attest some well-established technical achievements often attuned to novelties or particularities related to local workshops or stylistic trends. The material study of wall paintings is well established methodologically thanks to the past years developments of multi-technique strategies. This gives us today a fundamental knowledge of the materials and painting techniques. However, although the analytical identification of the nature of organic binding media in wall paintings has been put in focus the past years, several issues related to the understanding of the use of organic substances such as egg, glue or gums to reinforce the binding of the pigments either in fresh or in dry lime-based plaster remain unclear. This lack of understanding of the nature or manner of the organic binding media use before, during or after the carbonization process of lime, is due to obvious reasons. The original organic substance is originally added in low binder-to-pigment ratio and therefore remaining only in traces or residues which are often result of deterioration or complex interaction with the inorganic pigments or materials of the substrate further complicated due to possibly offensive weathering processes occurring in changing climatic environments through the years, [1], [2], [3], [4].

In the framework of IPERION-CH (*Integrated Platform for the European Research Infrastructure ON Cultural Heritage)* project a collaborative task is dedicated to the evaluation and comparison of different innovative methodologies and conventional diagnostic techniques for the investigation of markers related to alteration mechanisms and degradation products to obtain knowledge about original organic materials used in wall paintings. The non-invasive and microsampling methodology is first optimized on well-defined models been designed to simulate different painting techniques with limewater and five organic binders in different relative proportions while in a next step will be applied on archaeological samples.

In the present paper initial project results on a selected set of models submitted in different stages of a well-established artificial ageing protocol are demonstrating the specific complementary input of each analytical technique included in the analytical approach (FTIR reflectance and colour measurements, micro FTIR analyses in ATR mode in cross-sections, Evolved Gas Analysis-Mass Spectrometry and Pyrolysis Gas Chromatography-Mass Spectrometry). The comparative evaluation and interpretation of the results is a step forward the optimization of the approach in relating the analytical findings detected on the analysed samples to the original compounds and the possible changes for each group of binders (proteins / gums) due to degradation or interaction depending on the pigment / metal present.

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Depth Profiling of Paint Layers with a Conventional Handheld X-ray Fluorescence Analyser

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Handheld X-ray fluorescence (XRF) analysers are nowadays very common tools in the research of cultural heritage objects in which non-destructive analysis is demanded. XRF analysis is then simple to perform and the data evaluation is managed by provided software. The prices of portable devices are usually also reachable. In our contribution we focused on the advanced evaluation of data obtained from the measurement performed with a conventional handheld XRF device (NITON XL3t GOLDD+). The investigated samples consisted of at least 2 different paint layers and our aim was to get approximate information on elements present in particular paint layers.

We used the technique that is known as the Kα/Kβ technique and it is based on an evaluation of intensities of two X-ray lines of an element of interest. So it can be used with any conventional XRF measurement. We present calibration method and its application to the samples with different composition. We evaluate the effects of the analyte and matrix composition to the possible application and results uncertainty.

Such calibration procedure of the XRF spectrometer includes measurements of standards of several elements from thin to thick layer. The homogeneous standards were covered by a set of materials with different atomic number (Z) and known thicknesses. The measured standards, as well as covering materials, were chosen with the respect to the application in historical paintings survey. It means, the elements present in measured standards are often found in pigments. After the calibration of the XRF device, the samples consisting of paint layers of different composition were analysed and the inorganic pigments were identified in individual layers. Also we estimate the influence of the portable device, which are less mechanically stable than laboratory devices. This research is linked to the past work with K/K technique on laboratory XRF devices [1], so the comparison is also included.

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A complete Raman approach for the identification of synthetic colorants in works of art

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A staggering array of new synthetic organic pigments and colorants became available on the market after the accidental and revolutionary invention of the first synthetic dye in 1856 by William Henry Perkin, which marked the emergence of modern organic chemistry [1]. Their wide use as artistic materials makes their identification crucial to understand the materiality of modern and contemporary art objects and to plan proper preventive conservation protocols.

In this study, we focus specifically on the Raman analysis of azo, aniline and xanthene dyes. While many Raman databases present the characterization of red azo pigments, their water soluble counterpart have rarely been studied by Raman spectroscopy. To fill this gap, the red azo dyes most commonly used as artist's materials have been studied here by normal Raman and surface-enhanced Raman spectroscopy (SERS), and a proper protocol for their detection when used as inks in Japanese woodblock prints has been evaluated [2].

Figure1. Acid red 26 identified on a late 19th-century Japanese woodblock print

While azo dyes could be successfully characterized by normal Raman spectroscopy, SERS has proven to be a powerful analytical method for highly fluorescent aniline and xanthene dyes. Complexation of the colorant with metal ions to dye fabrics and produce lake pigments, as well as undesired interactions with other matrix components (i.e. substrate, binding media, fillers and extenders), are just some of the issues that typically complicate dye identification in actual samples from museum objects. These issues can be easily overcome by using proper sample treatments prior to SERS analysis [3]. In this work, an *ad-hoc* hydrolysis treatment based on the use of HNO_3 was key to detecting aniline and xanthene dyes by SERS in garments, paintings and gouaches on paper.

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Multi-analytical approach to evaluate $CaCO_3$ crystalline evolution in fresco paintings

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The fresco technique executed with lime putty as conglomerating material is well known since the ancient times. However, the crystallographic and physico-chemical processes which make the fresco painting possible have been described in a general way [1] as part of the carbonation process of the intonaco itself. When approaching this technique from the point of view of experimental archaeology, it has been observed that during the execution period (from 0 to 20 hours, approximately) the evolution of the superficial film does not correspond to the one observed for the stratums which form the intonaco layer, just beneath the film: its texture, stiffness and compactness are specific [2]. The aim of this study is to investigate the formation and development of this superficial film. For this purpose, a series of fresco paintings test-tubes have been prepared and characterized by applying a multi-analytical approach which includes polarized optical microscopy, particle count and measurement through image treatment, scanning electron microscopy coupled to an energy dispersive X-ray spectrometer, and Fourier transform infrared spectroscopy. In parallel, two ancient Spanish fresco paintings (the Roman fresco of the Nemesis of the amphitheatre of Tarragona, and the Romanesque frescoes of the Monastery of Sant Miquel del Cruilles in Girona) have also been characterized. The obtained results have been compared with those of the experimental samples, achieving a wider view of the evolution of the film over time. Results allowed to identify the presence of an amorphous gel composed by calcium carbonate over the surface of the intonaco/intonachino. Beneath this gel, there is an interface in which specific crystalline growths (split growth phenomena) are developed thanks to the supersaturated conditions. Below this interface, the intonaco/intonachino surface can be found. This layer contains compounds that contribute to change the composition of the film as to be transformed in a colloidal dispersion. The identification of this gel-film has implications in the field of investigation of the fresco painting, the lime putty as a conglomerating material, as well as in the preservation and restauration of fresco paintings and lime-based wall-paintings.

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How well constrained are Pb white provenance studies of paintings?

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The pigment lead white is a complex salt containing both carbonate and hydroxide ions that has been widely used in paintings since antiquity. In the last three decades, lead isotope analysis of lead white was used to determine the source of the lead ore and, by inference, the provenance of the painting. The assumption is that lead whites are homogeneous and have the same isotopic composition as the ore from which they were derived. This is potentially an oversimplification of the 'life' of lead in pigments as many factors could influence isotopic compositions. Another issue, especially in oil paintings, is that lead is often present as an added drying agent, and in grounds, thus occurring in different layers of the paint stratigraphy. It is unknown, however, if the various lead white pigments found in one painting have a common source. These observations potentially question the homogeneity of lead isotope compositions in individual oil paintings and thus the reliability of any provenance information based on that.

The overall goal of this project is to quantify the limitations of Pb isotope provenance studies of oil paintings. The latest generation mass spectrometric techniques will be used; doubled spiked lead analysis linked to new generation 10^{13} Ohm amplifiers. The approach allows the analysis of sub nanogram amounts of lead white and hence minimally destructive sampling techniques allowing analysis of parts of individual paint layers that are typically between 10-100 µm.

Here we report on an assessment of different minimally invasive sampling techniques for sampling individual paint layers for their isotopic composition that are precise enough to avoid contamination by other layers of the painting. Three techniques have been evaluated:

Ultra-microtoming of existing paint cross-sections that produces ultra-thin sections (~ 0.5 µm). The technique allows horizontal or axial slicing of the sample providing bulk samples or individual layers. Moreover the production of multiple thin layers allows storage of subsamples for future investigations and the isotopic homogeneity to be determined at the ~ µm scale.

Details will be presented of an in-house built *Micro-Scalpel* that allows 3D sampling of complex paint cross-sections.

A *Focused Ion Beam (FIB) Milling* technique was also used to sample paint cross-sections at a scale of 20x10x10 µm using a Ga ion beam. This technique appears to require multiple sampling steps to avoid introduction of contaminants due to the complex sample handling procedures.

Data will be presented for each sampling technique to quantify the level of contamination introduced and an initial assessment will be made as to the isotopic heterogeneity of individual lead white samples in a selection of paintings from the Rijksmuseum. Current work is designed to assess both the homogeneity of lead white in individual paintings in the time period 1500-1800, and the level of provenance discrimination offered by lead white pigments and how uncertainties vary over time.

A Unique Colours' Workshop in the Ancient Aegean World: Physicochemical characterisation of the iron-containing pigments found at the site

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A unique archaeological site comprised of numerous pigments, raw materials and tools, as well as the remnants of a ruined kiln was brought to light in 1984 by the systematic excavation in the southern sector of the Ancient Agora of Kos (Greece). The workshop was in continuous use since the Late Hellenistic period (150-50 BC) until the Early Roman period ((Late 1st century BC- 2nd century AD).Among the plethora of red, brown, green and yellow pigments, a great amount of Egyptian blue balls and numerous litharge tubes were also found.

The examination of the material culture of the site aims to shed light on the ancient manufacturing technology, the provenance of the raw materials and the applications of the final products.

This paper focuses on the study of the iron-containing pigments found at the site. A systematic protocol was developed in order to achieve the physicochemical characterisation of the materials.

The first step included the macroscopic and stereomicroscopic observation with photographic documentation of the samples. Subsequently, Environmental Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy detector was conducted (SEM-EDS), in order to examine the microstructure of the samples and obtain the elemental characterisation. The crystalline phases of the samples were identified using X-ray Diffraction analysis (XRD), leading to interesting results concerning the mineral origin of the samples.

The examination of the material remnants pointed out the importance of the site, indicating the high level of expertise of the involved craftsmen and the different types of raw materials that were processed in situ. Furthermore, this unique context provides an opportunity to observe the wonderfully colorful chemistry of iron.

Insights on multi–analytical study for documentation and treatment of the oil painted dome of Archangel Gabriel church

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This research is outcome of an integrated diagnostic study that has been carried out to understand the main causes of the overall color changes of the painted 20th C dome of Archangel Gabriel church, Haret El saqueen, Abdeen, in Cairo. Documentary, stratigraphic and chemical studies by the means of Multi-spectral imaging , Scanning Electron Microscope coupled with Dispersive Energy of X-ray spectrometer(SEM-EDS), Fourier Transformed Infrared Spectroscopy(FTIR), Gas Chromatography-Mass Spectroscopy (GC/MS), X-ray Diffraction (XRD) and colorimetry provided important clues about the original and non–original superimposed layers. The studies confirmed that the dome was executed on the drying plaster by the oil painting technique in the beginning of the 20th Century with the same European technique. The 20th C. paintings were applied on earlier paintings which are likely referring to the date of the church construction. Owing to the heavily over-painting process occurred during the previous intervention in 1994, the dome lost many of its historical and aesthetic significances.

For this purpose, this study presents the preliminary data for characterization the authentication features and the relevant conclusive decision making to retrieve the historical and aesthetic features of the dome.

Keywords: Authentication features, Multi- spectral imaging , Over painting

Experimental study for monitoring the physical changes in oil based wall paintings

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More recent treatises showed the interest of conservators in studying the causes of chemical and physical changes in wall paintings appearance with the aim of providing the good conservation state to those painted surfaces. This issue is more complicated process with oil based wall paintings as the changes in chemical and physical properties of the paints have begun from their preparation and continued to be influenced by the drastically surrounded environmental condition reactions with the multi-layered system. These influenced factors are considered to be triggering agents for alternation of organic and/or inorganic constituents of oil paints. In addition to that, mechanical stresses as flaking, brittleness and paint losses are often accompanied. For this purpose, Experimental samples have been prepared with the same stratigraphy of oil based wall paintings and painted by massicot, red lead and cinnabar. Samples were subjected to UV natural aging and salt weathering to study their possible changes in appearance under aging. Stereo Microscope, Colorimetric measurements and FTIR analyses were employed to monitor the changes occurrence. Further investigations will include the characterization of degraded painting materials by using Raman spectroscopy.

Pigments characterization for image reconstruction of wall paintings of Amărăşti wooden church

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The wooden church from the village of Amărăşti, Vâlcea county, Romania, dedicated to Saint Nicholas, is part of a special category of churches, namely, wooden churches with *fresco* painting [1]. The church was erected for the first time in the second half of the 18-th century, and then it was rebuilt in 1802. The church, initially without mural painting, only with icons on the iconostasis, was painted in *fresco* in 1841, the altar apse being decorated with a beautiful iconographic ensemble. It looks like the naos and the pronaos have never been painted. The micro-climatic conditions, the seismic movements and, not least, the incompatibility between the organic material - wooden walls, and the mineral painting substrate (lime mortar) produced important deterioration of the wall paintings. The *fresco* is detached from the wooden beam walls on large surfaces. These detachments lead to the fall of numerous fragments onto the pavement (Fig.1). In view of a future restoration aiming at regaining the iconographic image, the identification and classification of these *fresco* fragments is necessary. In this enterprise the identification of pigments used in mural painting is of the main importance.

Here we present the investigation of the painting materials employed in wall paintings using digital microscopy with visible and infrared light and portable X-ray fluorescence spectrometry (pXRF) combined with digital image processing and multivariate data analyses. Visible and infrared images together with pXRF spectra are used as data acquisition. For actual pigment recognition we follow by state of the art feature descriptors, such as color histogram computed on perceptual color spaces and histogram of topographical structures for pigment texture, by principal component analysis for selecting the most discriminative features and by machine learning systems for actual correlation. These techniques have been applied to characterize the pigments with the goal to put in evidence the similarity between the painting remained on the walls and the fragments fallen on the pavement. We aim at providing information for the reconstruction of the original image of the wall paintings.

Figure 1. Fresco fragments detached from the wooden beams of the Amărăşti church

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Study of the organic material in polychromed samples from the Alhambra using GC-MS

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This paper presents the results obtained from the identification of the painting materialsorganic, used in the polychrome decorations of Alhambra. The Alhambra monument, declared UNESCO World Heritage Site due to its universal beauty and exceptional expression of Moorish and Andalusian culture, was built in Granada (Spain) under the Nasrid dynasty, the last Muslim rulers on the Iberian Peninsula. Originally designed as a military area, throughout the thirteenth, fourteenth and fifteenth centuries, the fortress became a citadel, which house two main areas: the military area, or Alcazaba, and the medina or court city, the location of the famous Nasrid Palaces. Although many modifications took place after the Christian conquer and the palaces were partially altered to Renaissance tastes, much of the Alhambra retains its original character being the most important surviving remnant of the Islamic architecture in the Iberian Peninsula. Samples from polychrome motifs painted on different types of supports, namely marble, wood and gypsum, were studied. Marble samples were taken from the capitals of the columns from the Hall of the Abencerrages, the Hall of the Mexuar and The Court of the Myrtles and the Generalife. Wood samples belonged the Nasrid polychrome wood ceilings of the Hall of the Abencerrages and the Hall of the Two Sisters. Finally, gypsum samples were taken from the mocarabes in the plaster decorations of the Hall of the Kings.

First, the samples were investigated under a microscope. Due to the tiny amount (around 100 µg) of the available samples and their hardness, in the case of the marble and the wood was almost impossible to separate the paint layer from the preparation layer and the support though in some cases sub-sampling was attempted. The sample preparation consisted in a combined methodto extract the possible protein, lipid and carbohydrate material present. Once separated, each organic fraction was derivatized correspondingly and analyzed by means of Gas Chromatography coupled to the Mass Spectrometry (GC-MS)[1]. Despite of the small amount of sample and their antiquity (XIIIth-XVth century), results show that mainly proteinaceous materials, in almost all cases identified as animal glue, were used as binders in the different supports and periods studied. Moreover, wax and lipid material werealso observed, probably as restoration materials applied on the surface of thepolychromes on wood. Results, therefore, shed light into the painting technique of a unique work-of-art and an extraordinary example of Muslim art in its final European stages.

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At the archaeological excavation site: Spectroscopic investigation of pigments in Egyptian funerary artifacts

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The study of archaeological artifacts has to be conducted always minimizing the damage done to the objects. In cases like Egypt where it is illegal to take any archaeological artifact out of the country, there is a need for the use of portable and really non-destructive analytical techniques that can perform the analysis working directly on the object without sampling. Colorimetry, X-ray fluorescence and Raman spectroscopy can be interesting tools for these cases to gain information on site.

Here portable instruments were used for the investigation of wide range of excavated artefacts directly in the field during an archaeological survey in Egypt. These objects include antique Egyptian sarcophagi, cartonnage funerary masks, painted surfaces on gesso and lime, faience amulets and human remains.

An objective measurement of the colour has been achieved by colorimetry whereas elemental composition was obtained by X-ray fluorescence. Furthermore, Raman spectroscopy allows for the identification of molecular compounds gaining in this way a complementary information. The work illustrates some analytical challenges that arise when working on freshly excavated objects. They include strong fluorescence interference for the Raman measurements, diverse dimensions and shapes of artefacts and the need for urgent conservation treatments, sometimes prior to object investigation due to the fragility and poor condition of the objects.

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Technology and materials of ancient encaustic media

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The exact composition of the medium of encaustic, the wax-based painting technique used in antiquity for the production of wall and panel paintings, ceramics and polychrome sculpture, remains the subject of much debate. Ancient sources do not provide detailed descriptions for the technology employed to make encaustic paint formulations and our modern understanding of this medium is restricted to theoretical interpretations and empirical observation gained from reconstructions. The main uncertainties lie in whether treatment with alkali or the incorporation of additives (such as oil soaps or resins) to pure beeswax, would produce a workable paint capable of achieving the characteristics observed on works such as the Roman period Egyptian mummy (or Fayum) portraits, perhaps some of the best-known examples of encaustic painting. Attempts to provide evidence for the use of one such method over another have been fraught with difficulty. The detection of fatty acid salts for example, often invoked as evidence for saponification treatments, could be due to factors such as addition of oil soap, interactions with pigments and/or degradation of the medium.

A collaborative task dedicated to the investigation of markers, related to alteration mechanisms and degradation products was proposed as part of the IPERION-CH (Integrated Platform for the European Research Infrastructure ON Cultural Heritage) project. The work evaluates and compares innovative non-invasive methodologies and conventional diagnostic techniques for the detection of these markers, for a variety of organic materials, including encaustic paints. To understand how differences in the technology of production of encaustic media in antiquity would alter the composition of the wax and the extent to which these differences in wax composition are masked by the subsequent effects of aging, three different preparation approaches, based on historical and published procedures [1], [2], [3], were trialled and compared to untreated beeswax. Both unaged and artificially aged samples are investigated, including the influence of the pigment in the soap formation. For this purpose, red lead is added to one half of each preparation procedure, so that each sample has a pigmented and unpigmented variant. The study will then examine how the behaviour of these model materials can inform the interpretation of ancient paints in a case study object(s) (e.g. Egyptian mummy portraits) analysed by both invasive sampling and non-invasive methods, including GC-MS, and portable Raman and FTIR Spectroscopy.

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A multi-analytical approach for the non-invasive and micro-invasive study of inorganic and organic materials and for assessing conservation state of the 16th century Italian wall painting

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In this study a multi-analytical approach was carried out to characterize original and non-original materials, the stratigraphy structure and state of conservation of the wall paintings (16th century) painted by Antonio del Massaro da Viterbo, nicknamed il Pastura in the Vitelleschi Chapel in the Tarquinia Chatedral.

Portable XRF and mid reflection FT-IR spectroscopy allowed us to study the composition of pictorial layers evidencing original pigments, alteration compounds and restoration materials. Using unilateral Nuclear Magnetic Resonance (NMR) [1] and colorimetric measurements, a non-invasive monitoring was carried out directly in situ to evaluate the performance of different traditional and innovative cleaning treatments [2]. Further, by high resolution NMR spectroscopy in liquid and solid state [3] and ATR-IR spectroscopy performed on micro-samples the fully characterization of the organic materials was obtained.

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Multispectral Imaging Reveals New Insights on the Tomb of Iti and Neferu

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Multispectral imaging coupled to digital image processing and computing is an important tool for the non-invasive analysis of artworks. Multispectral and Hyperspectral imaging are non-invasive techniques that acquire the spectral reflectance of an object with accuracy comparable to a spectrometer. The methods are widely used to study the cultural heritage, to analyze their conservation treatments, for documentation and archiving.

In this research we will present the results on the application of LED multispectral imaging to the frescoes of the Tomb of Iti and Neferu (about 2000 B.C.) from the Egyptian Museum of Turin, Italy. A portable imaging system was used to acquire the multispectral images from these important frescoes that were detached from the Tomb of Iti and Neferu, situated in Gebelein near Luxor in Egypt, in the 1911.

The multispectral images were then processed using digital image algorithms, principal component analysis and statistics in order to read their illegible parts.

The analysis allowed the discovery of several scriptures and paintings and revealed new insights on the collocation of a *Stele* founded near the Tomb.

Luminescence of Egyptian Blue particle size - a parameter affecting the life time emission of the pigment?

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Egyptian Blue, one of the oldest synthetic pigments, which consists of Calcium Copper Silicate ($CaCuSi_4O_{10}$ or $CaOCuO(SiO_2)_4$) was commonly used throughout most of antiquity as a pigment in paintings, wall paintings, tombs, mummies, coffins and in ceramic glazing. Egyptian Blue became widespread in Egypt around 2600 BCE, although its first known use was earlier, possibly in the 1st Dynasty circa 2900 BCE. It was very commonly used during the Roman period, but later it occurred sporadically including in the Middle-Ages and beyond. Egyptian blue production knowledge and skills during ancient times must have been in the hands of very competent specialists. There is enough indication that pigments were prepared in very similar way at different geographic locations in the Aegean and eastern Mediterranean sites during the Bronze Age period [1]. Studies of the particle size of ancient Egyptian blue show great variation between eras and sites: for example Egyptian Blue grain size from 15 different Bronze Age Aegean sites, showing a great average size variation between 13 and 130 μm [1]. Recently, it was reported that Egyptian blue particles from Middle Bronze Age Aegean wall paintings of Tel Kabri, showing that their size varies between 30-100 μm. Comparisons of the particle size of Egyptian Blue from Aegean Bronze Age period to Roman period, show a significant reduction in the particle size in later period, suggesting a process of finer grinding of the pigment as part of its manufacturing. Particle size of Egyptian Blue from the Roman period from Caesarea Maritma werte measured approximately to 10-30 μm. More recent Egyptian Blue particle from the 6th Century CE of an early Christian wall painting at Shivta, in the Negev Desert, has particles size of the same magnitude as of Caesarea, between 20–40 μm. Egyptain Blue is well known for its strong infrared luminescence, but little work has been carried out on the characterisation of the lifetime of the pigment [2]. In this work analysis of historical samples from Israel containing Egyptian blue has been carried out using a time-resolved photoluminescence spectroscopy system based on the use of a pulsed laser source operating either at 355 nm or 532 nm (Nd:YAG) coupled to a time-gated intensified CCD imaging detector [3]. Analysis suggests that there are detectable differences in the microsecond lifetime in different samples of Egyptian blue from different sites and periods opening up key questions regarding the chemical composition and different physical phenomena which may be responsible for the modifications in the emission lifetime.

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In-situ characterization of the paintings found in the **Galleries of Punta Begoña (Getxo) by Raman Spectroscopy** and X-Ray Fluorescence

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The Galleries of Punta Begoña are located in the township of Getxo (Biscay) and were built in 1918. This construction has a high architectural and artistic value. It is composed of several rooms: two outer galleries (lower and upper), outside gardens and a main hall called living room. This main hall contains on each of its walls different iconographies but with a limited color range. Carlist and Falangist symbology, shields of Bilbao and Biscay and images and slogans contextualized in the pro-Franco regime appear in the different walls.

External stressor as marine aerosol and atmospheric acid gases from the nearby industrial port and road and marine traffic, together with the bad conservation state of the building increase the deterioration processes of the paintings. The characterization of the pigments is a fundamental step for a better understanding of the artworks and to determine the degradation processes in view of their possible conservation. However, because of the delicate state of preservation of the paintings, the analyses must be carried out in-situ without sampling. For that purpose, a portable innoRam spectrometer from B&WTEK^{INC} (USA), providing a 785-nm excitation laser and a hand-held energy dispersive X-ray fluorescence (HH-EDXRF) spectrometer X-MET5100 (Oxford Instruments, UK) equipped with a rhodium anode X-ray tube (operating at 45 kV) were used. The analyses were carried out with scaffolding.

In this sense, it was identify the use of lead carbonate ($PbCO_3$) or lead white as preparation layer. Moreover, lead sulphate ($PbSO_4$) was also observed. This compound was an indicative of the decaying process of the preparation layer by the atmospheric SO_2. Regarding red pigments, it was clearly identified vermilion (HgS) by both elemental and molecular analysis. In the case of gold pigments, yellow chrome ($PbCrO_4.PbSO_4$) was identified by Raman spectroscopy. In the case of blue pigments, lapis lazuli ($3Na_2O{\cdot}3Al_2O_3{\cdot}6SiO_2{\cdot}2Na_2S$) was observed. The identification of these pigments was unusual because they were in disused in the construction year. However, this date is clearly documented and therefore, the reason for the use of these kinds of pigments is still unknown. Thus, complementary analyses will be carried out.

Advantages and limitations of X-ray techniques in attribution investigations

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The techniques based on the X-ray radiation are widely applied in the attribution investigations due to the possibility for depth examinations of objects. In the thirties of the 20th century the X-ray photography was introduced to the examinations of the paintings [1]. Today, the X-ray techniques became the fundamental method of the non-invasive examination of art objects.

Recently the X-ray fluorescence gained importance in the authenticity investigations due to quite fast analysis of elemental composition and its applicability to wide range of objects such as paintings, watercolours, silver coins etc. As this is a point analysis, the number of measurement points and the selection of measurement areas strongly depends on the analyst`s experience. A more comprehensive information referring to the whole analyzed object provides the macro XRF. This technique enables us to collect information of the whole investigated area but it also gives access to XRF spectra of selected points or areas. The results are visualized as map of element distributions which makes the analysis more precise and user-friendly. Unfortunately, there are some disadvantages of XRF techniques - especially in the case of paintings; they provide information of the all layers of the painting. Therefore the noninvasive XRF investigations are usually supported by the SEM-EDS analysis of the cross-section prepared from the collected samples.

The presented study discusses the outcomes of the application of various X-ray techniques in the attribution investigations for diverse types of paintings: the unique wall paintings in the byzantine style from the Chapel of the Holy Trinity in Lublin, the painting "Saint Francis" attributed to El Greco rediscovered in southern Poland and oil painting "The Capture of Samson" whose attribution to M. Willman was questioned.

The methodology, incorporating various X-ray techniques, like X-ray photography, X-ray imaging, XRF and macro XRF, as well as SEM-EDS supported by IR, UV analysis and optical microscopy, was applied in these attribution investigations. The comprehensive analysis of the discussed projects proved both the potential and the limitations of X-ray techniques in the attribution investigation of objects of art.

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A multi-analytical approach for non-destructive in-situ characterization of early 20th century Portuguese Paintings

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The Ducal Palace of Vila Viçosa (southern Portugal) houses a collection of portraits of the Dukes of Braganza, who typically became the kings and queens of Portugal, executed in two phases, the first in the 18th century and the second in the early 20th century. The second phase comprises seven portraits of large format commissioned to some of the most important painters of the late 19th century such as José Malhoa, Veloso Salgado and Columbano Bordalo Pinheiro. Given the overall good conservation state of the paintings and hence that sampling was not possible, the material characterisation of these works was made, for the first time, by means of non-invasive in situ spectroscopic and atomic techniques that included portable FTIR spectroscopy, X-ray fluorescence (XRF), Fiber Optic Reflectance Spectroscopy (FORS), and colorimetry, which were later complemented with imaging techniques such as reflectography and infrared photography.

Many of the painting materials used at that time, in Portugal, were new pigments introduced at different rates during the fourth quarter of the 19th century and which influenced the painters in different ways. This study illustrates the complementarity of these analytical techniques, used in situ and when sampling is not possible, for the successful identification of painting materials. Thus, it contributes to determining the painters' preferred palette, some of which have never been studied before, and how it changed in time, as well as to the knowledge of this important artistic period, yet still insufficiently scientifically studied. This paper contributes to the study of the painting materials used by some of the most important Portuguese painters in the 19th-20th century transition.

Multi-analytical characterization of 18th-20th centuries votive paintings in southern Portugal

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Votive paintings were a very popular religious offering in Portugal during the 17th to the 20th century. These votive paintings were frequently made by popular painters depicting scenes related to the believer's personal situation. Often overlooked due to their popular characteristics when compared to their erudite counterparts displayed in museums, these paintings are a direct source of historical information that has almost not been studied so far. The Sanctuary of Nossa Senhora de Aires, in Viana do Alentejo (southern Portugal) houses 145 of these paintings in different supports (metal, wood, and easel) which were the base for this study.

This work describes the material characterisation of the painting materials used by these anonymous folk artists, spanning from the 18th to the 20th century, allowing the determination of their typical palette. The characterization of the painting materials was performed by optical microscopy (OM), Scanning Electron Microscopy coupled with Energy Dispersive X-Ray (SEM–EDX) microscopy, micro-Fourier Transform Infrared Spectroscopy (μ-FTIR), micro-Raman Spectroscopy, X-Ray Fluorescence spectrometry (XRF), Fiber Optic Reflectance Spectroscopy (FORS), and colorimetry. This multi-analytical approach was chosen to allow the complete characterisation of these paintings, which have never been studied analytically previously. Since the paintings were made anonimously, an analysis is also being attempted in order to classify the paintings by author.

The resulting data and materials of this work is then compared with those used by more erudite or academic Portuguese painters from the same time periods. Since the paintings span more than 200 years, including the introduction of new pigments during the 19th century, the study of the introduction and evolution of modern pigments and their potential use by these artists is of special interest.

Magritte on practice: multi analytical study of sixty-three paintings from 1921 to 1963

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Despite the abundant literature devoted to the most famous Belgian surrealist artist, very little is known about the painting materials and the making processes adopted by René Magritte (Lessines 1898-Schaerbeek 1967). In addition, it is known that between 1920 and 1935, for saving money, Magritte often re-used canvases of his previous paintings. The number and the significance of the sacrificed compositions remain unknown. Over the past several years, the X-ray radiography and high-resolution multispectral imaging (NIR, Vis and UV) techniques routinely applied on easel paintings led to the discovery of numerous hidden compositions, expected as well as unsuspected. However, to date, only very few of Magritte's early works were investigated through scientific imaging techniques [1,2].

Furthermore, early Magritte's oil paintings are substantially affected by specific visual damages. The origin and the mechanism of the involved degradation processes must be elucidated. Starting in 2013 [3], in collaboration with the Magritte Museum in Brussels, the on-going Magritte on practice research project, aims to overcome this lack of information, through a systematic and multi analytical protocol applied on an extended number of Magritte's works covering five decades of his career.

For this purpose forty-two oil paintings and twenty-one gouaches, made between 1921 and 1963 from the Magritte Museum collection, were selected to be investigated by complementary and non-invasive scientific methods, including hyperspectral imaging (Visible and SWIR), X-ray radiography, high-resolution multispectral imaging (NIR, Vis and UV), X-ray fluorescence (punctual and MA-XRF), and Raman spectroscopies. All the examinations and measurements are performed in situ thanks to portable instrumentation. An overview of the last results obtained on such extensive corpus will be presented for the first time.

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Study of organic materials in wall paintings by ^{1}H HR-MAS NMR spectroscopy.

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Wall painting is widely considered to involve a lime-based plaster and inorganic pigments dispersed in water, it is often executed using small additions of organic binders such as casein, glue, or egg. Organic materials play multiple, important roles in wall painting. For example, they are functional elements, used as final touches, to provide adhesion on plaster, or they are applied as protective layers or varnishes. The artist adds and uses organic materials to obtain revisions or changes immediately on the semidry or dry plaster, or introduces retouches and complements at the end of the work [1]. The aim of this study was to provide an analytical protocol to characterize organic materials used in wall paintings by HR-MAS NMR spectroscopy. The method of utilizing MAS for non-solid materials to produce liquid-like NMR lines was termed High-Resolution Magic Angle Spinning (HR-MAS). This is an excellent technique used to analyze semi-solid matter [2], it requires also a small amount of sample which was swollen in appropriate solvent allowing high resolution NMR spectra to be obtained.

Following ancient recipes, models of wall paintings with linseed oil, egg, wax, gum, and milk, were prepared and analyzed by NMR spectroscopy. A comparison between ^{1}H HR-MAS NMR spectra obtained with several deuterated solvents of both ancient and artificial organic samples were performed. Furthmore, a comparison between the results obtained by ^{1}H NMR spectroscopy in liquid state and ATR-IR spectroscopy was also carried out.

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Building a fingerprint with multispectral analysis for modern Brazilian artist: Tarsila do Amaral

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Technical scientific researches with multispectral non-destructives analysis are applied in the study of the modern art painting "A Negra" by Tarsila do Amaral of the Museu de Arte Contemporanêa (MAC-USP) collection. The analysis were carried out with multispectral imaging, elemental and compositional characterization and enable understand the materials and techniques used in the creative process and the manufacture materials. Imagens with visible light, infrared reflectography (IR), fluorescence visible with ultraviolet radiation (UV), tangential light and digital radiography are used to examine and document this Brazilian important historical landmark. Portable equipment with Energy Dispersive X-Ray Fluorescence (EDXRF) and Raman Spectroscopy are used in "situ" at the museum. The results of these analysis are providing valuable information on the artist producing process and is providing new information of this painting and will be used in the future exhibition that is co-organized by the Art Institute of Chicago and The Museum of Modern Art (MoMa-NY). The name of the exhibition is "Tarsila do Amaral: Inventing Modern Art in Brazil" and it will be opened in Chicago in October 2017 and then in New York in February 2018. Stephanie D'Alessandro, Gary C. and Frances Comer Curator of International Modern Art are the responsible for the exposition. Studies of Brazilian artists [1,2,3,4] are being carried out systematically in order to building a fingerprint database that are useful to historians, curators, conservators and restorers to the expansion of knowledge in art history, conservation science but also in determining and describing the artist technical characteristic.

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An hyperspectral database for modern and contemporary pigments and its application to ***La bête*** by Karel Appel

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These last decades have seen the emergence of lots of new pigments on the art market. It is obviously necessary to know these pigments properties to adjust at best the conservation processes of the paintings. For this purpose, we created a database for modern and contemporary pigments and we collected reference spectra for X-ray fluorescence, Raman spectroscopy and near-infrared hyperspectral imaging [1,2].

The data obtained were then used to study ***La bête*** painted by Karel Appel. The spots analyzed with Raman spectroscopy were chosen according to the main tones in this painting. The near-infrared hyperspectral images were acquired by scanning it *in situ* with a translation stage.

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Novel double pulse LIPS for metal characterization using passively Q-Switched laser source and CCD detector

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Recent technological and methodological improvements of Laser induced plasma/breakdown spectroscopy (LIPS or LIBS) contributed to promote the use of this technique in the field of cultural heritage. In particular, the possibility to perform rapid and relatively low-cost elemental depth profiles of metal artefacts in situ favoured a number of applications in archaeometallurgical studies of large bronzes [1]. However, the available portable devices have a lower sensitivity than laboratory instruments. To date, this did not allow to perform alloy composition analysis extended to low-concentration and trace elements. Past researches devoted to increase the sensitivity of the technique have led to the development of double-pulse LIPS (DP-LIPS) in which a large enhancement of the signal-to-noise ratio has been observed. Anyway, the double pulse lasers (two independent lasers or single laser with double electro-optic Q-Switch) and detection systems (echelle spectrometer coupled to intensified CCD detectors) employed so far prevented the implementation of compact and preferably low-cost DP systems. In this work, a novel portable DP-LIPS has been developed and successfully tested on metal alloys. Its excitation is provided by a passively Q-Switched Nd:YAG laser and low-cost Czerny-Turner spectrometer coupled to a non-intensified linear CCD detector. The two laser pulses achieved were temporally separated by about 80 μs and their energy was about 100 mJ. The spectral acquisition on the second laser peak was driven by an optical trigger allowing for a minimum delay of 1.3 μs. DP provided a significant enhancement with respect to the single pulse. The amplification observed ranged between a factor 10-30, depending on the specific emission peak. The novel instrument has been calibrated for quantitative analysis of copper alloy. Systematic tests were carried out on reference samples then the DP-LIPS prototype was validated by investigating an original statuette from the Egyptian Museum of Florence.

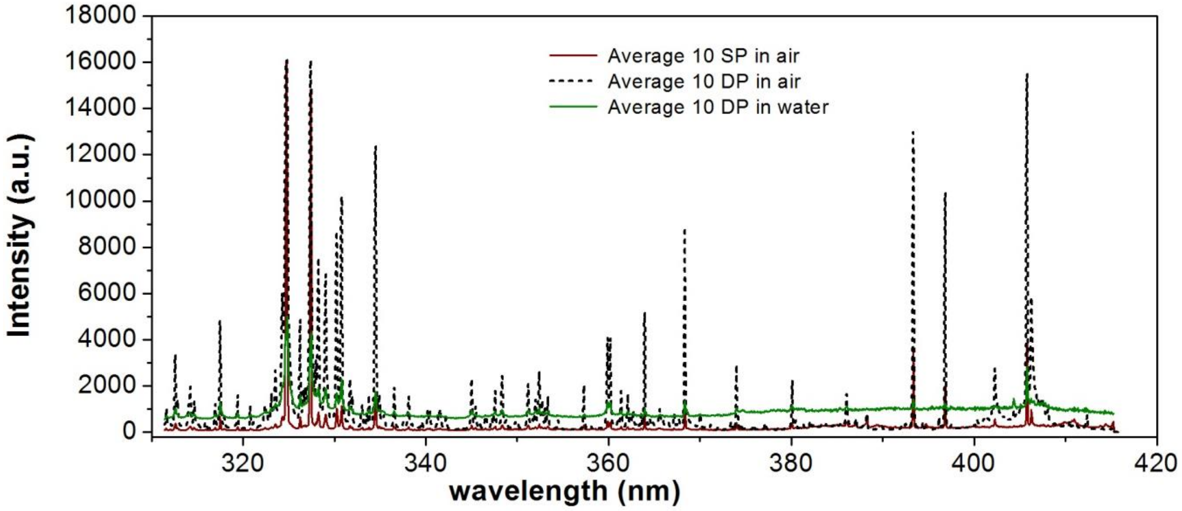

Figure 1. Comparison between spectra collected using single (SP) or double laser pulse (DP), respectively.

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Local structure of *Sb* through Synchrotron Radiation X-Ray Absorption Spectroscopy in 19th century glazed tiles from the Pena National Palace, Sintra, Portugal

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Unique majolica-type polychrome high relief tiles from 19th century Portuguese manufacture, precursors of the *Art Nouveau* period in Portugal, from the UNESCO World Heritage Pena National Palace (Sintra, Portugal), were chemically and structurally characterized using XRD, μ-PIXE, μ-Raman, Optical Microscopy and VP-SEM [1]. The glazes display a silica-lime-alkali glass with the addition of low melting point metals namely Pb (contributing to transparency and the brilliance of the glaze) and chromophores based on Sb, Co, Mn and Ni. An opacifier based on Sn was added to make the glaze opaque-white, resulting in the formation of a dispersed SnO_2 crystalline phase.

XANES (X-ray Absorption Near Edge Spectroscopy) was used in order to ascertain the chemical state of Sb in the vitreous matrix to clarify its role in pigment incorporation and the possible relationship between the chemical evolution and the ageing mechanisms of the glaze.

Speciation of fuser metals and colorants in ancient tile glazes allows for tracing chemical affinities and correlations in phase behaviour. This is the case of antimony-containing pyrochlore-type double oxides: the compound $Ca_2Sb_2O_7$ that gives rise to bluish/green colouring and bindheimite, a yellow pigment with approximate formulae $Pb_2Sb_2O_7$.

Samples analysed are minute glaze fragments from the 19th century with yellow, green and grey colour. The comparison with XANES spectra from model compounds along with theoretical modelling using the FEFF code [2] will be presented has they suggest the structural role of additives as glass network formers or modifiers or integration in crystalline colouring phases along with other XANES successful application to other type of tile glazes [3-7].

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Physical and Chemical Properties of Water-mixable Oil Paints Assessed Using Gas Chromatography and Single-Sided NMR

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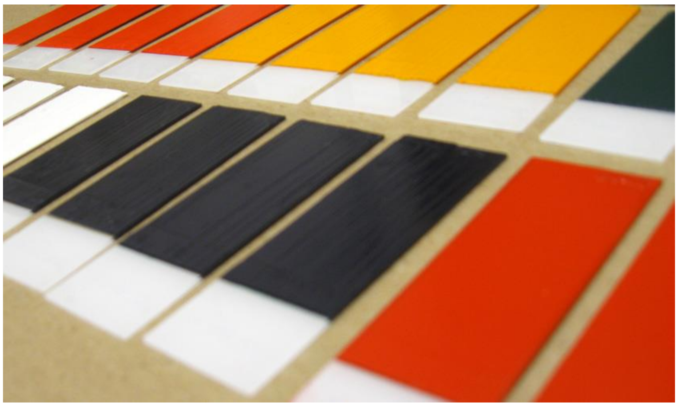

Figure 1. Some of the paint-outs of water-mixable oil paints used in this study.

Water-mixable oil paints have been formulated as safer and environmentally friendly alternatives to traditional oil paints since they require minimal organic solvents for dilution and clean up. Water miscibility is achieved by the addition of emulsifier in up to 10 weight percent. We used GC-MS and single-sided NMR relaxometry to investigate the effect of the emulsifier, polyethoxyethylene (40) sorbitol hexaoleate, on the curing rate and physical properties of the resultant paint films. Recent paint-outs on glass and paint-outs on prepared grounds made in 1995 were examined. GC and NMR results show that the addition of the emulsifier to oil paint reduces the curing rate and results in a less cross-linked paint film during the first six months. However, after six months, the stiffness of the paints, determined from NMR measurements, reaches a plateau which is relatively insensitive to the type of pigments present, evident from the results obtained from the 1995 paints. We infer that even as chemical changes in paint films continue for many decades, the extent of oligomeric network formation, as measured using NMR, plateaus. Naturally aged paints that have zinc-containing pigments have the lowest azelaic to palmitic acid ratio, but have NMR relaxation values similar to the other water-mixable paints, suggesting that as diacids form from β-scission the network does not become stiffer. As much attention has been given recently to the mechanical properties of paint films (in contrast with chemical properties only), this work extends the utility of NMR relaxometry in evaluating the *physical-chemical* properties of paint films.

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Preliminary scientific investigations on constitutive materials from Pagoda n.1205 Bagan valley (Myanmar)

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On 24 August 2016, a magnitude 6.8 earthquake struck central Myanmar. Bagan Archaeological Zone suffered extensive damage and more than 300 structures were partially destroyed. After the earthquake, information about the damage to cultural heritage was collected from the DoA, JICA and the UNESCO Bangkok Office. In addition, a post-earthquake damage assessment survey from Tokyo National Research Institute for Cultural Properties (TNRICP) was dispatched to Bagan from September in order to collect information on the structural damage to cultural heritage buildings.

As a part of the same project, a diagnostic project was carried out to acquire preliminary information on Bagan temples constitutive materials and construction technology, i.e. compositions of bricks and stuccoes. A further goal of the present study was to obtain sufficient technical-scientific knowledge to draw up a "pratical code" to be adopted in Bagan valley restructuring plain.

Preliminary non-invasive analyses were performed on the Pagoda n. 1205a with ED-XRF that allows to getting a general idea of the constitutive materials. Subsequently representative samples were collected and submitted to the following techniques: optical microscopy, scanning electronic microscopy with EDS microanalysis, XRD, ATR FT-IR spectroscopy, NMR, TG analysis.

The results allowed distinguishing two different brick typologies, one original and the other related to a restoration intervention, and two different typologies of stuccoes.

The SEM/EDS analyses showed the very interesting presence of yttrium, titanium, copper and tin in stucco samples, while in not original brick traces of rare hearths (cerium, lanthanum, neodymium, praseodymium) with vanadium, chromium and phosphorous were detected. As a matter of fact all of these elements are related to different deposits located in Mandalay Region [1, 2] and they could represent distinctive elements (markers) to recognize the constitutive materials provenance.

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The new monumental gate excavated in Tol-e Ajori (Fars, Iran): investigations on technology of bricks production and clay raw materials provenance

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This work deals with the characterization of the bricks, which belong to Tol-a Ajori Gate: one of the most important excavation in Persian plateau, closed to the World Cultural Heritage of Persepolis. The archaeological excavations of Tol-e Ajori (Fars, Iran) were carried out between 2011 and 2015 and a building structure came to the light. The wall structure is built with mud-bricks and fired bricks, some of which are glazed. In the outer face of the walls and in the collapse, decorated materials and glazed bricks were found showing parts of figurative motifs in reliefs. They are very similar to the bricks from Babylon's Ishtar Gate, although the colours are paler without the typical blue background of this gate.

A series of representative bricks from the found materials were selected for archaeometric analyses.

Several investigations were carried out in order to clarify firstly the compositions and the technology of the bricks production. A further goal of the present study was to compare the bricks composition with local clays data to determine a possible provenance [1]. Some clay deposits outcropping in the neighbourhood were recognised and clay samples were collected in order to possibly identify the raw materials used for the bricks material production.

Brick samples were investigated using different analytical techniques (Optical Microscopy, SEM/ESEM-EDX, FT-IR/ATR, XRD, XRF, TGA, STA and Micro-Raman) to point out differences in chemical and mineralogical composition. The clay raw materials have been submitted to XRD, XRF, SEM-EDX and FTIR-ATR analyses. In order to discriminate clays groups PCA and HCA were also performed on the chemical compositional data.

A wide homogeneity was present for all the considered bricks: Ca-rich clays with quartz-rich temper were used, this possibly suggesting a common origin. Firing temperatures were supposed on the basis of the presence of newly formed cristalline phases [2].

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(Un)stability of azurite and malachite in *fresco* mural paintings: the role play by high humidity environment

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This paper reports the experimental essays made to ascertain in which extent the pictorial technique and the atmospheric conditions can trigger the conversion of copper basic carbonates into tenorite. Azurite and malachite pigments were found in mural paintings from Antiquity to Renaissance in Europe and despite recommendations against, both pigments were often used in a lime-containing plaster in *fresco* with drawbacks but also with success [1-7]. Among the reasons for the pigments alteration raised by authors over the years are the granularity, the alkaline and the humidity environment but doubts still remain [4-7].

The present study was carried in mockup reference paint layers made with azurite and malachite in *buon fresco*, lime *fresco* and tempera *sul fresco* keep in environmental atmospheric conditions and in vitro in a high relative humidity (95-98%RH).

Changes in color appearance and in the pigments particles morphology were recorded by OM, SEM-EDS and XRD. First results with the paint set in *buon fresco* show that the exposure to high humidity is the main responsible for trigging the chemical-physical deterioration phenomenon. After 9 days of exposure in vitro, the paint layer surface has completely darkened into tenorite while the analogous paint layer keep on environmental conditions (65-85% RH) is still stable.

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Infrared spectroscopic study of the formation of fossil resin analogs with temperature using *trans*-communic acid as precursor

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The purpose of this work was to analyze the *trans*-communic acid with the temperature to provide spectroscopic evidences of possible chemical pathways that took place in the formation of fossil resins Class I [1]. The best known example of a fossil resin is the amber, a material used in many objects of the cultural heritage, and many aspects of its formation are still in debate.

With our experiments at variable temperature the natural polymerization process was mimicked in the laboratory by using pure *trans*-communic acid (a terpene derivative) as reactant. The process was followed and analyzed by infrared spectroscopy, differential scanning calorimetry and thermogravimetric analysis. Previously, a Raman study at different temperatures was reported [2]. In addition, we have studied with infrared spectroscopy the residue of *trans*-communic acid at room temperature, once the samples were subjected to a high temperature, which was varied between 453 and 613 K. Another issue considered by our experiments has been the influence of the used atmosphere, due to the temperature-induced reactivity has been studied in presence and in absence of an inert atmosphere.

Conclusions about the reactivity suffered by the *trans*-communic acid were discussed based on the changes observed in the conjugated double-bond, the exocyclic bond and carboxylic acid group of the monomeric unit. The implications in the formation of the fossil resins will be outlined.

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Identification of plastic bookbinding materials using system SurveNIR

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The Collection Preservation Division of the National Library of the Czech Republic (NL CR) has devoted special attention to the care also of the so-called modern library collections, which contain books and documents created within the range of last more than two hundred years, beginning in the year of 1801. These collections record development of Czech culture and national entity – they have invaluable historical, art, and social significance, and principal informative value. Unfortunately, the material from which the prints were produced after 1845 - lignin containing paper, plastics - as well as present changed technologies and materials, result in their poor durability. At the same time, this durability affects a number of degradation factors, above all external factors, which are ambient temperature, relative air humidity, impurities included in environment, light energy, biological pests, etc.

Poor quality of materials of modern book collections is accompanied even with large quantity of documents in this segment of collections: in the NL CR, there is up to 96 % of book collections, whereas their contents still increases. In term of care of modern collections contain variety of materials. After brief description of modern library collections this paper will be focused on methods of nondestructive analyses of composition, chemical structure and physical state of modern library collection exemplars - specially plastic materials using system SurveNIR and database for identification of plastic materials. SurveNIR is a portable systém used to determine 42 different kinds of plastic materials.

Roman glass tesserae: a combined Raman and XRF spectroscopic investigation

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Roman glass tesserae from the Coriglia (Italy) archaeological excavation site were characterized using Raman spectroscopy, handheld energy-dispersive X-ray fluorescence spectrometry and μ-energy-dispersive X-ray fluorescence spectrometry. Both intact and cross-sectioned samples were investigated through respectively, spot and line scan analyses. In total, 10 different glass colors were examined resulting in qualitative chemical characterization of the bulk glass, decolorants, opacifiers and coloring agents. The use of antimony opacifier confirms late imperial phasing as determined through numismatic, fresco, ceramics, and architectural evidence. Dealkinization of the exterior glass layers caused by the burial environment was confirmed. [1]

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A study of building stones from structures dating back to the period of Ivan IV the Terrible in Kazan Kremlin and the Island town of Sviyazhsk

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The work features the results of research with the purpose of determination of raw material source for stones used during the construction of 15th-16th century buildings in Kazan Kremlin and the Assumption Cathedral of the Island town of Sviyazhsk. The raw stone material was studied using four independent analytical methods. The chemical composition was determined by emission spectral analysis, whereas the mineral composition was studied using optical microscopy and petrography techniques. Additionally, a portion of samples was studied using the electron microscopy technique with the determination of elemental and mineral composition. Besides, X-ray patterns were obtained for a series of samples.

In accordance with research results, the four independent analytical methods have demonstrated the same result. Summarizing the data of all analyses one can make a definite conclusion regarding the source of raw construction material used for the erection of buildings in Kazan and Sviyazhsk. It has been determined during research that the masons who simultaneously constructed the Northern tower of Kazan Kremlin and the Assumption Cathedral in the 16th century acquired stone from the same quarry with dolomite deposits located on the Volga bank near Pechischi village. The 15th century Khan's Palace of Kazan Kremlin was erected using the same dolomite. Stones from the opposite bank of the Sviyaga in the area of Makaryev Monastery are different in that they are composed of “purer” dolomite.

Micro X-ray fluorescence and micro computed tomography applied to characterize the limestone of a quoin of Castello Svevo, Bari, Italy

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The conservation and protection of cultural heritage monuments is of primary importance for their environmental, economic, and cultural value for the society. Weather plays a relevant role in natural ageing of monuments and atmospheric pollution also affects the degradation of the constituting rocks due to chemical reactions induced by dry and wet depositions. Mining of limestones, which are widely spread in the Apulian region (Southern Italy), originated in ancient times and still represents a relevant economic resource for building purposes in the region. In particular, compact limestones were used to build several Romanesque cathedrals and many other relevant monuments such as the Castello Svevo in Bari. Compact limestones mainly undergo superficial degradation by dissolution of carbonatic components, sulphatation processes, and deposition of substances coming from the surrounding environment [1]. Besides the apparent negative aesthetical aspects, dirt on the surface is a threat for monuments preservation. In particular, the problem of surface deterioration is increasing in the urban context, where the impact of dirt involves relevant, expensive and frequent cleaning works.

The present work aimed at studying the alteration processes of a limestone sample of a quoin of the external wall of the Castello Svevo, in Bari, which was exposed for centuries to urban polluted air. This by analysing both the black crust and the stone material underneath using micro X-ray fluorescence (μ-XRF) and micro computed tomography (μ-CT). Results of μ-XRF analyses of limestone thin sections showed that S, Al, Si, Ti and Fe could be detected only in the black crust, whereas Ca and Mg signals increase in intensity passing from the black crust to the limestone underneath. The presence of S can be ascribed to gypsum formation in the black crust, while Al, Si, Ti and Fe would originate from atmospheric dust and particulate deposition. Results of μ-CT analysis highlighted the presence of three layers, i.e. the original limestone covered by an alteration layer consisting of a low density and porous material, over which an external crust of higher density containing small dispersed particles (particulate) was deposited. In conclusion, both μ-XRF and μ-CT techniques, allowed to perform successful analysis of the qualitative and quantitative composition and evaluate the alteration processes of the artifact under study.

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Identification of elemental markers in historical musical instruments through XRF spectroscopy combined with Principal Component Analysis

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The history of bowed stringed musical instruments hides centuries of experimentation performed by violin makers on shapes and materials. In several cases, these peculiar characteristics can help to identify the making period, the geographical provenance and, rarely, the Master's workshop [1]. These objects of art, played a lot over time, suffered in few cases of severe damage (i.e. crackings, woodworms) requiring substitution of some parts. Gaetano (1878-1959) and Pietro (1903-1990) Sgarabotto, two of the most eminent violin makers and restorer of the 20th century, collected lots of these substituted parts. These fragments represent groups of several Italian instruments of historical significance, made over a long-time period (1500-1800) and coming from different geographical areas. We had the unique opportunity to perform non-invasive and non-destructive analyses through portable X-ray fluorescence spectrometry (PXRF) [2] on 26 of them. Principal Component Analysis was applied to classify relics highlighting the most relevant elements in the data set. The principle of transformation is the extraction of maximum variance for each successive new variable. This procedure leads to a separation of valuable information from noise and to a selection of few influential and statistically significant variables [3]. The application of PCA lead us to (i) assess the existence of elemental markers of specific historic periods and/or production areas, (ii) identify correlations between different fragments. Preliminary results validated the application of PCA on XRF data set, as shown in Figure 1. Several groups of XRF data have been isolated from others for their PCA scores values with respect to the variation of the elements identified in the fragments.

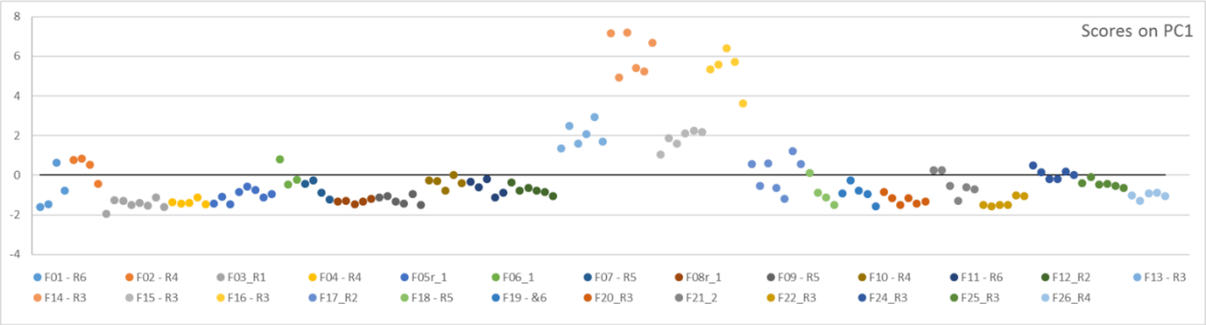

Figure 1. Scores on PC1 variation of selected XRF data collected on the musical instruments fragments

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μ-Raman spectroscopy of rock paintings from the Galb Budarga and Tuama Budarga rock shelters, Western Sahara

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Two Galb Budarga and Tuama Budarga rock shelters from the southeastern area of the Western Sahara have been studied by micro-Raman spectroscopy (μ-Raman) and scanning electronic microscopy combined with energy dispersive X-ray spectroscopy (SEM/EDX). An unusual white pigment has been used in the Galb Budarga shelter. Its main components are gypsum ($CaSO_4 2H_2O$) and the anhydrite ($CaSO_4$) polymorphs I and II [1], Fig.1. -Quartz (SiO_2), albite ($NaAlSi_3O_8$) and traces of hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] have been identified in the substrate. Accretions of calcium oxalates like whewellite ($CaC_2O_4H_2O$) are covering the painting panel of this rock shelter [2].

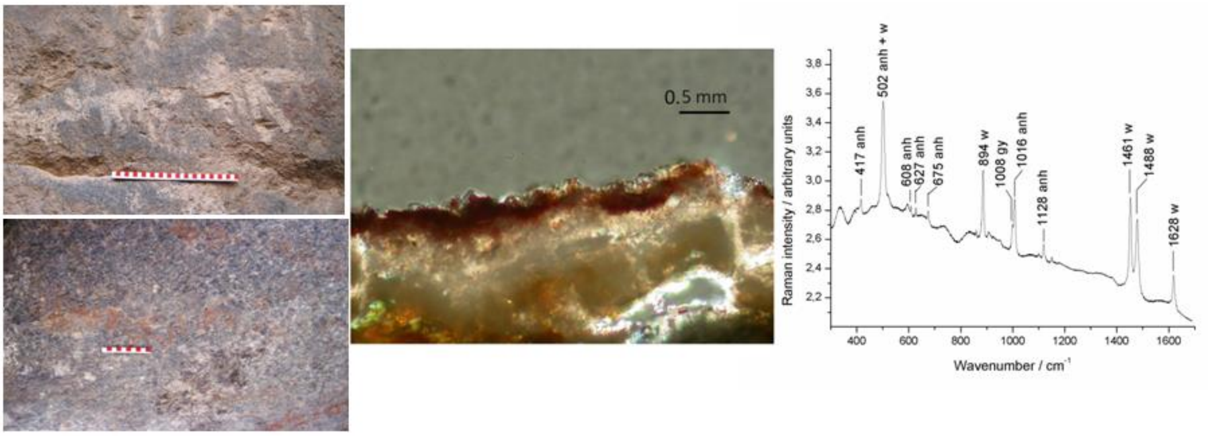

Figure. 1. (Left, up) Pictograph of Tuama Budarga; (left, down) pitograph of Galb Budarga. (Centre) Microphotograph of a cross-section of pigment from Tuama Budarga. (Right) Raman spectrum from a specimen of pigment from Galb Budarga showing bands of anhydrite (anh), gypsum (gy) and whewellite (w).

Red and orange zoomorphic figures and ancient bereber scripts have been painted in the Tuama Budarga rock shelter, Fig. 1. Haematite (α-Fe_2O_3) is the main component of the paints used; amorphous carbon, gypsum and anhydrite are also present. The substrate components are similar to those found in the Galb Budarga shelter, and layers of whewellite and weddellite [$CaC_2O_4\cdot(2+x)H_2O$, $x \leq 0,5$] have been detected on the surface of the painting panel. A microestratrigraphic study on specimens of red paint revealed a first layer of whewellite on the rocky substrate, haematite and amorphous carbon cover this layer and whewellite accretions appear on the surface, Fig. 1. Thus the red pigment is bracketed between oxalate layers. This is an excellent opportunity for AMS ^{14}C dating of the paint [3].

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The possible use of Mesopotamian bevelled rim bowls: results from organic content analyses

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The Middle and Late Uruk period (or Late Chalcolithic 4-5) in Mesopotamia has been characterised by the birth urbanism, including the first known system of writing. In the Middle Uruk period (3600-3500 BC) a diffusion of the Uruk culture started in the whole of Mesopotamia and surroundings, being the "Southern Mesopotamian Style" Uruk sites recognised by a special kind of pottery called bevelled rim bowls (BRBs). BRBs comprise up to 80% of all Uruk recovered pottery in excavations. BRBs are very basic, handmade bowls with very similar shape that were produced in large quantities in Mesopotamia. However, their use is still under debate. It has been proposed that the BRBs were produced with different purposes: cooking, measurement of cereal rations, salt making process or votive bowls among others [1], but none of those hypotheses have been supported by analytical evidence. One of the hypothesis is bread preparation [2,3], for which there are several archaeological indications. On one hand, BRBs are usually encountered intact (not fragmented) and found in large numbers and mixed with bones and vegetal remains. This indicates that they the bowls were not as important as their content and once consumed their content they were thrown away [4,5]. In some sites, they were also found near kilns and ovens [5], and BRBs are similar to bread moulds called *bedja* in a later period in Egypt [6]. On the other hand, in archaic Uruk texts the pictogram used to refer bread is very similar to the frontal view of a BRB [7]. To assess whether there is evidence that supports the proposed hypotheses we have studied eleven BRBs from two archaeological sites in the Middle Euphrates (Syria): Tell Humeida (TH) and Tell Sheikh Hassan (TSH). We have analysed small fragments by pyrolysis coupled to gas chromatography and mass spectrometry (Py-GC/MS) to identify organic molecules that could be related to any content of the BRB in the past. Additionally, we have experimentally produced BRBs and cooked bread to compare results. Results showed up to 93 organic compounds, including polysaccharides, lignin and fatty acids present. The results are compatible with the proposed hypothesis of leavened bread cooking, in particular the survival of 4-vinylguaiacol, which is a product of weakly charred lignin that was also found in experimentally charred bread heated below 450 °C.

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Calcium alkoxides for stone consolidation: investigating the carbonation process

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During the European NANOMATCH project (funded under FP7 GA no. 283182) two alkoxides, calcium tetrahydrofurfuryloxide and calcium ethoxide, were developed and tested as new products for stone and stone-like consolidation [1, 2]. Their behavior in atmosphere makes them suitable products for conservation of calcareous stone: in fact they react with humidity and carbon dioxide to give $CaCO_3$. In this paper we report the results of an investigation aimed to understand the influence of different parameters (RH, solvents, concentration) on the carbonation process and on the formation of the final coating, in particular as far as the crystalline form is concerned (vaterite, calcite, portlandite). Solution of alkoxides in different solvents (different alcohols, n-butylacetate, ligroin) were prepared at two concentrations (5g/L and 20g/L in Ca). Kinetic of carbonation was investigated through µ-FT-IR. The solutions were then applied on glass slides and maintained two weeks either at environmental conditions or at controlled RH conditions (50% and 90%). The resulting coatings were then characterized by -FT-IR, XRD and SEM. Results indicate that the most important factors influencing the kinetic and the final products are the humidity and the features of the employed solvents.

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Are the biocolonizations dangerous for the conservation state of Machupicchu? A multi-spectroscopic study of the Sacred Rock monolith

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Machupicchu archaeological site dates back to the 15th century and it is located 2,430 meters above sea level in the Cusco Region (Peru). It was erected on a white granite plateau in the Vilcabamba batholith. In 1983, it was declared World Heritage Site by UNESCO. Due to its location and climatic conditions, microorganisms and composite organisms such as lichen, algae, fungi, etc. can colonize the rocks present in Machupicchu. A good example is the biocolonization phenomena that are taking place in the Sacred Rock monolith, which are favoring surface exfoliation phenomena on this granodiorite rock. The hyphae of some of these (micro)organisms can penetrate this rock, promoting stress on it. Moreover, they can also extract the essential inorganic cations from the substrate, which can be chelated with different ions excreted by themselves (e.g. oxalates, sulfates, etc.) to give rise to biomineralization processes.

In this work, a multi-spectroscopic study based on the use of molecular techniques such as micro-Raman spectroscopy and X-ray Diffraction, and elemental techniques such as micro energy dispersive X-ray fluorescence spectroscopy (single point and mapping) was applied trying to understand better the biodeterioration action that these kind of (micro)organisms can produce on the Sacred Rock monolith from Machupicchu.

Thanks to the micro-Raman spectroscopy, beta-carotene and scytonemin were identified as the main biogenic pigments of the biofilms from the Sacred Rock monolith. In the literature, there are works that correlate the presence of beta-carotene with the lichen and algae existence, and scytonemin identification with the presence of cyanobacteria [1]. Indeed, thanks to Phase Contrast Microscopy, algae from the *Trebouxia* class and different mosses from the *Bryopsida* class were identified as main colonizers of the rock. Following a depth-profiling test, micro-Raman spectroscopy was applied to determine the penetration depth of these organisms in the rock, observing that the lichens and mosses, even algae, can penetrate till 200-300 µm and in some cases till millimeters.

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MALDI-FT-ICR-MS for the analysis of resinous materials

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This work focuses on the modified methodological approach for analysis of resinous materials with MALDI-FT-ICR-MS.

MALDI is a suitable ionization technique for MS analysis of almost any type of material (resin, polymer, oil, peptide/ protein, saccharide, etc.) and enables the analysis of very small samples that are not fully dissolved (even solid samples may be analyzed) [1, 2]. Coupled with FT-ICR-MS the method enables obtaining mass spectra with high resolution (up to 100000 in case of resins/ varnishes) and high *m/z* accuracy – mass deviations less than 2 ppm (in case of internal calibration).

In order to obtain high *m/z* accuracy the *m/z* axis of the mass spectra has to be calibrated. Unfortunately, the selection of (commercially available) calibration standards suitable for the analysis of resinous samples (offering a flexible selection of *m/z* values under *m/z* 1000) is very limited (few peptides, some polyethylene glycols).

One of the most important aspects of the MALDI technique is using the suitable matrix compound. We have demonstrated the suitability of 2,5-dihydroxybenzoic acid (DHB) for the analysis of resinous samples in the positive ion mode [1, 2]. However, this matrix is unsuitable for the analysis of resins in the negative ion mode. Therefore, a new matrix compound had to be found for this method.

This study presents a modified MALDI-FT-ICR-MS method for the analysis of resinous materials, utilizing both positive and negative mode. It incorporates a novel matrix compound, 2-aminoacridine (2-AA), for the analysis of resinous samples in the negative mode and extends the selection of internal standards with $m/z < 1000$ for both positive (15 different phosphazenium cations) and negative (anions of 4 fluorine-rich sulpho-compounds) ion mode in order to provide more accurate information about the composition of the samples.

The newly suggested internal calibration compounds and matrix material were tested for the analysis of dammar, mastic, sandarac, colophony and shellac resin, but also for the analysis of real-life varnish samples. The obtained high *m/z* accuracy mass spectra of the resins were used as references in the identification of unknown varnish samples. These results demonstrate the applicability of this approach for analysis on resinous materials with MALDI-FT-ICR-MS.

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Micro-chemical evaluation of ancient potsherd by mean of Micro-Libs-Scanning on thin section negatives

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In the study of ancient pottery fragments, thin section analysis represents the basic approach to obtain preliminary information about origin of archaeological ceramic finds[1]. In fact, composition of aggregates and clays usually reflects the geological context of artifacts production. However, even if thin section analysis allows investigating the textural and structural characteristics of archeological ceramics, peculiar features related to clay paste and temper composition can be detailed addressed only by quantitative mineralogical and chemical studies. In some cases, the relevance of artifacts prevents the sampling of large amount of materials to analyse by different analytical techniques and only fragments to preliminary study under microscopy light can be obtained. In the realization of thin sections,often a negative face is produced, similar to the thin section itself, which can be used for additionally analysis, such as high spatial resolution micro-chemical studiesusing a micro-laser induced breakdown spectroscopy (μ-LIBS) scanner.

LIBS is a spectroscopic technique that, exploiting the laser radiation, is able to bring into the plasma state micrometric portions of the sample, and to analyse its content through the study of the optical emission of the plasma itself [2]. Unlike other techniques,LIBS can detect and quantify light elements such asaluminium and magnesium, as well as add other elements, relevant in potteries studies [3].

The images produced by the μ-LIBS instrument show the spatial distribution of the chemical elements within a portion of the sample, which may have dimensionsfrom a few hundred microns up to several centimeters. The combination of these images with algorithms derived from image processing techniques may return interesting information and supporting data to go in-depth investigate potteries components detected by petrographic observations. Thus, in this contribute we present the results of an experimental study performed on thin sections negatives coming from some important Neolithic Italian sites different for grain size, surface treatments and aggregates, exploring the potential of the method in micro-chemical studies of ancient potsherd.

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NIR μ-Raman spectroscopy investigation on Early Bronze IV potteries from Khirbat Iskandar

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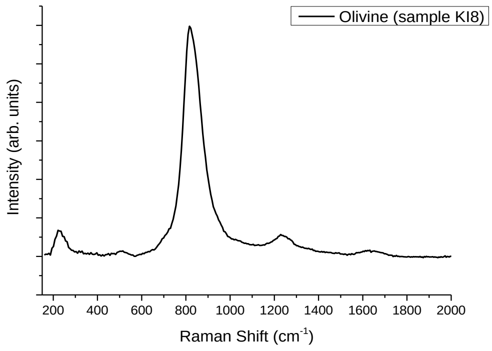
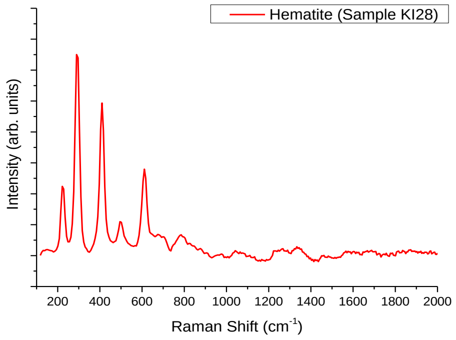
A group of pottery sherds from Khirbat Iskandar, Jordan, was submitted for analysis through micro-Raman spectroscopy. Khirbat Iskandar is a key-site in the study of the Early Bronze IV, ca. 2500-2000 BC, a critical period in the southern Levant. Excavations at the site revealed a multilayer Early Bronze IV stratum that allowed for the reconstruction of a trajectory of crisis, stability and growth. The selected samples belong to Phase 2 in Area C, when a domestic complex was transformed into a multifunctional complex interpreted as a gateway.

Near Infrared Micro-Raman spectroscopy was used, as a preliminary and non-destructive technique, in order to investigate the mineralogical composition of the samples [2]. Preliminary results show that the ceramic body is composed mainly of quartz, calcite, and minor amount of feldspars and hematite. In addition, the presence of olivine and Anatase (see figure), important markers to identify the provenance of raw materials, was detected. Furthermore, the occurrence of portlandite was related to both rehydration of calcite and burial alteration processes [3].

NIR μ-Raman spectroscopy was helpful to investigate the nature of the pigments of these ceramics: the red colour was obtained by hematite (see figure), the dark areas of the sample were associated to amorphous carbon. Mineral assemblage, especially the presence of Anatase, allowed us to estimate the maximum firing temperature of these pottery vessels between 600 and 700 °C [4]. These preliminary results suggest that μ-Raman spectroscopy could have a key role in the study of ceramic materials, especially the characterization of archaeological ceramic samples for which manipulation and/or consumption are not allowed.





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In situ analyses of Himalayan paintings to strengthen Ladakhi cultural identity

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The Matho Museum is an under-construction museum 3800 m above sea-level in the Himalayan mountains in the Indian region of Ladakh. The museum is built alongside the Matho monastery and is a collaboration between the Buddhist monks and international experts. The future opening of the museum (planned in 2017) is a great opportunity for a scientific investigation of its unique collection: precious Himalayan artworks, objects and documents. In this communication we focus on the thangkas which are scroll Tibetan Buddhist paintings on cotton or silk, usually depicting a Buddhist deity. The monastery has in its collection such unique pieces as 12th century Kashmiri thangkas, which truly deserve to be analysed despite their limited accessibility.

In-situ X-ray fluorescence analysis and near infrared spectroscopy have been performed on 28 thangkas of the monastery to address several questions concerning their technique and provenance. For the most precious ones, all of the colours have been characterized (traces and main elements), and for the others only the white pigments and preparation have been investigated to find evidence of local production. Preparation and white pigments were most probably found locally and can thus help to define the thangka's provenance. The results constitute the first database of white Himalayan pigments.

As a comparison, local clays have been quantitatively analysed by XRF, but also wall paintings and ritual ornaments from the same region. With this study we aim to emphasize the role played by local production in art, and thus to promote the Ladakhi culture, too often under-estimated. This is the first scientific investigation devoted to Ladakhi works of art, and one of the most important one on Tibetan thangkas.

Figure 1. On the left, the Matho monastery and the future museum (ladakh, india); on the right, in situ x-ray fluorescence spectroscopy of a thangka.

Wine organic biomarkers in archaeological potteries: detection by GC-MS at ultratrace levels

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Wine has been one of the most produced, consumed and traded fermented beverage throughout the world and throughout the ages. Ceramic vessels, such as Amphorae, have played an important role in the past in order to store or transport this product. The detection of organic residues that remain absorbed into the pores of these ceramic artifacts gives us the chance to differentiate among different merchandise, etc. Although many research works have been successfully accomplished on the study of organic remains in porous ceramics, the poor conservation state of the potteries and the low amount of the organic tracers are still an analytical challenge as well as the main drawbacks to get the relevant information concerning different aspects of past societies.

In this framework, the main aim of the present research work is to propose an improved analytical methodology to determine organic biomarkes related to wine in archaeological ceramics. Several analytical methodologies have been previously developed, but none of them have focused their attention on the improvement or maximization of the biomarkers' recoveries. Unfortunately, sometimes this fact could lead to false negatives, that is, ignoring samples that really contained wine.

An analytical approach based on the extraction of wine biomarkers (tartaric, fumaric, succinic, benozoic, malic and syringic acids) by means of Focused Ultrasound Solid Liquid Extraction (FUSLE) followed by a preconcentration step by Solid Phase Extraction (SPE) using mixed-mode strong anion exchange (Oasis MAX) cartridges and a derivatization step prior to analysis by means of Gas Chromatography-Mass Spectrometry (GC-MS) was developed. For the optimization and validation of the whole procedure, synthetic ceramics were spiked with the previously mentioned biomarkers and were subjected to analysis. Additionally, synthetic ceramics were immersed in wine during 8 months and subsequently analyzed with the developed methodology and other methodologies described in literature in order to compare the obtained recoveries.

Finally, the optimized procedure was applied to archaeological ceramic samples found in Azores (Portugal) suspected to have contained wine or oil.

Unraveling the composition of coloured glass by the comparison of complementary spectroscopic methodologies: the case of beads from the Kongo Kingdom

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The KongoKing project, focuses on the history and development of the Kongo Kingdom, before and after their first contact with Europeans. European glass trade beads play a significant role in this project, as they are ubiquitous in funerary contexts.

Following previous research on beads from the Democratic Republic of Congo [1,2], in this study, the glass was initially characterized, in terms of matrix (stabilizers, flux, etc.) and colouring/opacifying agents, by micro-Raman spectroscopy. In fact, from the Raman spectra of glassy materials information regarding the glass network itself and crystalline phases affecting the colour and transparency of glass can be successfully identified.

XRF analysis was then used to clarify the chemical nature of some colorants with trace level elemental sensitivity. The hXRF used during previous studies [1,2] is very well suited for relatively homogeneous samples, but due to its large spot size, finely structured objects are more difficult to examine in detail. Hence, microscopic XRF analysis (μXRF) and subsequent data-mining techniques will be employed to resolve the different layers of coloured glass with their respective elemental compositions. Using these techniques together with the complementary Raman spectroscopy will maximize the information extracted from the glass samples. Furthermore, 3D Hirox microscopy was applied on the beads in order to macroscopically investigate the multi-coloured fine layered samples.

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A fixative fixation: Historical and analytical study of fixatives for pastel paintings

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Pastel paintings are characterized by a velvety and matt surface, as a result of the irregularly shaped particles, which diffuse the incident light. These particles are not incorporated in a binding medium, like in the other paintings techniques, but the pastel sticks are applied dry on the support. Because of the poor adhesion of the pastel powder onto the support, artists have always looked for a fixative able to stabilize the pastel powder without altering the hues or modifying the velvety texture of the medium. Starting from the 18th century, this quest led to numerous recipes reported in treatises, journals and letters.

This poster will present an ongoing Rijksmuseum research project dedicated to the analysis of fixatives applied for pastel paintings, starting from the mock-up design, detailing then the analytical methods used and concluding with the results obtained and the challenge of their interpretation. After a technical study of the pastel collection, mock-ups were designed and produced to represent the most common 18th-century supports (paper and parchment) and the fixing procedure used by one of the most famous pastellist of that time, Jean-Étienne Liotard (1702-1789). This recipe was used by Monsieur Jurine (1722-1779) and disclosed at the Académie des Sciences in 1753 [1] by Antoine-Joseph Loriot (1716-1782) [2]. It consists of a 0.5% solution of sturgeon glue in water and ethanol, sprayed a few times over the pastel medium. Aged and unaged samples taken from the mock-ups were then analyzed. The results obtained will be used in this poster to expose the benefits and limits of the analytical techniques used: Raman Spectroscopy, FTIR (Fourier Transform Infrared Spectroscopy), SERS (Surface Enhanced Raman Spectroscopy), GC-MS (Gas Chromatography-Mass Spectroscopy), HPLC (High Performance Liquid Chromatography), ELISA (Enzyme-Linked Immunosorbent Assay), SAWN (Surface Acoustic Wave Nebulization). The presentation of both conclusive and inconclusive results will be the opportunity to share with the scientific community the challenges faced today by the researcher teams and to look for new tools to overcome them.

Figure 1. Sampling

Figure 2. Fixative mock-up

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Non destructive chemical analyses of the "Red Marble" from Santa Maria del Fiore Cathedral (Florence, Italy)

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The Cathedral of Santa Maria del Fiore in Florence (XII-XV centuries) plays a fundamental role in the historic architecture of the city; it was decorated by using three stones of the different colour: white marble, red limestones (so-called "red marble") and green serpentine (so-called "green marble"). White and green marbles have been widely studied, whereas not sufficient data are available on the red marbles; different types of this latter have been used as a cladding of the Cathedral, and it is difficult to distinguish them and consequently to obtain information on their provenance. A research carried out at the Archive of the Florence Cathedral, made it possible to know that since the XV century, stones of different provenance were used both for the original decoration and for the following restoration works until today. As a matter of fact, many of these stones come from three geological formations of the Central Apennine: Scaglia Toscana and Rosso Ammonitico (Tuscan Sequence), Scaglia Rossa (Umbrian Sequence). It is easy to differentiate at naked eye the claddings belonging to Rosso Ammonitico showing nodular aspect from those belonging to the groups Scaglia Toscana and Scaglia Rossa which instead show massive appearance. Furthermore, different supply quarries were used for each of the three formations and macroscopically it is not possible to recognize the single quarry of provenance. To this regard the chemical composition and, in particular, the trace element abundances could help in the identification but, due to the architectural and historical importance of the Cathedral, it was not possible to collect samples. Therefore XRF analyses with the portable instrument (model TRACER III SD by Bruker) have been carried out in situ on the red claddings; the traditional XRF technique (model WD-XRF Rigaku Primus II) was, in addition, used to determine the composition of the stones coming from the different quarries sites. The results permitted to obtain a chemical database of the different quarries; these data have been compared with those acquired through the portable X-ray Fluorescence. The comparison permitted to achieve an important result: the different typologies of red marbles can be distinguished through the abundances of some trace elements (e.g. Sr and Ba) which are thus discriminant of the various typologies of red stones.

Preliminary considerations on the technology of manufacture of glass mosaics tesserae of the Rotunda in Thessaloniki, based on *in situ* colour and XRF measurements

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Rotunda is one of the most significant monuments of Thessaloniki, Greece. Its dome mosaics, a magnificent work of art of the Early Byzantine period, has no parallel in quality, but neither in iconographic motifs nor in stylistic traits. This uniqueness explains to a certain extent the various theories developed by scholars devoted to the study of the monument, concerning its interpretation and dating proposed diverging over a timespan of two centuries, from the early fourth to the early sixth century AD [1].

Analytical investigation of the colour and the chemical composition of the glass (in the main) tesserae in the third lower and better preserved zone of the dome decoration, based exclusively on noninvasive methods, has been carried out *in situ*, in November 2015, a few weeks before the monument was liberated from the long standing – required for conservation works [2] – scaffolding, to regain part of its original majesty.

About 80 diffuse reflectance (colour) and X-Ray Fluorescence (XRF) measurements on representative individual tesserae of coloured glass, gold/silver leaf or stone, appearing different in colour to the naked eye, have been carried out in various iconographic details of the mosaic compositions in two, out of the eight, panels of the lower zone of the dome decoration. The measurements have been grouped into distinct areas in the L*a*b* CIE 1976 colour space corresponding to different perceived colours and have been characterized according to their chemical composition, with respect to the technology of manufacture including raw materials, basic glass network oxides, colouring agents and opacifiers. Through this study it was possible to determine the basic technological features of manufacturing and attempt comparative assessments, based on analytical data, published by other research groups, on exhaustively studied mosaics of other early Christian monuments, in Italy [3].

Based on the physicochemical composition, it was possible to group the measurements taken in the wide range of colour shades of the tesserae into diverse categories, the number of which seems concise relatively to the infinite colour and lightness contrasts or gradations obtained and the incomparable wealth of aesthetic plurality and ingenuity of varied visual effects produced. These visual effects, based on the masterstroke juxtaposition of tesserae resulting in distance either the interaction of adjacent contrasting colour areas or the optical colour mixing of individual tesserae, would be further multiplied thanks to the varying natural lighting effects on the multi-faceted compositions of the Rotunda dome [4].

These results have a preliminary character and are considered, as a modest contribution to the study of manufacturing technology of the Rotunda mosaics glass tesserae, to be further discussed and evaluated together with the technical, iconographic and stylistic data obtained through the long uninterrupted studies by many scholars, on this unique mosaics ensemble.

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On-site analysis of Limoges enamels from the 18th c. Research of technological links with painted enamels from Qing Dynasty

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The analysis of the archives, in particular of the Jesuit missions, indicates that both enamelled objects and glassmakers or enamellers were sent during the reign of Louis XIV at the Chinese Court [1]. These exchanges were at the origin of the development of (***cloisonné***) painted enamels, on metal as on porcelain under the reign of Emperor *Kangxi* [1,2]. Also we undertook the joint study of *falangcai* porcelain and ***cloisonné*** painted enamels [3]. A great difficulty in enamelling is the realization of coloured zones well defined, without burrs: the enamel being liquid at the firing temperature and the colouring ions diffusing rapidly, this requires the use of pigments and opacifiers in order to obtain on metal or on porcelain paints similar to oil painting. On the contrary, the colouring by ions gives images similar to the watercolour. The first *falangcai* porcelain would have been made in the imperial workshop of the Forbidden City (*falang* is the name used to designate France at that time)[1-4] and the scarcity and high value of these objects imposes non-invasive analyzes. Raman mobile micro-spectrometry has proved its efficiency [5], particularly for studying both hard and soft porcelain enamels and bodies [6] and for identifying the colouring agents of enamels, particularly from Limoges [7,8]. Limoges productions from the Middle Ages to the 17th century are highly prized and studied, but later productions, those likely to have served as models for Chinese craftsmen, are poorly documented. We present here the first results of the on-site analysis of Limoges enamels from the 17th/18th centuries collection of the Fine Arts Museum (MAD), Paris, and compare their colouring techniques with those of *falangcai* porcelains [4] and to ***cloisonné*** enamel on metal [8,9], in order to be able to discuss the knowhow exchange between France and China.

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Why the cement is not proper to consolidate stone monuments? The case of Tello Obelisk, Lima (Peru)

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Over years, numerous consolidation formulations and procedures have been developed and tested on lithic materials. It was clearly proven that some consolidation protocols applied on stone monuments years ago were not the best ones, jeopardizing the state of conservation of the intervened artwork. An example of this was the use of modern cement to fasten the Tello Obelisk (Lima, Peru) from its base and to repair a fracture visible in its upper part in the year 2010. After some years of this consolidation, the cement used suffered structural problems, since cracks and cement material loss were observable, losing in this way the strengthening action of this cement used as consolidant.

The Tello Obelisk is a prismatic granite monolith (2.52 m high and 0.32 m width) belonging to the archaeological site of Chavin de Huantar in north-central Peru. According to the historic knowledge, this sculpture is probably a *Wanka* or an object of religious cult and belongs to the Early Horizon period (900 B.C to 200 B.C). The surface of the obelisk is covered with carved designs, representing mythic deities whose interpretation is still under discussion today. After its first consolidation, a new one was conducted during 2015 inside the National Museum of Archeology, Anthropology and History of Peru (Lima), were the obelisc is nowadays displayed and preserved. For this last restoration, conducted by experts from the Rietberg Museum of Zürich (Switzerland), only biodegradable materials were used.

This work is focused on the characterization of the cement material used in the 2010 consolidation of the Tello Obelisk. For that purpose, different cement fragments used in its consolidation were analyzed in the laboratory by micro-Raman spectroscopy, X-ray Diffraction (XRD) and X-ray fluorescence spectroscopy (wavelength and energy dispersive) in order to determine its composition, which can be responsible of future problems in such kind of stone monoliths. After the analysis of different salts crystallized on the internal part of the cement, different types of sulfates such as gypsum ($CaSO_4·2H_2O$), anhydrite ($CaSO_4$), starkeyite ($MgSO_4·4H_2O$), epsomite ($MgSO_4·7H_2O$), thenardite ($NaSO_4$), etc. were identified. These kinds of salts can migrate to the porous structure of the stone and cause later problems. Apart from the single point analyses, imaging studies were conducted using micro-Raman spectroscopy and micro energy dispersive X-ray fluorescence spectrometry on a cross section sample, to determine the distribution of the main components of the cement material.

Chemical Composition of the Ancient Silk Road glasses determined by Portable XRF

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It is known that glass artifacts and glass-making technology had spread over Eurasia through the Silk Road. As a result, many ancient glasses were imported to Japan from 2nd c B.C. to 12th c A.D. from all over Eurasia. We have been investigating the glasses imported from Eurasia to Japan to characterize and classify origin and distribution of the glass in ancient Japan [1]. The final goal of this study is to reveal how the ancient glasses excavated from Japan were imported. A large number of ancient glasses in South Asia, Southeast Asia, Central Asia and Siberia were analyzed using portable XRF. This study is still in progress and we report some of the results.

OURSTEX 100FA portable energy dispersive XRF spectrometer designed by our laboratory equipped with Pd X-ray tube and SDD detector with polymer window was brought to museums of each country and used for the analyses of glass. Quantitative analysis was done by two modes (monochromatic X-ray mode: 40 kV 1.0 mA, white X-ray mode: 40 kV 0.25 mA) for 200s (live time). The spectrometer is approximately 17 kg in weight. The glass chemical compositions were determined by calibration curve method and expressed as oxide weight percent (wt%). We will discuss the chemical compositions of the ancient glasses based on the analysis of 850 glass samples excavated from South Asia (India), Southeast Asia (Cambodia, Laos and Vietnam), and Central Asia (Kyrgyz and Tajikistan).

The chemical compositions of glass from these countries were classified into three types from their major components: i.e., soda lime silica glass (Na_2O-CaO-SiO_2), potash silica glass (K_2O-SiO_2) and high alumina soda lime silica glass (Na_2O-Al_2O_3-CaO-SiO_2). The glasses were then classified into sub-groups based on their minor components. The results revealed the compositional features of ancient glasses excavated from each region. In South and Southeast Asia, potash silica glass and high alumina soda lime silica glass had been used for a long time (8th c B.C 17th c A.D.). Especially, as previously reported [3], the results show that the number of high alumina soda lime silica glasses is largest in the glass samples excavated from this region. We analyzed many glass beads which have various chemical compositions distributed in this region. In Central Asia, there are few previous analytical studies of ancient glass. It is found that the number of soda lime silica glasses is largest among the glass samples excavated from this region. Next, we focused on the cobalt colorant in ancient blue glasses based on MnO vs. CoO plot and CuO vs. CoO plot. The results show that these colorants have different chemical compositions by glass types. Similarly, the ancient blue glasses containing copper as the colorant were also characterized based on SnO_2 vs. CuO plot and PbO vs. CuO plot. The present study revealed that the ratio of three glass types is different among South and Southeast Asia and Central Asia and the chemical compositions of the colorants are different among three glass types. We have successfully revealed the chemical characteristics of ancient glasses excavated from Asian regions based on on-site non-destructive XRF.

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X-ray computed microtomography of Late Copper Age decorated bowls with cross-shaped foots from central Slovenia and the Trieste Karst (north-eastern Italy): a provenance and production technology study

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The Deschmann's pile dwellings, located in the Ljubljansko barje (central Slovenia), are one of the main 3rd millennium BC sites in the south-eastern Alpine region. The well preserved ceramic finds have been included in various typo-chronological analyses to define the cultural development in this area during the Late Copper and Early Bronze Ages. In the Deschmann's pile dwellings two main phases have been identified. The oldest one is characterised by pottery typical of the Late Copper Age Vuedol culture, widespread from the Balkans to south-eastern Central Europe; the second phase is defined by finds of the so-called Ljubljana culture and Somogyvár-Vinkovci culture. Most of the 3rd millennium BC pile dwellings of Ljubljansko barje is associated to the latter. The Ljubljana culture is mostly attested in the Deschmann's pile dwellings and also in many caves of the Trieste Karst and eastern Adriatic coast [1].

From central Slovenia and the Trieste Karst - the two areas investigated in this contribution - decorated bowls with cross-shaped foots are reported. This type of vessel is a typical form of the Vuedol culture. In the Deschmann's pile dwellings, where this type is abundant, several variants are known, while in Trieste Karst only a few bowls were discovered. Despite the small number, the latter are heterogeneous in terms of shape and decoration.

A selection of these bowls from both areas have been studied to define their production technology and possible origin. All samples have been characterized by X-ray computed microtomography (μCT) at the Multidisciplinary Laboratory of the "Abdus Salam" International Centre for Theoretical Physics of Trieste, Italy [2], using variable parameters and recording 1440/1800 projections over 360°.

The preliminary results show similar constructive techniques of the vessels, generally characterized by quite homogeneous lithic-tempered pastes (clay\lithic inclusions ratio: from about 10 to 50) with the exception of a few finds, whose technological parameters probably suggest a completely different origin.

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SEM and Micro-XRF analysis to investigate stained glass windows

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Several restoration projects of stained-glass windows have been performed in Poland since 2010. The aim of the projects was to protect stained-glass windows against environmental impact of industrial pollutants and acid rain by installing a protective glazing[1]. Chemical analysis of glass samples was performed with SEM/EDX on a FEI ESEM-XL 30, (EDX-EDAX) and with Micro-XRF (M4 Tornado, Bruker). The EDX analysis was carried out within the high vacuum setting of the microscope, for which samples needed to be prepared by grinding and polishing and to be coated with carbon. The images of the cross section of the glass samples were acquired in the high vacuum mode, but it is also possible to use the low-vacuum mode (purging with water vapor in the sample chamber). The chemical composition of medieval glass samples and of glass samples of the 19th Century have been determined. Within this method it was possible to determine the concentration of glass ingredients higher 0.5 wt. %. Corrosion products and the gel layers of the corroded medieval glass samples can be seen within the cross section images. EDX analysis is indicating the distribution of elements within the cross section. The gel layer underneath the glass surface is wider than 20 m and is covered with micro cracks. Within these cracks a high concentration of Barium (Ba) was found. Further information on the glass' composition has been determined by Micro-XRF-analysis. This technique combines the low detection limits down to the ppm level for most elements with atomic number higher than Ca with the spatial resolution of ~ 20 µm given by the polycapillary optic. For this study a M4 TORNADO (Bruker) was used to determine the contribution of trace elements and their distribution. A sample preparation was not necessary. This approach allows for quick and easy distinguishing of different types of glass by their composition as well as their color giving elements (Co, Cu) in the glass. Micro-XRF scanning proved a valuable tool for the non-invasive study of glass samples.

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Ceramic glazes from Gaudi's Modernism Architecture:
Non-destructive study of tiles from Casa Vicens

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Antoni Gaudí was an architect from Catalonia, Spain, who belonged to the Modernist (Art Nouveau) movement and was famous for his unique style and highly individualistic designs. Gaudi is the author of many of the most famous and representative buildings of Barcelona architectural landscape, such as the Sagrada Familia basilique, the Park Guell, Guell Palace, Casa Milá and Casa Batlló.

Gaudí obtained the title of architect in 1878 and one year later Gaudí's name first appeared on the books of the Pujol&Bausis ceramic factory which mention a shade of special yellow color called "Gaudí". All of Gaudí's works display a notable wealth of ceramic decoration, well represented in one of its first work: Casa Vicens, built between 1883 and 1888. Casa Vicens suffered several architectural modifications around 1925 and also some restoration ending the 1990's. In each of these modifications some of the tiles were replaced with new identical colour but different manufacturing process.

The aim of the present work is focused on identifying the composition of the body ceramic pieces and the characterization the glazes, approaching to their production techniques and the process they were decorated. The complete characterization of the materials used in Cultural Heritage monuments is a crucial step, enabling to make decisions about restoration and preventive conservation methods. We mainly used non-invasive instrumentation, such as "in-situ" and laboratory Energy dispersive X-ray fluorescence, X-ray diffraction, SEM/EDX and optical microscopy.

X-ray diffraction of the ceramic bodies reveals an increasing content of feldspar in the newest tiles with a lowering in gehlenite content. Mineral assemblages suggest an improvement of firing conditions along time. Design of glazes consists in leaves and flowers drawings, then white, green and yellow-orange colours are predominant. Optical and SEM microscopic observations allow concluding the presence of a two layers glaze structure: a) base white enamel and b) an upper colored layer. The total thickness of layers is 100 to 500 microns. Original glazes from Casa Vicens (dated 1880's) and those from 1920's restoration are based on lead and tin enamel (white). Green colour is obtained by the presence of zinc, cobalt and chromium in different proportions and yellow is based on antimony addition. Tiles from 1990's are based on white zirconium-titanium enamel, chromium cobalt green glaze and the yellow colour is produced by the presence of Pb-yellow and minor antimony content.

A non-destructive protocol for the evaluation of dual wavelength Nd:YAG laser cleaning of gypsum black crusts on granite

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This study refers to a multi-analytical approach for the evaluation of laser removal of gypsum black crusts from granite and specifically to the development of a non-destructive monitoring protocol to ensure their complete removal. The methodology aims at establishing guidelines for reliable non-invasive multispectral control of the laser ablation process with emphasis to the assessment of any crust remains and/or potential damage on the surface.

Gypsum black crust in one of the most severe deterioration forms affected to cultural built heritage worldwide. As was reported by carbonate stones but scarcer studied, thick black crusts have been also found in granitic surfaces[1]. Therefore, the cleaning of these alteration forms is being remarkably studied nowadays. Also, it is important to highlight that in the granitic stones the aim is to extract the whole overlayer (carbonaceous pollution particles and the neo-formatted gypsum matrix layer) without leaving any remains or induce any damage. In this sense, more complex cleaning strategies should be employed. Laser cleaning with a single wavelength was already evaluated to extract black crust on granite[2], but the results were not satisfactory and thus further laser cleaning methodologies were investigated. Based on the encouraging results that have been reported for the combination of different wavelengths in the cleaning of black crust on marble[3], the simultaneous use of 1064 nm and 355 nm laser beams was investigated for the complete removal of gypsum black crust on fine grain-size granite.

For the purposes of this study, multispectral data from the laser irradiated surfaces (in various parameters and to different extends) have been studied in comparison to the reflectance values registered for the granitic surface without any kind of crust. Thus the cut-off conditions that will establish a total encrustation removal[4] or will denote any damage were determined. The remains and the possible damages on the substrate were also evaluated by means of optical and electronic microscopy, Fourier transform infrared spectroscopy and Raman spectroscopy.

Acknowledgements: This work was partially supported by the BIA2014-54186-R project. J.S.P.A. was supported by a postdoctoral contract within the framework of the I2C Galicia Plan for 2014.

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On-line photoacoustic monitoring of laser cleaning on stone: Effectiveness evaluation and induced microdamage detection

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Photoacoustic effect is the generation of acoustic waves following the absorption of intensity-modulated optical radiation in a material, typically emitted by pulsed lasers, and has been recently introduced as a non-destructive monitoring process in laser-assisted removal of unwanted layers with encouraging results[1]. The aim of this paper is to evaluate the suitability of photoacoustic technique for monitoring laser cleaning in terms of material removal in Cultural Heritage (CH). Emphasis is put on the determination of the substrate's damage threshold upon intentional overcleaning conditions.

Laser assisted removal of unwanted overlayers from CH surfaces has gained a wide acceptance during the last decades, since it has been proven to be effective, residue-free, whereas it also provides the possibility of process automatization[2]. However, in real practice, it is often difficult to control the cleaning in terms of overlayer extraction, as well as, microdamage induction on the substrate, i.e. melting and damage. In this direction, several spectral techniques have been applied[3,4] to evaluate non-invasively the material removal. On the other hand, the non-invasive, *in situ* evaluation of the substrate damage has not been deeply studied, and in most cases, it requires to collect samples and proceed with multianalytical evaluation tools. In this context, the exploitation of the intrinsic photoacoustic signals generated upon pulsed laser ablation of materials is expected to enhance the non-destructive diagnosis and monitoring of laser cleaning interventions.

To investigate this possibility, a simple and straightforward case application of laser cleaning has been considered; namely the removal of black graffiti from medium coarse white marble. A Q-switched Nd:YAG laser (=1064 nm, 8ns FWHM) was employed for irradiating the sample at several fluence values ranging from 0.6 to 3.5 $\mathrm{J\ cm^{-2}}$. The photoacoustic detection setup employed a 5 MHz ultrasonic transducer, a RF amplifier and an oscilloscope, which was used for the recording of the generated photoacoustic wave. In order to validate the results provided by the proposed approach, state of the art techniques were additionally applied. Graffiti extraction was evaluated by means of stereo and electron microscopy, as well as, hyperspectral imaging. The respective substrate micro-damage assessment was done through electron and confocal microscopy.

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ToF-SIMS study of pentacyclic triterpenic acids and birch bark pitch

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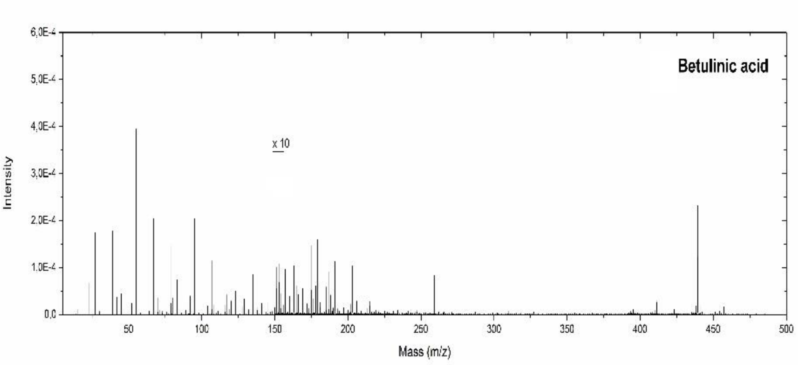
Birch bark pitch was used as adhesive since Neanderthal times. The production of this kind of glue was done by a controlled heating of white birch bark; the dark and odorous substance obtained from this process was used in the production of common and hunting objects [1]. From a chemical point of view, this natural resin is mostly constituted by volatile and non-volatile terpenoid compounds. In particular, pentacyclic triterpenoids with lupane skeleton are recognized to be markers of the birch bark pitch [2].

In this work, we have coupled Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) technique and Multivariate Statistics in order to identify characteristic fragment ions coming from the ion bombardment process of lupenone, lupeol, betulin and betulinic acid. This analytical approach has proven to be successful in the identification of characteristic fragment ions and discrimination of very similar mass spectra [3, 4]. At the same time, Finnish and Italian outer white birch bark pitches have been characterized by ToF-SIMS. All analytical results have been treated with PCA analysis to evaluate similarities and differences in terms of geographical origin and pitch sample preparation method. Finally, a real sample of pitch from an ancient sickle has been studied by comparison of ToF-SIMS with FTIR data.



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Metal Nanoinks as Chemically Stable Surface Enhanced Scattering (SERS) Probes for Analysis of Blue BIC Ballpoint Pens

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The elucidation of ink composition in commercial ballpoint pens has been the object of forensic investigation for many years. However, recently this field of research has become increasingly relevant also for art conservation applications. Since their wide spread introduction in the market in 1945, ballpoint pens have been used as a versatile medium for artistic productions which are nowadays found in many museum collections all over the world. Unfortunately, inks suffer fast color fading when exposed to light and the proper conservation of ink-based artworks requires the development of novel active conservation and long-term preservation solutions. In this context, the identification of ink formulations is of paramount importance for the establishment of artwork's dating and originality as well as for the elucidation of the photo-degradation mechanisms causing color fading.

In this paper we report on the use of chemically stable metal nanoinks for SERS analysis of a blue BIC ballpoint pen. Metal nanoinks were constituted by Ag nanospheres and Au nanorods and were used in combination with Thin Layer Chromatography (TLC) to identify the dye components in the pen. While normal Raman conditions required the use of two laser wavelengths to obtain spectra of all separated spots on the TLC, SERS illumination at either 514 nm or 785 nm was successful in obtaining enhanced spectra for all separated spots. High intensity and good signal-to-noise SERS spectra were obtained, due to the matching of the laser illumination with the plasmon resonance of the used nanoinks. In addition, the contribution of molecular resonance, electromagnetic and chemical effects were evaluated by further SERS analysis carried out in non-plasmonic resonant conditions. Enhancement Factors (EFs) between 5×10^3 and 3×10^6 were obtained for the separated spots, allowing identification of phthalocyanine Blue 38 and triarylene crystal violet (CV) in the pen ink mixture. In contrast with what reported in literature, both nanoinks gave stable SERS signals for days after deposition and did not necessitate the use of additional aggregating or charge-adjustment agents.

Byzantine glass bracelets from the Lower Danube

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Twenty three glass bracelets fragments of different colors and appearances discovered at Pcuiul lui Soare, Dobrogea, Romania and dated to the 10th-11th centuries AD were analyzed for their chemical composition using Particle-Induced X-ray Emission (PIXE) and Particle-Induced Gamma-ray Emission (PIGE) techniques at AGLAE accelerator of Centre de Recherche et de Restauration des Musées de France (C2RMF), Paris.

The historical hypothesis that triggered this study was to check if these finery items were imports - i.e. products of imperial workshops located in Constantinople - or resulted through the manufacturing procedures in local glass workshops.

The measurements led to the determination of the bulk composition of the glass fragments; thus, clues about the employed glass-making recipes and raw materials were obtained. Additionally, the compositional data provided information about glass chromophores, as well as hints about the pigments used to decorate the external surface of some of these archaeological artifacts.

The analytical data indicated that the bracelets were soda-lime-silica glass of intermediate recipes, with compositional patterns situated between the natron and plant ash ranges. This, in turn, suggested extensive glass recycling procedures, most likely practiced in local workshops that had access to vitreous artefacts of different compositions.

As concerning the glass color, it turned out that the blue color was correlated with the presence of small amounts of cobalt, while the green color was linked with high concentrations of iron and/or copper.

For the painted glass bracelets, the most likely candidate for the yellow pigment decorating the outer surfaces was lead tin yellow, while lead white seems to be responsible for the white hues.

The experimental data on Pcuiul lui Soare samples were compared to the ones previously obtained on coeval bracelet fragments excavated in the neighboring Byzantine archaeological sites from Nufăru [1] and Isaccea [2]. The comparison worked up to a certain point, the conclusion being that recycling was the major mechanism characterizing the glass manufacture during the Byzantine period in the Lower Danube region; most likely, this is also the main explanation for the production of such an outstanding number of colored glass bracelets in that period [3].

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Multidisciplinary approach on prehistoric pottery from South East Romania

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Local production or import? This is a long debate among the archaeologists that, in the case of the Eneolithic tell settlement of Sultana-Malu Rou [1] from South-East Romania, we tried to address through a series of physico-chemical studies. To reach this goal, we analyzed several shards from two dwellings, as well as clay samples from around the settlement. In order to obtain mineralogical and chemical information about our samples, we performed petrographic analyses on thin sections and chemical analyses using X-ray fluorescence and X-ray diffraction. The sampling covered the whole spectrum of vessels, from fine to coarse ware, painted and unpainted etc. The main goal of this presentation is to explore the connection between the pottery from Sultana-Malu Roşu tell settlement and the nearby clay sources, in order to prove the local origin of the analyzed pottery. Unfortunately, we have no other similar studies of KGK VI pottery or clay sources, studies that might had helped us to get comparison terms and identify possible imports/exchange networks. Most of the previous researches used similar technological approaches and explored Cucuteni pottery, but they have mostly dealt with mineral pigments [2-4].

All these analyses helped us identify the procedures used by the prehistoric potters to make their vessels. We used similar recipes in our experimental workshops when we tried to replicate prehistoric vessels. In this way we recorded how pots behave through all stages of manufacture, from modeling to firing [5].

The investigation process of both prehistoric and experimental pottery was complemented by imaging analyses using X-ray radiography and X-ray computed tomography, in a trial of getting a better picture of the *chaîne opératoire* for pottery production.

Alongside with the development of a strong reference database for Gumelnia pottery, another important achievement of this study is that we have proved that the ceramic vessels from Sultana-Malu Roşu were made using local clays.

Acknowledgements: This work was supported by a grant of the Romanian National Authority for Scientific Research, CNCS – UEFISCDI, project number PN-III-P2-2.1-PED-2016-0742.

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Green Thessalian Stone: The Roman and Byzantine ornamental material characterization

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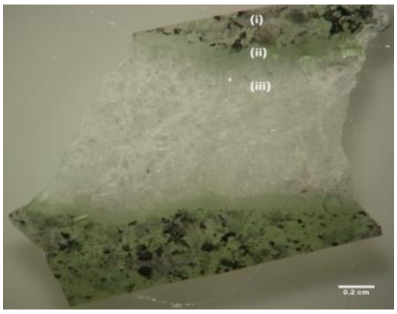
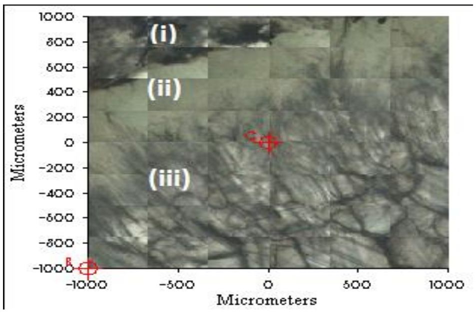
Green Thessalian stone, known also as 'verde antico' in the recent times, is an ophicalcite, a brecciated rock comprising an inhomogeneous material that consists of mixtures of serpentine (mainly antigorite with minor lizardite and chrysotile) and calcite [1]. This rock was formed under complicated tectonic, hydrothermal and sedimentary processes at the bottom of the Tethyan ocean during Jurassic period. It is a hard, resistant material containing fragments of various dimensions with contrast colors: white (calcite) and light to dark green (serpentine) (Fig. a). The calcite fragments are surrounded by an emerald green colored rim, up to 1cm wide, demonstrating a reaction process during its formation [1]. Green Thessalian stone was used for decorative purposes in Imperial Rome and Byzantium and also during Renaissance until recent times [2]. It was a proper material for pillars, column shafts, sarcophagi, tubs, ambones, iconostasis, facing slabs and baptismal fonts. The quarries that provided the stone are found at the Chasanbali hill, in Larisa area, central Greece. [1,2]. Monuments of this grandiose material can be found in places from Syria to Britain, from Tunisia to Germany and especially in Rome and Constantinople[1].

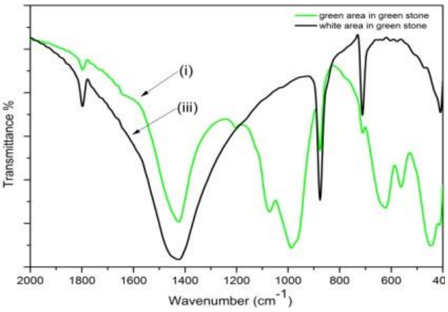
Polished-thin sections of the rock samples were studied mineralogically and chemically by FTIR microscopy. In serpentine spectra, the characteristic bands of the group were identified and the different polytypes of the crystal were distinguished (Fig. c). Comparison of the spectra clearly showed that calcite bands existed even in the spectra of dark green specimens. Aim of this study is to describe the thermodynamic processes that took place during the rock formation and led to this brecciated structure. A unique aureole is revealed at the reaction zones (Fig. b) and the kinetics, mechanisms and conditions under which it occurred are to be discussed. Gibbs description of this heterogeneous system and projections of this material are to be presented.



a. Section of the studied rock:(i) ophicalcite breccia, (ii) reaction rim, (iii) calcite



b. FTIR microscopy photo: (i) ophicalcite breccia, (ii) reaction rim, (iii) calcite



c. FTIR spectra:
(i) ophicalcite breccias, (iii) calcite

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Single-point and imaging procedures to analyze non-destructively the decorative glazes on ceramics from **Punta Begoña Galleries**

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The Galleries of Punta Begoña, located in Getxo (Basque Country, Spain), and erected in 1918 are a construction of high patrimonial interest. One of their main characteristics resides in the decorative coatings, formed by a great surface of tiles, which was created by the technique of "basin or edge". These are ceramics with polychromatic decorations including, tiles, slabs, panels and baseboards among others.

In this work a non-invasive multianalytical approach has been applied to analyze the composition of the ceramic glazes, including the pigments that give the final colors (e.g. white, honey, blue, green and black) to these decorative coatings. For the molecular analysis, infrared spectroscopy and micro-Raman spectroscopy (single-point and imaging analyses) were used, whereas for the elemental analysis scanning electron microscopy coupled to electron dispersive X-ray spectroscopy (SEM-EDS) was applied. Furthermore, the single-point analyses and the elements distribution images acquired by EDS were compared to the ones obtained by micro energy dispersive X-ray fluorescence spectrometry at 20 µm spot size.

The obtained results have revealed the use of elements such as manganese, iron and cobalt associated with black color. This last element was also associated with blue color (see Figure 1). In addition, the use of iron in form of magnetite has been identified to obtain the honey color, as well as tin for the white opaque glaze, along with cassiterite and quartz. Tin was also identified in the blue decorations from the glaze and lead in all the glaze areas (see Figure 1).

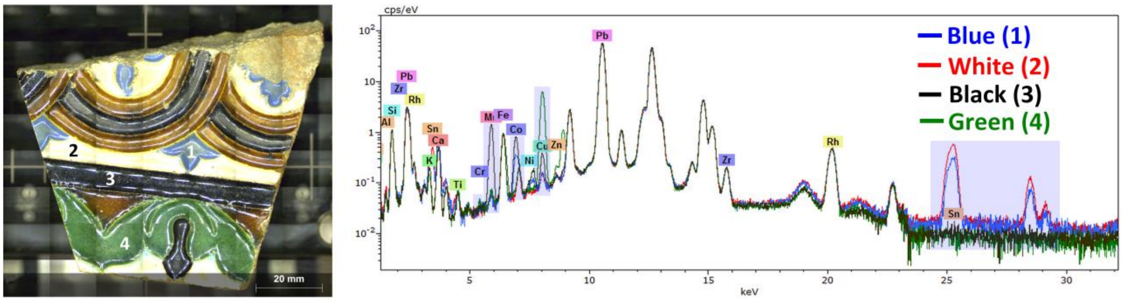

Figure 1. A ceramic fragment from Punta Begoña Galleries showing all the colors used in the decorative glaze (left) and representative energy dispersive X-ray fluorescence spectra obtained from each color (right).

Colorimetric analysis of Balearic medieval stone polychromy through Digital Image Analysis

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Five examples of Gothic sculpture in polychrome stone have been studied with different techniques. Digital image analysis (DIA) was used to guide a correct selection of sampling points and their colorimetric characterization.

Although there are few documentary evidence of the specific techniques and activities of the painter who polychrome stone in the Balearic Islands, there are numerous works that attest it. Five examples of this typology, dating from the late 14th to the early 15th centuries, have been analyzed.

The most common support is a local variety of sedimentary stone known as *Piedra de Santanyí*. In many cases, the small amount of polychromy present in these works is conserved only inside the pores of the support. The organoleptic examination of the samples have been complemented with DIA processed photography. This technique is based on the use of image processing software, which allows us to modify the lighting, contrast and saturation values. Thereby, DIA reveal the traces of conserved polychromy, characterizing its colour and guide the sampling process. In many cases, pigment colors assessed by this methodology coincide with the colors identified by laboratory techniques. The samples haven been also characterized by optical microscopy, scanning electron microscopy (SEM-EDX) and the study of organic binders.

DIA has been able to show the existence of hidden valuable polychromy which merits recognition and protection.

Transparency of blue paint layers probed by OCT

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The quest for the non-invasive analyses is a key issue in the diagnostics of cultural heritage. Since about 15 years, Optical Coherence Tomography (OCT) has been applied to study different processes, including the cleaning, and materials related to cultural heritage.[1,2] The method provides a virtual cross-section of analysed object, with depth resolution increasing proportionally with the width of the excitation source and diminishing with the increasing wavelength. The information about the physical make-up of the examined artefact can be obtained, provided the semi/transparency of probed layers, which generally improves with the wavelenght. Most of the varnishes are detectable by OCTs using infrared light whereas the pigments' transparency may be limited. [3,4]

Contemporary art is particularly delicate because the synthetic materials used for their realization are of poorer quality and durability than the traditional materials. It follows that the contemporary artworks often require imminent restorations: for this reason, the materials require in-depth analytical studies. The non-invasiveness of the analytical methods is another key issue in the diagnostics of contemporary art because it minimizes the need of sampling.

In this respect, we have studied the optical and chemical properties of contemporary blue paint materials in comparison to the traditional ones. Our goal was to examine the OCT potential to probe the internal structure of the commercial acrylic paint layers, as a function of their thickness. In support of these measurements, micro-profilometry, an interferometric technique with micrometric resolution, has been used to measure the paint layer thicknesses. Fiber-optic reflectance spectroscopy and multispectral infrared imaging were employed to obtain spectral information of the probed layers and to compare the visibility of the underdrawings.

Liang et al. has already pushed the OCT applicability towards new frontiers by visualising the underdrawing layers in paintings.[3] Here, we show proof of this concept both on the specimens and on *Madonna dei Fusi* painting.

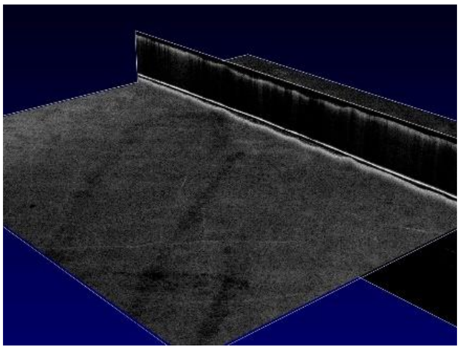

Figure 1. OCT 3D volumetric measurement on a real painting: the black lines of the underdrawing are evident in x-y plane.

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Islamic polychromatic glazed pottery technology in South Western Iberia: the case of the town port of **Mértola** (Portugal)

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This study presents the results of a multi-analytical research program on Islamic polychromatic glazed ceramics developed by Hercules Laboratory in collaboration with the "Campo Arqueológico de Mértola". It provides the analysis of several fragments of "*Green and Manganese*" glazed ceramics recovered in different areas of the old Islamic fortified Mértola town (Alcaçova), inside the old Islamic castle, as well as seven kiln rods (partially glazed) and one sample of white painted ceramic recovered within two different archaeological contexts. Green and manganese glazed decorated ceramic is known to be prepared using Ca rich clays. The ceramic body, fired or unfired, is subsequently covered by a silicon-lead based white glaze on both sides opacified with tin oxide (or not). The decorative motif is then outlined using a black glaze and completed with a green glaze. Nevertheless, different technical solutions have been documented [1-2].

Glazed decorated ceramics have been classified as bowls and jugs, with zoomorphic, epigraphic, naturalist or geometric glazed decorations, and they are chronologically dated between the second half of the 10th century and the end of the 12th century. The final goal of the study is to understand glazed pottery characteristic, its production and its dissemination in Mértola (Portugal), an important river port located in the river Guadiana at 60 km from the Atlantic coast.

Ceramic samples have been analyzed using non and partially destructive analytical techniques including portable XRF spectrometry, mineralogical analysis by XRD and FT-IR spectroscopy, petrography, microstructural analysis by SEM-EDS of the ceramic body and of the glazed decoration and by ICP-MS spectrometry of the ceramic paste. Results are giving important clues on glazed ceramic pottery technology and its distribution in South Western Iberian during Islamic times.

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Method development for the detection of indoor sources of styrene in museums

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The conservation of highly degraded wood artefacts by gamma irradiation is a technique with perspective of increased usage, implying the impregnation of the wood with a standard unsaturated polyester resin and styrene, in liquid state, which are then crossedlinked *in-situ* by gamma irradiation. Furthermore, the disinfection of artefacts is done based on the biocide effect of gamma irradiation, with the application of a dose that does not affect the physical-chemical properties of the material. The impregnation consists in the insertion into the pores of the deteriorated artefact of unsaturated polyester oligomers dissolved in styrene. In the presence of gamma radiation, the free radicals from the styrene molecules will interact with the free radicals on polyester, creating styrene bridges between the linear polyester oligomers, the result of this radiation-curing being the formation of a three-dimensional macromolecular structure that fills the pores, ensuring enhanced toughness to the artefact.

Latterly, styrene's toxicity to humans was progressively questioned both in the USA and in Europe. The objective of this study was to develop a TD-GC-FID method to determine the level of residual styrene from artefacts consolidated by radiopolymerization, to determine the optimum irradiation conditions and the minimum absorbed dose for a complete radiopolimeryzation. The sampling and the concentration were performed using a Unity thermal desorption injector, produced by Markes International Ltd. UK, the separation was made utilizing a gas chromatograph GC 6890N, made by Agilent Technologies USA and the styrene detection was made with the flame ionization detector.

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Spectroscopic analysis of white pigments and substrata of prehistoric paintings of Prado del Navazo rock-shelter (**Albarracín,** Spain)

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The application of non-destructive multianalytical techniques is necessary for the elemental and molecular characterization of the components of prehistoric paintings. Relevant information about alteration processes, biochemical and geochemical changes is obtained as well by means of these techniques. In the last years, several *in situ* analytical techniques like Raman spectroscopy (RS) and energy dispersive X Ray fluorescence (ED-XRF) have been extensively tested in open-air rock art sites with prehistoric paintings included in Rock Art of the Mediterranean Basin of the Iberian Peninsula [1,2,3], minimizing this way sampling and associated damages to rock art. The results have demonstrated their utility for rock art studies.

One of the aims of our projects was the characterization of white pigments used in Levantine art of the Iberian Peninsula. White paint was used in some sites but most of the examples are concentrated in Albarracín (Teruel) district, so it is relevant characterizing them to produce archaeological hypotheses that explain the specific use of this colour. Several rock art sites were analyzed with the indicated techniques, but the more significant results were achieved at Prado del Navazo rock shelter. Several large size bulls, other animals and some archers are preserved in this rock art site, and most of them were painted in white. This is one of the best examples of Levantine art in Albarracín district.

In situ preliminary analyses using a hand-held energy dispersive X-ray fluorescence spectrometer (HH-ED-XRF) and RS were applied on this panel. The surface elemental composition was identified, but it was not possible the molecular characterization of white pigment for the intense energy of fluorescence and an oxalate layer on the panel. The *in situ* analytical campaign was complemented with some analyses in the laboratory by micro-RS (m-RS), Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Analysis (EDX) and X-ray diffraction (XRD) on micro samples with substrata and white pigments. Most of the pigments in the color range from white to grey were found to consist of quartz, gypsum, dolomite, calcite or whewellite (a hydrated calcium oxalate).

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Raman Spectroscopy and X-Ray Fluorescence as a restoration tool in the removal of whitish crusts in ceramics of the 20th century (**Punta Begoña**, Getxo)

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The galleries of Punta Begoña (Getxo, Spain) were built in the beginning of the 20th century object of an intense project of renovation of the area. This building is rich in several artistic representations, being ceramics the most common ones, which cover great part of the galleries. However, these ceramics present a very high degree of degradation. In this sense, the whitish crusts have special interest since their origin is unknown and because of their capacity of hide (even totally) the ceramics.

In the field of classic restoration it is very common to use the technique of "trial and error" using different cleaning products to recover an artifact. However, this procedure can have serious consequences with the piece to be restored and, also, a high economic and personal cost because of the use of unnecessary harmful substances. In contrast, the use of analytical techniques helps restorers to understand the decaying processes and the original materials and therefore, to select the best restoration process. In this way it is possible to carry out in-situ analysis, without sampling and avoiding the "trial and error" methodologies, even without the requirement of future actions. Thus, analytical techniques help to make restoration faster, more efficient, economical and safer for both the artifacts and restorers.

In this work, in-situ Raman spectroscopy and portable X-ray fluorescence were used to identify the nature of the white crusts observed in the Punta Begoña ceramics before selecting the appropriate restoration procedure avoiding unnecessary damage to the ceramic pieces. For that purpose a portable innoRam spectrometer from B&WTEK^{INC} (USA), providing a 785 nm excitation laser and a hand-held energy dispersive X-ray fluorescence (HH-EDXRF) spectrometer X-MET5100 (Oxford Instruments, UK) equipped with a rhodium anode X-ray tube (operating at 45 kV).

Thanks to these analyses different types of white crusts were identified. First, crusts produced by marine aerosol and constituted by NaCl, were identified by HH-EDXRF. This crust was successfully removed by aqueous solvents. The second type of crust was clearly identified by Raman spectroscopy, as calcium carbonate ($CaCO_3$), presumably from the leaching of adjacent materials such as mortars and concretes. Moreover, hydrated calcium sulfate ($CaSO_4 \cdot 2H_2O$) was also identified as secondary compound due to the atmospheric acid attack (SO_2) to the calcium carbonate. For this type of crust a moderately acid aqueous mixture was selected to the restoration of the ceramics. Anyway, it was suggested the analysis of the construction materials to stop the formation of the crust and therefore, avoid future actions.

Thus, thanks to the use of analytical techniques as a restoration tool, crusts were eliminated choosing the best chemical products from the beginning and understanding the processes of formation, to act on the origin, avoiding subsequent restorations.

Pigments and colouration in the 18th century Chinese court paintings of Giuseppe Castiglione (1688-1766)

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Ming and Qing Dynasties, especially from Kangxi's reign (1662-1722), saw the arrival to China of many missionaries and, with them, a number of elements and materials of Western crafts and arts. Among such imports, the enamel and painting pigments used inside and outside the court have been a subject of academic interest and discussion. As the use of a new material or new pigment may bring a new look to artwork, a study into the relationship between colouration and pigments of an artwork may lead to a better understanding of changes in the aspect of artistic styles. Despite a number of previous studies on the application of such pigments with literature researches, mainly through the Crafts Archives of the imperial workshops, further conclusion has been difficult to reach without physical examination of actual examples.

Giuseppe Castiglione (1688-1766), a.k.a. Lang Shining, was an Italian missionary born in Milan. He arrived in China in 1715 during Kangxi's reign in Qing dynasty and served as court painter for Kangxi, Yongzheng and Qianlong in the next 51 years. Castiglione was a key person in eastern transition of western painting in Qing dynasty. In addition to Western perspective and shadowing techniques, Castiglione also adopted a different colouration from that of traditional Chinese paintings. The impact of pigments is a subject that can not be ignored in a study related to the eastern transition of western painting and the Sino-Western cultural exchanges. What exactly are the differences between his usage of pigment and that of traditional Chinese paintings? Having studied Western painting in his early years, Castiglione was certainly fairly familiar with materials used in Western painting since seventeenth century. Did he apply pigments imported from the West to his court works? What were the colouration techniques for creating his proper Chinese paintings? To answer these questions, it is essential to scientifically analyse the pigments actually used in his paintings.

In order to identify the pigments applied in Castiglione's works and to apprehend his colouration techniques, in this study, several non-destructive analytical techniques, including multi-spectral imaging, XRF and Micro-Raman spectroscopy, etc., are employed to investigate a number of Castiglione's paintings.

Mastic incrustations: a study of the medieval sculptures of the San Nicola Church in Bari (Italy)

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Mastic incrustation sculpture can be found from the XI century onwards in various important churches such as San Marco in Venice. It was used to decorate different types of objects by filling the marble incisions with an impasto containing *cocciopesto*, molten glass or lithoid fragments, and was employed both in Byzantine and Occidental areas [1].

The decorations in the presbytery of the San Nicola church of Bari date back to the governance of the Benedictine Abbot Eustazio (1105-1123) [2]. The marble panels (Fig. 1), as well as the famous pulpit probably commissioned by the Abbot Elia (1098), are decorated with the mastic incrustations technique in different shades ranging from reddish brown to dark green or grey.

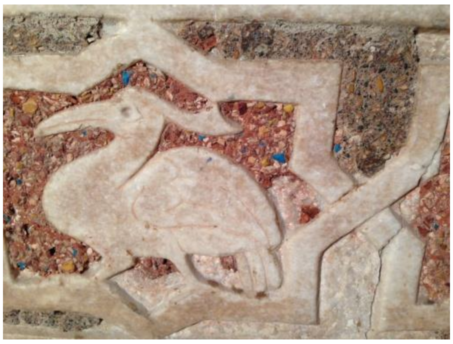

Figure 1. Marble panel with mastic incrustations – Presbytery, San Nicola Church (Bari, Italy)

Although their widespread use and conservation problems, the composition and technique of the mastic incrustations have never been thoroughly studied. Here we present the results of the examination of several samples taken from the rises of the steps and bench in the presbytery as well as from the pulpit. The matrix was analysed with Fourier Transform infrared spectroscopy and pyrolysis gas chromatography mass spectrometry. Organic binders could be found and, in particular, the occurrence of *Pinaceae* resin that had most likely been submitted to heating was assessed. The clasts among which different types of lithoid fragments were also characterised with optical microscopy and scanning electron microscopy.

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Trace element and isotopic analysis for the study of marble provenance

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Trace elements are commonly used for fingerprinting of ancient copper, coins, silver circulation, among others applications for culture heritage [1,2]. In this work, trace elements quantification was used with the aim of recognizing the different provenance of visually identical white marbles.

Ten white marbles from Estremoz and Carrara were analyzed by PIXE-PIGE to determine the marbles composition and μ-AMS for strontium isotopic analysis.

Carrara (Italy) and Estremoz (Portugal) marbles may be undistinguishable from the point of view of macroscopic observation [3]; the Mg content and Sr isotopic ratio turned out to be valuable parameters for their characterization [4]. In white marbles, Mg, Fe, Mn, and Sr are incorporated in the carbonate lattice and Mg is mainly related to a dolomitic component. For thick samples the X-rays of light elements are masked by heavier elements and, although thin window X-ray detectors have reasonable efficiency for Mg X-rays, the analysis is not accurate, particularly in presence of Ca. Hence, PIGE becomes the reasonable choice for light elements quantification. In order to quantify Mg and other light elements present in the samples, we used a standard free method for PIGE in thick samples, based on a code – Emitted Radiation Yield Analysis (ERYA) [5]. Tests will be perfomed with the microAMS system present at CTN_IST to determine the ^{87}Sr/^{86}Sr isotopic ratio directly on the marble samples. These tests will determine if this technique can achieve the necessary precision for provenance studies of this kind.

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Multi-analytical characterization of glasses from South Spain

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Multi-analytical characterization has been carried out of Spanish ancient glasses from different chronology (Roman and Arabic period).

The aim of the present work is the characterization of a set of historical glasses of different chronological periods to compare their technology, chemical composition, colouring agents, conservation state and degradation products or corrosion crusts.

The characterization techniques have been optical microscopy (OM), scanning electron microscopy (SEM-EDX) with energy dispersive X-ray microanalyses, X-ray fluorescence spectrometry (XRF) and proton-induced X-ray spectrometry (PIXE & PIGE).

The results of the chemical composition of major components (SiO_2, CaO, Na_2O, K_2O, MgO) allow us to classify the origin and the state of conservation. Most glass fragments from the Roman and Arabic period are of sodium-calcium nature. The main forming material is the silica, and as a flux, a sodium source such as natron or ashes from plants should be used. This type of vitreous-calcium composition makes them vulnerable to de-alkalization that cause leaching of alkaline elements, which cause on the surface irisation in an early phase, and formation of crusts enriched in silicon. Some Islamic glasses contain lead and suffer less de-alkalization.

The transparency of the samples are conditioned by the presence of iron and manganese and opacifiers (lead and tin), while main chromophores are vanadium, chromium, cobalt, nickel and copper.

The combination of nondestructive techniques SEM-EDX and PIXE/PIGE is useful to classify these glasses and evaluate their conservation degree.

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Ancient beads from the Late Minoan cemetery of Armenoi in Crete (Greece): non-destructive examination using Raman Spectroscopy

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Raman Spectroscopy was used to identify the nature of ancient beads from the Late Minoan cemetery of Armenoi in the island of Crete, along with examination under the stereoscope and photographic documentation.

The aim of the study was the contribution to the knowledge of the materials that were available and used in the region at the period 1400 BCE – 1200 BCE [1].

The beads have a variety of colours, degrees of transparency, shapes and sizes.

Opaque white – whitish beads of various shapes were identified as calcite, while others also whitish opaque as well as one colourless almost transparent bead as quartz.

The red beads as well as those consisting of red and beige areas are made of carnelian (a mixture of a-quartz and moganite, a polymorph of SiO_2) [2, 3]. The colorless translucent beads were identified as fluorite [4], the purple as quartz (amethyst), the gray as steatite (talc) [5] and the grayish as chrysotile [6, 7].

In a group of beads that present the same specific features (granular texture - gray grains in partial or total contact and whitish to brown depositions in the interparticle regions), quartz was mainly detected, while in the whitish to brown areas calcite was also present. In two beads of this group, silicate glass was also detected. Their image under the stereoscope and the results of the examination using Raman Spectroscopy imply that these beads are made of a composite material consisting mainly of quartz that was placed in molds and heated at high temperatures.

According to the results of the examination, the late Minoans used both natural (minerals) and artificial materials to make beads for jewels. In the minerals used, very soft (talc), soft (calcite, chrysotile), medium hard (fluorite) and hard (quartz, carnelian, amethyst) are included.

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Integrated study of a Late Bronze Age axe mold by optical imaging, pXRF, SEM-EDS, XRD, µFTIR and µRaman

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The shape of metal artefacts is often obtained in a mold. Simple mold shapes are known since the Chalcolithic, but by the Bronze Age molds became more complex as a result of the development of technical skills and demand for sophisticated artefact shapes. Molds are objects which are relatively rare in the archaeological collections compared to their metal artefact counterparts. Thus, detailed or systematic studies of ancient molds are not common, despite their importance for a broad understanding of the ancient metallurgical productions.

In the present work, a fragment of a mold made of stone recently found in Galicia (NW Spain) was studied by a multi-proxy approach involving 3D optical imaging reconstructions, pXRF, SEM-EDS, XRD, µFTIR and µRaman to obtain data about the shape of the mold, typology of artefact produced in the mold, mineral composition of the mold, and composition and nature of a black residue present on the casting surfaces.

Results show that the mold is made of aplite, and that the original mold was composed by at least 3 pieces. It was used to produce axes, likely socketed axes with a side loop, a typology attributed to the Late Bronze Age/Early Iron Age in Western Europe. The alloy cast in the mold was probably a ternary bronze, since Cu, Sn and Pb were detected by pXRF and SEM-EDS in the black residues. Also, the presence of P, the detection of remains of proteins and oxalates by µFTIR, and a carbon black by µRaman in the black residue, can suggest that the mold was dressed with an organic material, such as bone grease or smoky flame from burning bones, prior to metal casting.

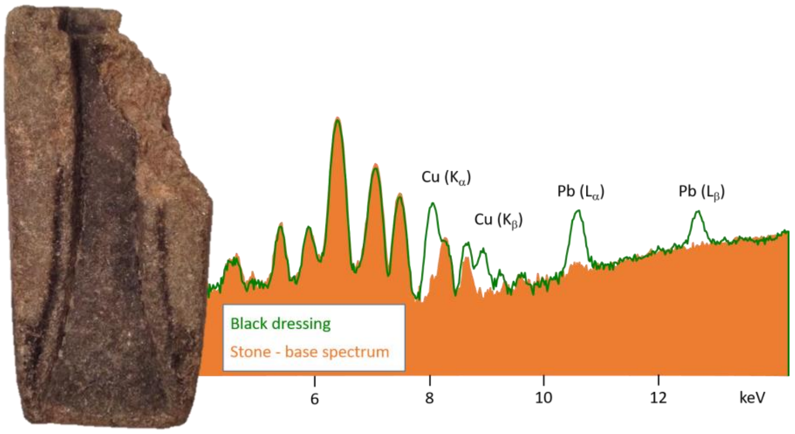

Figure 1. Photograph of the mold fragment studied in the present work and representative pXRF spectra taken over the 'black dressing' and the stone material (base spectrum).

Mortars and binders: from Roman times to 20th century reconstruction periods in built heritage. The case studies of the aqueduct of Carthage, the fortress of Safim and the Knossos palace

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A major question in the conservation and restoration of built heritage today relies on materials compatibility, requiring the knowledge and understanding of ancient and new materials in respect to its chemical composition, phase constitution and structural information. For that purpose, cultural heritage materials are being studied with advanced non-destructive characterization techniques in order to understand degradation phenomena, ageing mechanisms and ancient manufacturing techniques, allowing for the identification of manufacture periods, used techniques, historic economic routes and authentication procedures and resulting in consistent restoration approaches that do not compromise the value of the items under analysis.

Three case studies will be presented where different characterization techniques were applied such as X-ray diffraction, X-ray fluorescence, scanning electron microscopy, optical microscopy, differential thermal analysis and thermogravimetry and synchrotron radiation X-ray based techniques.

Binders, mortars and conduit crusts from the Roman Aqueduct of Carthage in Tunisia from the 2nd century (comprised mostly of sandstone and occasionally limestone) were characterized allowing for the clarification and distinction of different reconstruction periods as well as the identification of different water supply sources to the city of Carthage [1].

Original and different reconstruction periods mortars from the fortress of Safim in Morrocco (16th century) were also analysed allowing for a comparison with other studies regarding Portuguese settlements in African countries.

Profiting from the recently approved European Union Horizon 2020 HERACLES project [2], results will be presented concerning 20th century reconstruction materials used by Sir Arthur Evans and today conservators from the Minoan Knossos Palace in Creete, Greece.

Results will enhance comprehension on materials with cultural value and conservation approaches for their preservation for future generations.

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Photoacoustic approach to the assessment of stone consolidation

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Along the last decades significant advances have been achieved on the consolidation of stone materials, which led to the introduction and testing of several polymeric, inorganic, and composite consolidation products. Despite substantial steps ahead have been made evident through rigorous analytical insights, the direct non-destructive or microdestructive measurement of the mechanical properties of the treated surfaces still remain rather challenging. Available methods, such as those based on the tape test, rebound hardness testing, and sound speed measurements present serious limitations, although the latter approach is very attractive.

Ultrasonic Testing (UT) is widely used in various fields of application ranging from the well-known diagnostics of the living tissues to the characterization of polymers and many other materials. It is useful for detecting surface and bulk defects, measuring the thickness of multilayered materials, and other. In particular, UT has been widely exploited for investigating the mechanical properties of building materials and then their alteration due to deterioration processes. However, common ultrasonic wavelengths up to ~100 kHz are still too long for detecting weathering effects in proximity of the outer surface, as well as for assessing the effectiveness of consolidation treatments within such a spatial range. On the other hand, the consolidation effects within the order of ~10 μn-1 mm have a crucial importance in conservation of stone reliefs and wall painting. In order to overcome this limitation, the present work proposes a novel laser-based photoacoustic (PA) tester, which has been designed and developed in order to perform pulse-echo ultrasonic characterization of deteriorated stone artefacts, before and after the consolidation treatment. The device includes a fiber-coupled Q-Switched Nd:YAG (1064 nm) laser with a variable pulse duration and an efficient PA source, which allow producing strong pressure waves with peak frequencies between ~1-20 MHz, and PVDF piezoelectric transducer. Such a PA probe was comparatively tested on quarry samples and strongly deteriorated original marble artefacts, before and after consolidation treatments using acrylic-siloxane polymer, ethyl-silicate, and a fluoride-based elastomer. The results achieved are very encouraging and could represent the first step towards the introduction of a novel assessment instrument in conservation of cultural heritage.

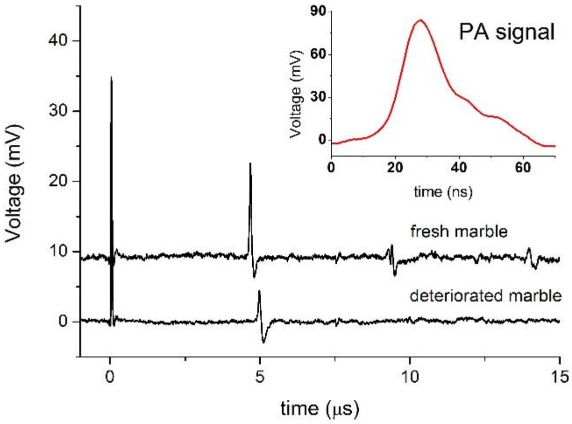

Figure 1. Examples of the laser produced PA pulse and associated reflection from different marble surface.

The multi-disciplinary approach to determine and monitor the state of conservation of the wall painting of Our Lady of Mellieha (Malta) before, during and after the restoration works

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This contribution aims to describe the approach followed during all the steps of the diagnostic project of the wall painting of Our Lady of Mellieha (Malta). The diagnostic activities started before the restoration interventions in order to understand the state of conservation of the wall painting, define the nature of the original materials, the presence of previous interventions and the processes of degradation. The activities were extended during the restoration intervention to acquire an immediate understanding of the decay phenomena and after the restoration to monitor the quality of the intervention, its effectiveness and durability

The Siculo-Byzantinesque wall painting of Our Lady of Mellieha depicts the Virgin Mary and Child, it is found in a semi-hypogea environment on the rock-cut apse aedicule of the Sanctuary of Mellieha, in the north side of Malta. It is painted directly on the local carbonate rock with iron based pigments and organic black. Along the years, the environment underwent several changes and interventions (partly documented), owing to its use as a sanctuary for worship. Before the restoration intervention the painting was heavily altered by the presence of an acrylic product, applied during a previous restoration. The acrylic product was of consistent thickness, numerous over paintings were also present. However, the most important conservation problem was related to the substantial presence of salts acting on the cohesion of the plaster layer causing pulverization.

The environmental conditions (temperature, relative humidity, moisture content and the presence of salts) and materials have been investigated through the use of non-invasive and micro-invasive techniques in order to determine the factors causing the deterioration and to suggest methods of prevention.

The approach presented in this study was developed on a preliminary survey based on non-destructive investigations using infrared thermography, evanescent field microwave dielectrometry and imaging techniques (UV) together the thermo-hygrometric monitoring of the environment. The results of this preliminary survey highlighted areas characterized by a high index of decay (humidity, presence of salts and of organic products related to previous restorations). Results from the scientific investigations have led through targeted micro-samples in areas of interest, for further laboratory investigations (FT-IR, XRD, microscopy, SEM-EDS).

The type of salts identified, (chlorides and nitrates) and the environmental conditions clarified the critical factors for the preservation of the painting and the development of a conservative intervention.

The most significant results of the project will be discusses during the presentation.

Acknowledgments: The authors wish to thank Rev Joe Caruana, Parish Priest of the Sanctuary of Our Lady of Mellieha, for his hospitality and useful suggestions and critical discussion. A special thank to Prof Giovanni Gardini, Prof Aldo Messina, Prof Mario Buhagiar and A. Martinellli for the useful discussions during and after the restoration works and to L. Scaletti (CNR-ICVBC) for their continuous interest in our activity and for the fruitful discussions on technical solutions for monitoring.

Portable FTIR spectroscopy to monitor conservation treatments applied on archeological surfaces in Pompeii

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This activity aims at proving the effectiveness and usefulness of portable Fourier Transform Infrared (FT-IR) reflectance instrument in monitoring the durability and chemical stability of conservation treatments used for consolidation and protection of archeological stone surfaces, a crucial issue in the scheduled maintenance.

The conservation problems in the archeological site of Pompeii are due to a combination of factors. The first one is the use of poorly durable stones, such as *Campanian ignimbrite* and *phonolitic tephrite* (volcanic rocks) or *Sarno limestone*, typically suffering from high rate of cohesion loss. The second one, but equally important, is due to the severe weather conditions characterized by strong rainfalls (mainly in spring and autumn) strong solar radiation. Also the non-negligible hydro-geological risk in this area must be included among the main causes of stone deterioration. Typical methods to consolidate and protect the stone exploit the adhesive and hydrorepellent properties of polymeric products, as well as the aggregating capability of silane-based materials. However, the applied materials may have limited durability due to chemical degradation or leaching caused by rainfall and other atmospheric events. As a consequence, the in situ monitoring on the treated surfaces is necessary to check the presence of the product, its composition and its chemical stability. In addition, the monitoring of surfaces is a powerful tool to evaluate the appropriate application of product, enabling to take informed decisions during the treatment. All the results of monitoring practice are useful for conservation scientists to plan a scheduled maintenance of large surfaces exposed to environmental agents.

The suitability of portable FTIR reflectance instrument for monitoring conservation treatments was preliminarily tested in laboratory and then on site, on a wall of the Macellum in Pompeii. Two polymeric products (one acrylic resin and one polysiloxane), and the tetraethylorthosilicate, traditionally used on stone surfaces, were firstly applied on different sets of specimens coming from the Macellum. The lithoypes considered were the above mentioned *Campanian ignimbrite*, *Phonolitic tephrite*, *Sarno* limestone and red Brick. Standard methods and techniques (colorimetric analysis, sponge test method, microscope investigation and SEM analysis) were also used to assess the appropriate application of the conservation treatments. Spectroscopic investigation by FTIR reflectance was performed on untreated and on treated specimens, before and after artificial ageing in solar box and climatic chamber. After these preliminary tests, the same lithotypes on the wall of the Macellum were treated according to the laboratory results. In the framework of a one-year monitoring, the on site tests were carried out four times: before the products application, one day, one month and eight months after the treatments.

The spectroscopic investigation proved the portable FT-IR reflectance instrument useful and capable of monitoring the permanence of conservation treatments also on site.

Acknowledgments: The authors wish to thank Piero Tiano (CNR-ICVBC) for the useful suggestions and critical discussion of results and Luciano Scaletti (CNR-ICVBC) for the design and arrangements for the on site setup.

TIO$_2$ Nanostructured silica-epoxy resins as photo-bioactive and protective consolidants

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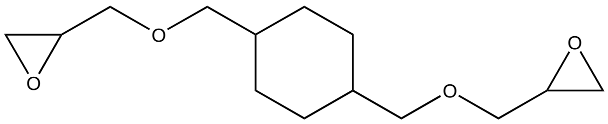
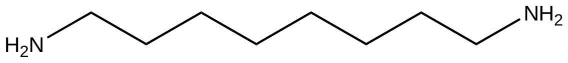
Aliphatic epoxy resins represent one of the most investigated and applied class of resins for stone conservation due to the whole of modulable physico-chemical properties such as viscosity, curing rate, penetration capability, discoloration resistance and easy handling application. Eponex and EP 2101 constitute representative examples of commercial epoxy resins. Alkoxysilanes, on the other hand, have been the most widely used stone consolidants over the last two decades as they easily hydrolyze inside silica stones affording Si-O linkages with the substrate.

Taking in mind the properties of these two classes of resins we have developed novel protective/consolidant materials, i.e. hybrid silica nanostructured epoxy resins, resulting from mono- and di-glycidyl epoxy precursors and amine functionalized alkylsiloxanes as curing agent [1].

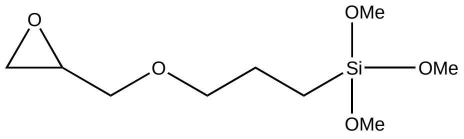
Here, we report on a novel class of hybrid cycloaliphatic siloxane@epoxides resins obtained by reaction of 1,4-cycloexanedimethanol diglycidylether (DCEE) with different siloxane precursors, namely GLYTS, TEOS and IBUTMS (see Figure), using ODTA (1,8-diaminooctane) as epoxy curing agent.



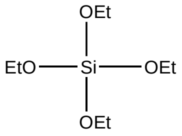
1,4-cyclohexanedimethanol diglycidylether (DCEE)



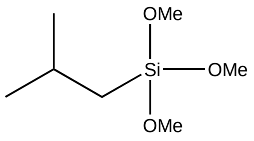
1,8-diaminooctane (OTDA)



(3-Glycidyloxypropyl)trimethoxysilane (GLYTS)



Tetraethyl orthosilicate (TEOS)



Isobutyl(trimethoxy)silane (IBUTMS)

On the basis of a preliminary screening aimed to assess film formation capability, transparency, curing rate, hydrophobicity, etc. some samples are selected and characterized and then treated with nanostructured titania- and Gd- and Ce-doped-titania to induce the required photo- bioproperties. All the products are characterized by spectroscopic techniques (NMR, IR, Raman), thermal studies, SEM, XRD and BET. The samples showing the best performance will be tested on different typologies of stone materials. Studies aimed to investigated their photocatalytic activity towards microorganisms coming from degraded materials (bacteria, algae, black fungi, etc) both as isolated and as biofilm have been also planned.

Acknowledgements: O. Gómez-Laserna is grateful to the University of the Basque Country (UPV-EHU) for her post-doctoral contract.

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Comparison of two direct mass spectrometric methods for the analysis of paint samples

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Two direct mass spectrometric methods have been compared for the analysis of samples from paintings: direct temperature-resolved mass spectrometry (DTMS) and atmospheric solids analysis probe (ASAP) mass spectrometry.

DTMS is an established technique which has been extensively applied for the analysis of oils, resins, waxes, synthetic media, synthetic organic pigments and other organic compound types in tiny complex paint samples [1]. The combination of DTMS with high-resolution time-of-flight mass spectrometry has recently opened new avenues for analysis, for example detection of proteinaceous compounds in complex samples that is notoriously difficult with traditional low resolution mass spectrometry. The availability of accurate mass information adds another dimension to the data which has been visualized in 'Kendrick plots' [2].

ASAP is a recently developed sampling technique based on atmospheric pressure chemical ionization [3]. While temperature resolution is maintained in ASAP, a main difference with DTMS is its preference to produce pseudomolecular ions which improves the specificity of the peaks observed in the complex mixture mass spectra. ASAP has also been used in combination with high-resolution time-of-flight mass spectrometry.

Both techniques provide a wealth of information on a large range of organic materials and indication of the degree of curing and degradation of these materials in varnishes and paint binding media. Sample preparation is straightforward and allows for combined use of the techniques rendering partly complementary information.

The paper will compare the two analytical techniques through a series of reference samples. Furthermore, the analysis of varnishes and binding media from 17th, 19th and 20th Century paintings from Dutch museum collections will be presented.

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A XANES study of archaeological glass beads

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The International Atomic Energy Agency (IAEA) operates jointly with Elettra Sincrotrone Trieste a multi-purpose X-ray spectrometry facility at the X-ray fluorescence (XRF) bending magnet beamline. Exciting energies from 3.65 to 14.5 keV are currently available using a Si(111) double crystal monochromator with a resolving power of 1.410-4. The synchrotron beamline end-station was developed to operate primarily under ultra-high vacuum (UHV) conditions, but non-UHV compatible samples can be also accommodated. Research groups associated with the IAEA Coordinated Research Project G42005 [1] have already utilized the facility during the last two years carrying out research in various fields such as advanced materials, biology, biomedicine, air pollution studies and cultural heritage.

In this work, an X-ray absorption near-edge structure (XANES) study is presented for the transition metals used to produce various coloring variations of ancient glass beads. The analysed soda-lime glass beads (six bead fragments) showing blue, green and red colorations, belong to a sub-set of a larger collection from an ancient cemetery discovered in the outskirts of Thebes, Greece, were dozen of graves from late Archaic to early Hellenistic times (ca. 6th–4th century BC) [2, 3] were excavated. Due to the obvious difficulty to export archaeological objects outside the country of origin, similar X-ray absorption spectroscopy studies are rather scarce [4-6].

The aim of this study is to determine the oxidation state of the chromophore transition metals and enlighten their coordination environment in order to better understand how different colors and shades are produced. The XANES measurements were carried out in the fluorescence and transmission modes across the K-edge of the chromophore elements (Fe, Co and Cu), on the glass beads and on corresponding standard compounds. Supporting information regarding the beads elemental composition was gathered by means of scanning electron microscopy energy dispersive X-ray spectroscopy and micro-XRF analyses. Finally, in order to assess the influence of the glass corrosion in the chemical environment of the chromophore elements, XANES measurements were performed on a polished area and the intact surface as well.

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Analytical pyrolysis of proteins in samples from artistic and archaeological objects

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In this study proteins found in artistic and archaeological objects were investigated by analytical pyrolysis. Proteins (mainly egg yolk and/or egg white, casein, animal glue and collagen) have been extensively used as paint binders, adhesives and varnishes in mural and easel paintings, and they can be found in archaeological findings, such as bones and skin tissues. In order to overcome limitations of wet chemical methods arising from the reduced solubility of aged proteins in samples of cultural heritage, a combination of analytical pyrolysis techniques was used to characterise reference materials, paint reconstructions and samples from different historical periods (2nd century BC-20th century AD) and geographical origins, which were collected from paintings and archaeological findings. Analytical pyrolysis was used to characterise proteinaceous materials in reference samples, ancient paintings and archaeological findings. Evolved gas analysis coupled with mass spectrometry (EGA/MS), pyrolysis coupled with gas chromatography/mass spectrometry (Py/GC/MS) and double shot pyrolysis gas chromatography/mass spectrometry (DSP/GC/MS) were used as analytical pyrolysis techniques. EGA/MS allowed us to investigate the thermal behaviour of proteinaceous materials. DSP/GC/MS was used to support the interpretation of the EGA/MS data. Both Py/GC/MS and EGA/MS were used to characterise the different proteinaceous materials and highlight changes occurring with ageing. This analytical approach allowed us to characterise and differentiate the proteinaceous media, investigate their thermal behaviour and evidence changes occurring with ageing. Data clearly indicate that egg, casein and animal glue can be identified and distinguished in a sample of unknown composition using each of the analytical pyrolysis technique used. With time though differences tend to disappear to the extent that extremely degraded samples present pyrolytic profiles extremely similar to each other, irrespective of the nature of the proteins present. Data also indicate that proteins tend to became significantly more thermally stable with ageing, suggesting extensive intramolecular and intermolecular aggregation, and/or covalent cross-linking, offering the first insight into the correlation between the degree of aggregation and/or cross-linking of the proteins and ageing. Although more research is still necessary to better understand what is the role played by aggregation and covalent cross-linking in determining the thermal behaviour of proteinaceous materials in artistic and archaeological samples, the data presented clearly highlight that analytical pyrolysis has the potential of contributing to our understanding of the ageing and degradation of proteinaceous materials by overcoming solubility limitations affecting wet chemical sample pre-treatments

Microbiological extraction of sulfur compounds from simulated waterlogged wood

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Archaeological waterlogged wood encounters serious problems after excavation due to the accumulation of sulfur and iron compounds during burial [1,2]. In sulfate-rich anoxic environments, sulfate-reducing bacteria (SRB) produce hydrogen sulfide. This latter combines with the iron ions present, as consequence of the corrosion of iron parts, leading to the formation of iron sulfides. These phases are responsible for serious structural damage after excavation. Indeed, exposure of these compounds to oxygen results in salts precipitation and acidification [3]. In order to overcome this phenomenon, a preventive extraction of sulfur compounds using bacteria is proposed here. Such extraction could be done by immersing wood in bacterial cultures and using a trap for sulfates produced.

In this study, the capacity of the bacterium *Thiobacillus denitrificans* to oxidize sulfur compounds commonly found in waterlogged wooden objects, was evaluated. Oak wood samples impregnated with a solution containing iron and sulfur were used to assess the efficiency of the bacterial treatment. The model wood samples were characterized before and after treatment with environmental scanning electron microscope coupled with X-ray energy dispersive spectroscopy (ESEM-EDS), micro-Raman spectroscopy, and X-ray diffraction (XRD). Additionally, synchrotron-X-ray fluorescence (Sy-XRF) allowed the distinction of the oxidation state of sulfur present in the wood. The formation of sulfate ions by bacteria was also measured by ion chromatography. Finally, non-invasive techniques such as Fourier transform infrared (FTIR) spectroscopy, were carried out to assess the possible consequences of the biological treatment on the wood structure.

Before treatment, mackinawite (FeS) and mineral sulfur (-S_8) were detected in the impregnated wood. Sy-XRF maps showed mostly reduced sulfur. After treatment with *T. denitrificans*, mineral sulfur was observed but not mackinawite. Also, the presence of oxidized sulfur was predominant in Sy-XRF maps. The formation of sulfates was then confirmed by ion chromatography. Furthermore, the lignin/carbohydrates ratio obtained from FTIR spectra was not significantly different between untreated and treated samples, indicating that no degradation of wood cells was induced by the bacteria. These results showed that *T. denitrificans* is able to metabolize sulfur compounds present in wood. This suggests the feasibility of an alternative biotechnological procedure for the preventive extraction of sulfur species from archaeological waterlogged wood.

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A comparative analysis of the gesso ground of frescoes in the Cathedral of the Protection of Most Holy Theotokos (Moscow) and the Cathedral of the Assumption of Most Holy Theotokos on the Island of Sviyazhsk (Russia)

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Cathedral of the Protection of Most Holy Theotokos (Saint Basil's Cathedral) was erected in the 1555—1561s at the order of Tsar Ivan IV the Terrible in celebration of the conquest of Kazan. Unfortunately, due to numerous fires and repaints of the 16th-18th centuries the original wall painting of the temple only remained on the walls of the upper octagon, the dome of the central church, and fragmentarily on the arch of its altar. The major portion of fresco painting in the Cathedral of the Protection of Most Holy Theotokos dates back to late 17th century and represents an "al secco" technique of painting on a thin gesso. Almost simultaneously with the Moscow Cathedral, the Cathedral of the Assumption of Most Holy Theotokos was being constructed 30 km away from Kazan on the Island of Sviyazhsk. Its construction was dedicated to the same event as that of Saint Basil's Cathedral. All fresco paintings of this cult structure have remained in their original appearance. With this unique historical experience of a simultaneous construction of two Cathedrals directly related to the history of Kazan campaign, of interest is the determination of certain similarities in the preparation technique and chemical composition of gesso. This work features a comparative analysis of the ground material for fresco paintings from two architectural monuments.

Its authors studied gesso samples from a surviving Sviyazhsk painting dating back to the period of Ivan the Terrible together with certain gesso samples collected in the lower sections of the altar walls in the central church of the Cathedral of the Protection of Most Holy Theotokos. These sections are presumed to be the initial ones. Sample analysis and research were conducted using the electron microscopy technique with an energy-dispersive XRF analyzer. Research work has revealed a number of similarities characteristic of gesso from both Cathedrals, such as the use of dolomite-containing dust as a basis for fresco paintings.

The conducted work represents a significant experience in the comparison of monuments from a single time period. Yet, the aggregate picture of the comparison of gesso layers is at the initial stage, as only the paintings on the uppermost section in the central church of the Cathedral of the Protection of Most Holy Theotokos can be considered authentic and original layers. However, they are currently unavailable for research due to fact that these sections of wall painting are located at a considerable height.

The ceramic bodies of Hispano-Moresque tiles: chemical and mineralogical characterization

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With this work, important 15th-16th century Portuguese and Spanish Hispano-Moresque tile collections were studied and compared using micro-Particle-Induced X-ray Emission (µ-PIXE) and micro-X-ray Diffraction (µ-XRD) analysis data. The comparison involved tiles from the National Palace of Sintra (Portugal) (PNS), Monastery of Santa Clara-a-Velha (Coimbra, Portugal) (SCV), Instituto Valencia de Don Juan (Madrid, Spain) (IVDJ), Casa de Pilatos (Seville, Spain) (CPS) and Museo de Cerámica y Artes Sumtuarias "González Marti" (Valencia, Spain) (MCV) collections. The methodology relied upon a non-destructive, minimally invasive approach with complementary analytical techniques that will allow for replication in future studies with other Hispano-Moresque tile

In flat tiles, the ceramic body acts only as a base on which the pictorial layer is applied and painted. In *arista*, *cuerda seca* and relief tiles, however, the ceramic body plays a fundamental role in the aesthetics of the pictorial layer, since the separation of the coloured glazes and the definition of the motifs is directly related to the quality of the mould print.

Three types of ceramic bodies were identified among the studied collections: calcareous (CaO >10 wt.%), less calcareous (CaO <10 wt.%) and non-calcareous (CaO <2 wt.%). The calcareous group represents the vast majority of the tiles and show high lime contents (20±4 wt.%), even when compared with other calcareous tin-glazed ceramics from the literature. The non-calcareous group contains two red paste samples (PNS) with very high SiO_2 and Al_2O_3 contents. Another four samples were considered as less calcareous because of the lime content below 10 wt.%. These are four IVDJ tiles with red-coloured ceramic bodies. The most important mineral phases identified in the ceramic bodies were quartz (SiO_2), calcite ($CaCO_3$), gehlenite ($Ca_2Al(AlSi)O_7$), diopside ($MgCaSi_2O_6$), hematite (Fe_2O_3) and plagioclase (likely anorthite $CaAl_2Si_2O_8$), further allowing estimation of the firing temperature between around 900 °C.

The chemical composition of the calcareous clays is very similar among all the studied collections and no major differences were identified. However, the set of tiles with a Valencian provenance (MCV) are the ones that stand out the most for their higher CaO contents, as well as stronger presence of gehlenite when compared to the other collections.

Chemometric studies of analytical data obtained from **water sensitive Winsor & Newton Artists' Oil Paint** Swatches and twentieth century oil paintings

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Water sensitivity of twentieth century unvarnished oil paintings is widely documented[1]. Recent studies have involved systematic analytical investigations of water sensitive oil paintings[2] and Winsor & Newton (W&N) Artists Oil Paint swatches[3]. Results indicate split carbonyl absorptions at ~1737 and 1713cm^{-1} in FTIR spectra of samples taken from water sensitive paint passages which is suggestive of medium oxidation and/or hydrolysis[4]. Electrospray ionisation mass spectrometry investigations have also indicated that azelaic acid content, oxidation and hydrolysis all appear to relate to water sensitivity[3]. Statistical analysis of large and complex data sets generated by investigations into water sensitivity has the capability to reveal new insights and trends that may be otherwise obscured. One preliminary study used chemometrics to analyse electrospray mass spectrometry data (ESI-MS) relating to three W&N swatches, which highlighted interesting relationships between pigment type and degree of oxidation [5].

W&N produced paint swatches in order to check the drying times of each batch of manufactured paint. Samples of paint were applied to primed canvas or a paper support using a palette knife or draw-down bar with colour names and drying times recorded under each sample. A group of 27 water sensitive and non water sensitive W&N Artists' Oil Colour swatches dating from 1945-2003 were selected for study. In addition samples were taken from 16 water sensitive unvarnished oil paintings belonging to Tate's collection. A total of 112 samples were extracted using ethanol and analysed using an established ESI-MS protocol[6]. Negative mode data yielded the most interesting information about the content in extractable glycerides and fatty acids. Fragment ions of interest were identified in the mass spectra, and a matrix containing the relative abundances of significant ions from each sample was produced. Mass spectral data were put in relation to the chemical composition of the samples and evaluated by means of principal component analysis (PCA). Unsupervised multivariate pattern analysis permitted the comparison of the chemical composition of the lipids in the various samples, highlighting differences and similarities between the materials present in the swatches and in the paintings. Correlations were investigated between the chemical information contained in the mass spectra, the water sensitivity of the paint, and the influence of different pigments in determining specific oxidation or alteration phenomena.

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Analysis of Roman Imperial coins by combined PIXE,-XRF and LIBS techniques

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Development of non-destructive or micro-invasive scientific diagnostic techniques gained an outmost importance in field of Cultural Heritage, contributing to asses authenticity, provenience and age of the objects, as well as to supply additional information to the archaeologists, useful for the restoring and the conservation procedures. However, each diagnostic technique has its own advantages and limitations, thus in many cases the optimal sample characterizations require a synergy between different analytical approaches.

In this context, Particle Induced X-ray Emission (PIXE), micro X-Ray Fluorescence (-XRF) and Laser Induced Breakdown Spectroscopy (LIBS) techniques were applied to characterize the composition of the samples, both to the bulk materials and to the top layers. The samples analyzed were four Roman Imperial coins belonging to different periods, namely: two "Asses" coined under Emperor Claudio (41-54 A.D.), one "Sestertius" from Vespasian's period (69-79 A.D.) and one "Dupondius" by Augustus (4 B.C.). It is already known that the first two coins mainly contain copper, while the last two are based on "auricalcum" (a Cu-Zn alloy), but the content of the main constituents and, in particular of minor elements could vary significantly, depending on the production date and place. On the other hand, the surface composition is strongly affected by the conservation conditions.

The measurements were carried out in a multi-analytical approach combining results from three different techniques, which allow multi-elemental analysis: i) PIXE with 3 and 18 MeV pulsed proton beam accelerated by a linear high frequency accelerator; ii) -XRF equipped with a Mo X-ray tube working at HV=50 kV and I=100 A, and polycapillary optics with focal beam spot size of 80 m; iii) LIBS detecting simultaneously the high resolution spectra in the wide range, covering 235-790 nm [1].

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Non-destructive investigations of set of French golden coins

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This work is a continuation of the study of coins from precious metals by means of various non-destructive methods [1].

The objects of study were considered French 20 franc gold coins.

Napoleondor (fr. Napoléon d'or) is a French 20 gold coin of 900 fineness of gold, the total weight is 6, 4516 grams of 5, 801 pure gold in grams.

It was produced in France as a means of payment from 1803 to 1914. 84 coins of this period were investigated.

Napoleon I introduced a standard franc. Later "Napoleondor "became known as any 20 francs gold coin made in this standard even if not bearing the Emperor's image.

Then the kings were portrayed on them. During the second Empire Napoleondor was made with the image of Napoleon III.

The following characteristics of the coins were measured:

- chemical composition using portable energy dispersive X-ray spectrometers PRIZMA-M Au (Russia) and InnovX-System Omega (USA).

- changes micro- and macro-components of these objects for a specified period of time and the parameters of the crystal lattice using X-ray diffractometer Rigaku Ultima IV (Japan).

- conductivity parameters measured on "Sigmascope" Gold C (Germany).

- density using balances with built-in density measurement Sartorious AG (Germany).

The purpose of the study was the identification and interpretation of the obtained data to determine time ranges for the production of the investigated objects.

The range of methods was expanded due to the use of X-ray diffraction and the phase sensitive eddy current. The Rietveld method for the accurate determination of the structure of solid solutions was used and substructure components (mosaicity and microstresses) from the broadening and shift of diffraction lines were defined.

The results of the investigations:

For each period of the Board the dependence of these parameters on the period of time was built. The results are useful to interpret the time of production (mintage) of the coins and the authenticity of the objects was considered on the relevant structural components and chemical composition.

Nowadays, the investigation continues. The obtained data will be used for identification of the coins and included in database.

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Technical characterization of the necklace of El Carambolo treasure

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Since its accidental discovery in 1958, El Carambolo treasure (Camas, Seville) has been considered the most emblematic of all the treasures belonging to the Orientalizing period of the Guadalquivir Valley in Spain. It is an example of the economic heyday and the interrelations between native and oriental population during the VII-VI centuries BC. This impressive group consists of 21 artifacts. The archaeological and scientific studies carried out so far divide the pieces of the treasure into three groups [1], depending on style, composition of the alloy and manufacture techniques. Some studies have already dealt with the analysis and interpretation of Group 1, consisting of two bracelets, a series of 8 rectangular plaques and a pendant [2] and Group 2 that involves another series of 8 plaques and a pendant. Group 3, consisting solely of a necklace with pendants in the form of signatory seals, has not been characterized yet. The stylistic characteristics, along with the symbology of the seals, covers this necklace with mystery.

Thanks to previous studies on ancient joining methods and production techniques by micro-XRF spectrometry on several archaeological gold jewels (Group 1 of the El Carambolo treasure among others) [2, 3], it is possible to distinguish the different types of welding procedures and to reconstruct the manufacture steps used for a metallic object. In this work, we apply this study to interpret the micro-XRF results of the necklace of *El Carambolo* treasure.

For the analysis of the objects, a portable micro-XRF experimental set-up was used. This system is equipped with a portable X-ray source with a Rh anode, combined with a polycapillary full-lens in the excitation channel. This lens provides a 30 μm FWHM spot size at about 10 mm distance to the exit lens. A Super Silicon Drift Detector from Amptek, positioned at 45° from the source, has been used for the acquisition of the X-ray spectra.

The bulk composition of the alloys, the welding/soldering zones and the decorations of the jewels were characterized. The results allow identifying the manufacturing method and shedding light on the provenance of the necklace.

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Electrochemical screening of Spanish maravedis from different mints

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When Philippus IV started his reign in 1621, the financial situation in Spain was not favorable. The currency in use was mainly made in copper (*maravedis*) so that falsifications were frequent. In order to avoid this practice, Philippus IV ordered some modifications in the coinage, among which the most important was the change of the composition of the coins. Thus, new issues of currency, prepared from a copper-silver alloy, started to be produced in 1661 in the different official Mints located in Burgos, Córdoba, Coruña, Cuenca, Granada, Madrid, Segovia, Sevilla, Toledo, Trujillo and Valladolid.

The voltammetry of microparticles methodology has been applied to the discrimination of Spanish *maravedis* produced in different mints between 1661 and 1664 using characteristic signatures for the reduction of cuprite and tenorite in the patina of the coins. The variation of the apparent tenorite/cuprite ratio with depth was fitted to potential laws differing from one mint to another for A Coruña, Burgos, Córdoba, Granada, Madrid, Trujillo, Sevilla and Valladolid coins. Electrochemical data suggested that significant differences between the diverse mints existed possibly associated to variations in the silver content and thermomechanical treatments involved in the mint process.

Figure 1. Maravedi (Philippus IV, 1664) minted in Córdoba.Courtesy of the authors. ©Universitat Politècnica de València. Obverse (left) reverse (right)

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Study of submarine lead objects using solid-state electrochemistry techniques

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From the point of view of the conservation of heritage the marine milieus is one of the most complex environments for conserving artifacts due to the variability of conditions (mud, deep ocean, continental shelf, shallow water, tidal, splash or atmospheric) [1]. Additionally, corrosion studies on archaeological lead objects present some difficulties inherent to the scarcity of available samples for destructive analysis, to the variations of sample composition and lack of knowledge of objects history. Moreover the metal and its corrosion layer have to be taken into account simultaneously.

Voltammetry of microparticles is a solid state electrochemical technique that has been previously applied with success in the study of the corrosion processes taking place in buried lead objects [2] as well as in dating [3,4] and authentication [5,6] of buried lead objects. In the present work, the voltammetric response of submicrosamples from the corrosion layers of different lead objects proceeding from submarine archaeological sites was studied upon sample attachment to graphite electrodes in contact with aqueous electrolytes by means of portable equipments. $PbSO_4$ and $PbCl_2$ were identified as main corrosion products whose distribution in depth in the corrosion layers was studied based on thermochemical and kinetic considerations suggesting that the relative amount of such corrosion products varied systematically with the immersion time.

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Biogenic characterization of archaeological organic residual soils using n-alkanes ratios from a stable rock-shelter, Los Husos II, (Upper Ebro Basin, Spain)

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The use of n-alkanes concentration in faeces for determining the diet of the ruminants has been used in several works with success [1-2]. The main objective of this work is the use of n-alkanes concentration ratios to classified archaeological organic residual soil strata from a stable rocksheler sited in Los Husos (Cantabria mountain range, Araba/Álava, Upper Ebro Basin, North of Spain) in different kind of herbivorous residues such as goat, sheep, horse or cow.

For that purpose faeces from goat, 2 type of sheep (Rasa and Merina), horse and cow were collect from different livestock near the sampling site. The concentrations of 9 n-alkanes (C_{25}-C_{30}, C_{32}, C_{34}, C_{36}) were determine using a simple solid-liquid extraction with 1 g of homogenized sample and 10 mL of n-hexane and an analysis by means of a gas chromatography mass spectrometry. The archaeological organic residual soil samples were analysed in the same way using 5 g of homogenized sample.

The odd-chain n-alkanes were present in higher concentration than the even-chain ones, mainly in the archaeological samples. Therefore just odd-chain n-alkanes were use for the classification step.

As the objective is to compare nowadays faeces with archaeological ones, different ratios between odd-chain n-alkanes were used for the classification. Principal component analysis (PCA) was used to make a model with the faeces samples and a good grouping was obtained for all the herbivorous groups. That grouping was used as the models for a SIMCA classification (95%). Good model was obtained for classified the residues from nowadays.

This model was applied to 19 archaeological samples in order to determine their biogenic origin. Contradictory results were obtained depending on the ratios used including samples in the classification model or not.

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Investigation of proteins in samples of a mid-18th century colonial mural painting by MALDI-TOF and nano-LC-ESI-hybrid-Q-orbitrap mass spectrometry

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With the aim of investigating the presence of proteinaceous materials in a wall painting from the church of Our Lady of Copacabana de Andamarca (1723) in Bolivia, seven micro-samples have been extracted before the restoration. Historically, artists have used different proteinaceous binders as egg, casein, and animal glues, depending on the painting technique and their availability. Identification of proteinaceous binders plays an important role in conservation and offers insights into the manufacturing technique of a work of art.

In this investigation, we report for the first time the application of proteomic tools to the study of colonial samples. The analysis of proteinaceous binders was performed on references, model samples and micro-samples from a wall painting. In the first stage of our study, we applied MALDI-TOF mass spectrometry and then, we used nano-LC-ESI-hybrid-Q-orbitrap to achieve more reliability in the identification of the protein binders.

By MALDI, we found weak signals presumably of egg peptides in several of the micro- samples. By nano-LC-ESI-hybrid-Q-orbitrap, one sample yielded several peptides from seven egg white different proteins, particularly ovoalbumin, ovotransferrin, lysozyme, and two egg yolk proteins, vitellogenin-2 and apolipoprotein B, were detected in another sample with one high confidence peptide each. These results confirm our previous GC-MS results indicating that egg tempera was used as the painting technique [1]. In all the samples, the presence of collagen from animal glue was established by MALDI-TOF and nano-LC-ESI-hybrid-Q-orbitrap. This finding supported our previous assumption that animal glue was applied as a primer onto the ground layer. In order to identify the origin of the collagen isoforms, a search against a Uniprot database containing collagen proteins from all the species was performed. The results suggest that this glue was prepared from a mixture of several sources.

In conclusion, both mass spectrometry techniques are efficient tools for identifying proteinaceous binders in old tempera paintings. The advantage of nano-LC-ESI-hybrid-Q-Orbitrap over MALDI-TOF lies in the highest accuracy to identify proteins. However, MALDI allowed a quicker screening and faster comparison between samples and references.

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EDXRF analysis of Iberian votive figurines from the southern Spain (4th-3rd centuries BC)

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Studies on Iberian votive imagery have allowed us to increase our knowledge of Iberian culture and to provide valuable information on technological aspects related to the metal processing and, on the other hand, on the social and religious patterns. In this work, we present energy dispersive X-ray fluorescence (EDXRF) analysis of the copper alloys of a selection of 32 Iberian votive figurines and 2 fibulae (4th-3rd centuries BC) from the Juan Pablo Pérez Caballero private collection. This collection is on exhibit at the "Museo de Prehistoria de Valencia" and is made up of 97 bronze objects from the Iberian sanctuaries of the "Collado de los Jardines de Santa Elena" and the "Altos del Sotillo de Castellar" (Jaen, Spain). Our aim is to characterize the bronze alloy of the votive figurines and to compare the absolute composition of the bulk alloy and corrosion patinas.

The analyses were performed on polished and patina/crust coated areas of the figurines by means of a home-made EDXRF spectrometer equipped with a Peltier cooled semiconductor Si-PIN detector (FWHM =165 eV @5.9 keV) and a low power X-ray transmission tube (silver anode) operating with an excitation potential of 35 kV, an intensity of 0.012 mA and an acquisition time of 300 s. The X-ray beam is collimated by an aluminum pinhole on a sample surface of about 15 mm^2. Data acquisition was controlled by a "pocket" multichannel buffer board. X-ray tube and detector were fitted on a mechanical device with an excitation-detection geometry of 45° and about 2 cm sample-detector distance. Quantification of the spectra was performed by the fundamental parameters software XRS-FP (Crossroad Scientific) and 6 bronze reference samples (Cu-Pb-Sn). The results reveal a diversity of Cu-Sn-Pb alloys among the votive figurines, which include copper, leaded copper (Pb >2%, Sn <2%), binary bronzes (Sn >2%, Pb <2%) and ternary bronzes (Sn >2%, Pb>2%). Significant differences between the concentrations of Cu, Pb and Sn in polished areas and corrosion layers are found.

Photography unveiled: a multi-analytical approach for the study of 19th century ambrotypes

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Photography withstands time and unveils the past, preserving our memories. Since its invention in the mid-nineteenth century, numerous photographic processes emerged, introducing different techniques and innovations. One of these is the ambrotype. Ambrotypes are direct positives produced in coloured glass plates or in transparent plates backed with a black varnish, paper or cloth. A glass plate was coated with a solution of collodion (a syrupy liquid composed of soluble gun-cotton, ether and alcohol) mixed with iodide or bromides of different metals. Then the plate was immersed into a solution of silver nitrate in order to precipitate the silver halide, obtaining a light-sensitive surface [1, 2].

These photographic items are subjected to various types of degradation, being the most frequent mechanical damages, cracks, flacking and surface roughening. Chemical degradation can be observed as image fading and stains. Silver mirroring is one of the most prevalent form of degradation of the silver image forming particles and appears as a bluish iridescent metallic deposit on the binder's surface, with a mirror-like effect [3].

In this work an in-situ non-invasive approach was used to study three historical cased ambrotypes from the 19th century. Visual examination and technical photography under different illuminations were the first step to define methodologies for the analysis. Optical microscopy was used to gather information on the morphology and to evaluate the degradation patterns. Variable pressure scanning electron microscopy with energy dispersive X-ray spectroscopy coupled (VP-SEM/EDS) was a valuable tool to complement the study of the morphological aspects in higher magnification and to obtain chemical information on the materials used on the ambrotypes' production and on the degradation compounds formed meanwhile. Micro-Fourier transform infrared spectroscopy (μ-FT-IR) was particularly helpful with the analysis of the organic binder, confirming the use of collodion (cellulose nitrate), and micro-Raman (μ-Raman) spectroscopy confirmed the formation of silver sulphide degradation products.

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Ancient and Modern Paper: study on degradation process by means of NIR Raman Spectroscopy

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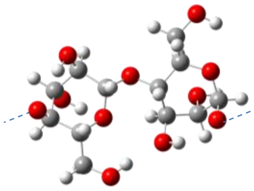
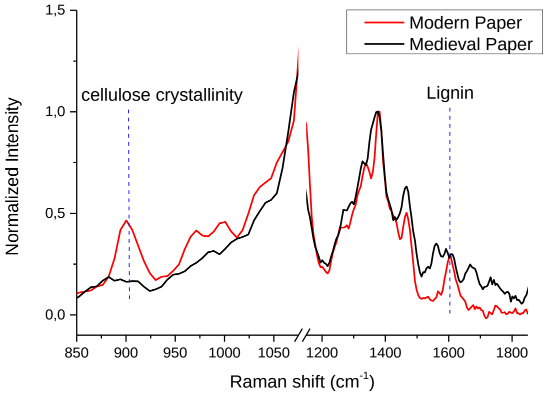
For many centuries paper has been the main material for recording cultural achievements all over the world. Archives represent the historical memory of our past, many books and documents kept in libraries and archives are at risk because of their fragility [1].

The present study demonstrates the extraordinary power of the non-destructive NIR Micro Raman Spectroscopy, recently applied in the field of the Cultural Heritage [2, 3] , to gain new and different information on paper and inks analysed in a set of ancient and modern documents. Micro-Raman scattering measurements have been carried out within back-scattering geometry in air at room temperature neither moving the ancient documents from their seat nor exposing them to possible damages. With the help of Raman spectra, determined after computer simulations, we determined the conservation state of the samples by studying the structure and the grade of crystallinity of the paper. The Figure shows the raman spectrum of modern paper compared with a medieval paper.





Paper composition is ascribed to mostly treated and bonded cellulose fibres constituting by linear polymers of glucose (-D-glucopyranose) monomers linked by -1,4-glycosidics bonds. Molecular chains are held together by strong intermolecular hydrogen bonds that have an important role in the aggregation of single chains into highly oriented structure. The aggregates are ordered up to even 80% ("crystalline" forms). The rest, considered disordered, is called "amorphous" form. The presence of the 900 cm-1 band is very sensitive to the amount of crystalline versus amorphous structure of cellulose. This band is assigned to the angle around the -glycosidic linkages and hydrogen bond rearrangement and then it depends on the deformation of COC, CCO, CCH and stretching vibrations of C5 and C6 atoms [4].

Prior to the XIX century, paper was made entirely from rags, using hemp, flax and cotton fibres. After this period, due to the enormous increase in demand, wood pulp began to be commonly used as raw material, resulting in the rapid degradation of paper. The band centered at 1602 cm-1 is typically assigned to the presence of lignin in the composition of the paper, responsible of the principal degradation processes due to its photo-oxidation properties [1].

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Investigation on metal adornments from ancient Eastern Europe

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The paper focuses on the investigation of some bronze jewelry objects from the first Iron Age, between 9th – 8th c. BC. The objects belong to two metal hoards discovered in the present Romanian territory, in the Tărtăria – *Podu Tărtăriei west* location, in Alba County. Part of the objects found at Tărtăria were included in a study concerning the development of a pilot platform for transdisciplinary investigation and valorisation through linked data-bases, which aims at creating a web platform for easing the access of specialists from various field to large collections [1]. This platform represents an example of how inter-disciplinary fields – archaeology, science, computer science, can be used together to spread knowledge about cultural heritage objects. For this study, several adornments were selected and were subjected to laboratory investigations, aiming at revealing as much information as possible about them. The selected objects included bracelets, bracelet fragments, torques and spectacle fibula. They were investigated using non-destructive methods, such as X-ray fluorescence spectroscopy, radiography, laser-induced breakdown spectroscopy and digital 3D scanning. The results offered information not only about the materials from which they were created, but also regarding the environment in which they were buried and their current preservation status. The importance of the study derives from the significance of the discovery made at Tartaria, the hoards found here probably being the most complex findings of the Bâlvăneşti-Vin series from the Eastern part of Europe, in Romania, Hungary and Serbia [2].

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Complementary non-destructive investigations of two Lipovan-style icons

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The non-invasiveness and precision of art investigation methods has been the golden goal of art restorers and conservators for the past decades. There a well-defined tendency to try to obtain as much information and as accurate as possible about art objects, especially those which are about to undergo restoration or conservation processes. The CERTO laboratory [1] tries to meets these needs and come up with new ways to get information about art objects, such as paintings or icons. Thus, a current practice protocol for investigation of icons includes imaging documentation, elemental documentation and molecular documentation, performed, as much as possible, or even solely, on non-invasive techniques, in order not to damage in any way the integrity of the art objects. The present study shows the application of our investigation protocol to the characterization of two Lipovan-style icons on wood support, with the aim of easing the restoration process. Thus, the investigation protocol included imaging (photographic, X-ray radiography, macroscopic and microscopic analysis, hyperspectral analysis), elemental (X-ray fluorescence spectroscopy) and molecular (Fourier-transform infrared spectroscopy) techniques.

The first icon is a depiction of St. Sergius of Radonezh and the other shows the Virgin Mary and Jesus (see figure 1). The icons come from private collections, but their origins are not well known. The Virgin and child icon is dated to approximately 17-18th century, while the St. Sergius of Radonezh icon is presumed to have been created around 19th century.

Figure 1. a) St. Sergius of Radonezh; b) Virgin Mary and Jesus

The results obtained with these methods allowed the assessment of the current preservation status of the objects, the detection of hidden defects and nonetheless an extensive characterization of the painting layers that allowed the identification of the existing binders, varnishes and pigments.

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Elemental characterization (gold, silver, copper) in Ancient gold jewelry using X-ray fluorescence

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One of the most important preconditions in the analysis of historical/artistic materials is the use of nondestructive techniques. For this reason, X-ray fluorescence techniques are the most suitable and used in the analysis of these types of materials in Museums. The X-Ray Fluorescence (XRF) technique allows a nondestructive qualitative and quantitative multi-elemental analysis on a great variety of archaeological samples [1, 2]. In the present work we analyzed ancient gold artifacts from different ages using an XRF portable system. Ten different types of gold samples were analyzed: earrings, pendants, figurines and clothing adornments. All samples analyzed are part of the gold collection of the Instituto de Pesquisa Histórica e Arqueologica do Rio de Janeiro (IPHARJ). The XRF analyses were performed using an XRF commercial system (ARTAX 200, Mo anode, 40 kV and 250 μA). The concentrations of Cu, Au and Ag were obtained from calibration curves obtained with gold standards of 24 k, 18 k, 16 k, 14 k, 12 k and 10 k. The results showed that the samples have different gold concentrations. Thus, it was possible to classify the samples with respect to gold purity (karat gold). Besides that, two samples were identified as Tumbaga, since their copper and gold concentrations were very similar to those found in the literature for this kind of alloy [3].

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Goa cathedral former altarpiece: a Portuguese feature? Material and technical assessment to the work of Garcia Fernandes, Portuguese painter from Lisbon workshop

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Goa Cathedral former altarpiece is one of the oldest set of paintings in India. The seven remaining paintings from the first altarpiece of Goa Cathedral, nowadays in the sacristy, are attributed by some art historians to Master Garcia Fernandes (act. 1514-1565), Portuguese painter from Lisbon workshop. The 16th century was the "Golden age" of Portuguese painting. In this context the Royal Lisbon workshop played a predominant role, where the activity of the royal painter Garcia Fernandes and his workshop can be distinguished. This painter stands out from the coeval artists not only for his particular pictorial technique but also as one of the few painters to be known for having produced works for India, as confirmed by his own testimony in coeval documentation [1-3]. His work is recognized by some art historians in the paintings that constituted the first main altar devoted to Saint Catherine, in Goa Cathedral. In this new research approach, these paintings will be studied and compared with other works in Portuguese territory attributed to Garcia Fernandes, as the S. Bartholomew altarpiece of Lisbon Cathedral.

Comparing stratigraphic technique with pigments, binders and ground layers using complementary microscopy techniques (μ-X-ray diffraction, Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy, μ-Confocal Raman, and Gas Chromatography and High Performance Liquid Chromatography coupled to Mass Spectrometry) will bring a new insight on the techniques and materials used and highlighting to the conclusion if Goa Cathedral former altarpiece is of Portuguese feature.

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Trading and stories behind a ***Bull's eye*** stamp: unveiling **the placement's authenticity of early Brazilian printed** stamps through *in-situ* spectroscopic analysis

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Although mail delivery systems date back to Antiquity, it was only during the 19th century that an effective solution was implemented to overpass the problems behind the payments of mail delivery, with the invention of the stamp. The first postage stamp (known as *Penny Black*) was printed in 1840 in the United Kingdom. The second country to introduce the use of postage stamps was Brazil, in August 1st 1843, with postage rates established for land and sea routes: 60 *reis* for a letter carried by land weighing up to 4 *oitavas* (around half-ounce), and double the land rate for mail carried by ship. The land rate increased at 30 reis increments for each additional 2 *oitavas* (quarteronce), and the sea rate increased at 60 reis increments [1]. For these first printed stamps, known as ***Bull's eyes*** for its resemblance to the animal's eyes, three values were printed: 30, 60 and 90 *reis*. For this, a Perkins-Bacon-style equipment was used, from which plates of 54 stamps were prepared, each plate comprising panes of 18 of each of the printed values [2]. The printing of ***Bull's eyes*** stamps ceased at the end of 1843, being than replaced by the *slanted numeral stamp* style [2].

The value behind the trading of primitive stamps is highly dependent on its conservation condition and on its original placement: if a primitive stamp is found in its original envelope, its prize increases expressively. This work involves the study of two Brazilian *Bull's eyes* stamps based on *in-situ* FTIR-ATR, μ-Raman techniques, and optical microscopy to evaluate the authenticity of its original placement. Some of the results here presented and discussed turned to be surprising, once the molecular information contradicted the statements of authenticity declared previously by some philately experts.

Figure 1. The Brazilian ***Bull's eyes*** stamps analyzed through *in-situ* spectroscopic techniques to evaluate the authenticity of its original placement.

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Colours and fibres in ancient Siberian textiles

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The Altai Mountains, situated on the Russian border with Mongolia and China, represent one of the most important archaeological sites concerning early Scythian nomadic cultures. Several excavations have taken place since Rudenko started in 1947-9. A series of burial mounds (*kurgans*) was revealed in exceptionally good state of preservation, as freezing occurred inside the barrows. In particular, large amounts of organic materials were found, including horse and human mummified bodies, the most ancient carpet ever found (the Pazyryk carpet, 4th century BC), as well as garments, saddles, rugs, jewels, ornamental and objects from everyday life [1, 2]. This confirmed the existence of an early nomadic culture in this region making efficient use of natural resources and developing a distinctive form of "Animal Style Art", including body art such as tattoos that are still visible on some of the human bodies.

In this work, performed in collaboration with the State Hermitage Museum of St. Petersburg, we present some preliminary results obtained by SEM-EDX and HPLC-ESI-Q-ToF. The techniques were applied to various textile samples from different Siberian archaeological sites with the aim of characterising the fibres and identifying the dyes. The textiles were taken from Arzhan, Chertomlyk, Pazyryk and Oglakhty *kurgans*. Their dates range from early 9th century BC to 4th century AD, thus offering the opportunity to compare the results over a significant geographical and chronological scale.

Cotton, silk, wool and felt were identified as the fibres used to produce the clothes, carpets, rugs, horse-trappings, *etc*. In most cases the wool was found to be consistent with that of Altai sheep [3], but the manufacture and the decorations were sometimes consistent with Asian regions or Achaemenid inspiration. Mixtures of dyes of plant origin (madder, indigo and tannins) and animal origin (cochineal, kermes, lac-dye) were identified, confirming different trade contacts for the Scythian Nomads. In addition, the frozen burial environment offers a rare opportunity to examine material preservation in terms of both structural (fibres) and molecular (dyes) changes that occurred in these specific conditions.

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Lixiviation pathways of metals in the Corten steel façade of the Euskalduna Palace

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Corten steel is a very used material, both from artistic and constructional point of view. Due to its self-protection capability, its use in outdoor public sculptures and structures (stairs, facades, balconies, etc.) is in vogue. This quality is achieved thanks to the addition of certain metals (such as Mn, Cu or Cr) to the alloy [1]. However, depending on the environment where the material is exposed, the self-protection capability can decrease, increasing at the same time the corrosion rate with its corresponding consequences. The most worrying affections, when dealing with art or architecture, are those affecting to the aesthetics of the artwork or the building, but also colored stains observed in the floor down to the materials.

In Bilbao city, Corten steel is a widely used material, being very representative of the city. Actually, several artworks exhibited in the river side are made of this material. Besides, one of the most emblematic buildings in Bilbao is the Euskalduna Palace, the concert and conference hall of the city, whose facades are made also of this material.

The present work is focused on the analyses of these facades to widen the knowledge about the behavior of Corten steel when using it in construction. To attain this aim, a field analytical study was performed using Raman spectroscopy and X-ray fluorescence portable devices.

The analytical data obtained on the water runoff areas, which are grey instead of reddish as the rest of the façade (Figure 1), showed systematically higher concentrations of all the alloy metals, especially Mn, Cu and S, in comparison with the areas of the façade not affected by water runoff. Moreover, there are some horizontal ledges where the water is accumulated; there, the XRF analyses revealed that the concentration of those elements is even higher. Raman spectroscopy elucidated that the lixiviation of metals is taking place due to their reaction with SO_2, since different sulfates were identified composing the grey areas. Finally, the analyses of the stains formed on the stone made floor revealed the enrichment on the same metals that are leached up to the floor, so that degradation of the Corten steel of the façade affects the aesthetics of the whole architectural complex.

Element (% w/w)	S	Cr	Mn	Fe	Ni	Cu
Reddish area	0.34-0.48	0.28-0.34	1.16-1.33	98.23-98.60	0.27-0.32	0.11-0.19
Water runoff	0.09-0.21	0.32-0.37	1.45-1.57	98.08-98.26	0.37-0.39	0.21-0.25

Figure 1. XRF in situ analyses on the water runoff and summary of the XRF results (% w/w) of the reddish and grey areas formed as a consequence of water runoff.

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Neutron and X-ray imaging techniques for the investigation of structures of pearls

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Natural pearls were considered precious and rare gems for many centuries, in comparison with cultured ones and imitation of pearls. As the cultivation techniques have improved, the distinction between natural and cultured pearls has become a challenging task and still an open question for gemologists.

All pearls are biogenetic structures, mixing inorganic and organic components and consist prevalently of calcium carbonate, in the form of calcite and aragonite phases, and of a minor amount of organic tissues and water [1]. For decades, the analysis of the pearls was mainly based on the X-ray radiography [2] that allows to visualize slight variations in X-ray absorption. However this technique has several limiting factors due to the instrumentation and to the intrinsic structure of pearls. Only recently, the X-ray computed micro-tomography was used to better reconstruct the inner parts of the gems [3-4].

In this study we analyzed a selected set of natural and cultured pearls by means of two non-destructive techniques: the X-ray Phase-Contrast Imaging (PCI) - performed at ID17 beamline, European Synchrotron Radiation Facility (ESRF) - and the Neutron Imaging (NI) - performed at ICON beamline, Paul Scherrer Institute (PSI).

PCI basically takes advantage of the phase shift that occurs when an X-ray beam passes through an object. This technique shows a better image contrast compared to the conventional X-ray attenuation-based imaging, especially for low atomic number samples, and so for biological samples (e.g. conchioline). On the other hand, neutrons are strongly absorbed by hydrogen and easily transmitted through metals, as a consequence NI gives complementary results respect to X-ray attenuation-based imaging. In this regard, neutrons could be a suitable probe in order to observe the various kind of pearls structures and differentiate organic tissues from inorganic carbonate phases and possibly disclose the origin of pearls in uncertain cases.

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Energy-resolved (4D) neutron tomography of natural and cultured pearls at a pulsed spallation source using a microchannel plate camera

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Neutron-based tomography is a non-destructive analysis technique with several advantages, such as the ability to distinguish among isotopes of the same element, the high sensibility to hydrogen and the penetration capability towards bulky materials.

The MCP (MicroChannel Plate) detector developed by Tremsin et al.[1] is a novel device capable to perform radiographies and tomographies with thermal and cold neutrons. The time- resolving pixel camera allows for energy discrimination of neutrons at a pulsed spallation source, and thus provides options for bulk microstructure and element mapping. The MCP consists of one ^{10}B-doped microchannel plate (8 μm pores on 11 μm centers) as neutron converter, followed by a standard glass MCP (10 μm pores on 12 μm centers). The charged particles produced in the first MCP produce an electronic avalanche in the following plate which is collected by the Timepix, a CMOS pixel readout chip developed at CERN. At present, small objects with a maximum size of 28 × 28 mm^2 can be analyzed, with a best spatial resolution of few tens of microns [2].

In the presentation, a brief explanation of the MCP detector will be provided, as well as its characterization with respect to efficiency, resolution and software post-processing. Furthermore, the performance of the MCP will be demonstrated with the analysis of natural and cultured imitation pearls , and the effectiveness of the new technique will be evaluated.

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FTIR and Raman spectroscopy determination of Japanese armour's material composition

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Japanese armour (Fig. 1), which has been a part of an important collection of the National Museum of Slovenia since 1961, consists of different parts such as helmet (*kabuto*), neck guard (*nodowa*), facemask (*menpo*), chest plate (*do*), armoured sleeves (*kote*), armoured shorts (*haidate*), etc. In this work, its material composition was defined by means of different microscopic and spectroscopic methods (optical microscopy, Raman microscopy, FTIR spectroscopy).

Figure 1. Japanese armour, property of National Museum of Slovenia. (Photo taken by Marko Habič).

As derived from the analysis of the stratigraphy of samples taken from this armour, the presence of several thin layers (usually at least six) and their composition suggest the classical Japanese armour manufacture. Thin paint layers (of about 20 μm) are applied on a classical ground layer [1], which consists of different clay materials (*i.e.* quartz, kaolin) along with iron-based pigment (hematite). *Urushi*, the significant resin, was detected by FTIR spectroscopy in almost every layer. The characteristic IR bands for *urushi* are placed at ~ 3400 cm^{-1} (OH stretching), ~ 2932 and 2960 cm^{-1} (CH stretching of aliphatic side chain), 1712 cm^{-1} (carbonyl band), 1630 cm^{-1} (C=C stretching within the benzene ring), 1457 and 1375 cm^{-1} (CH bending), and 1275 cm^{-1} (CO bending) [2]. Furthermore, the identified pigments characteristic of *urushi*, such as vermilion and carbon-based black pigments, were also found as main constituents of red and black layers, respectively. The challenge of utilising Raman spectroscopy in the detection of pigments was related to strong fluorescence emission, which probably has its origin in the presence of organic compounds building a distinct *urushi* work. In addition to the conclusions of the art history research, the identification of *urushi*, which is a resin derived from Chinese lacquer tree *(Rhus Verniciflua)* cultivated in East Asia, is another proof of the origin of the mentioned armour.

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Recent advances in XRF spectrometric analysis combined with Monte Carlo simulation for the non-destructive chemical characterization of museum metal collections

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Archaeological and historical metals often show a stratified structure composed by different superimposed layers that can be the result of: a) specific manufacturing techniques (i.e. gilding treatment); b) metal alteration during the burying as consequence of surface enrichment phenomena and/or environmental factors; and/or c) restoration-conservation works (i.e. application of protective layers).

The presence of these outermost layers prevents a good quantitative characterization of the bulk alloy, unless they are removed. Since the removal of these superficial compounds is not always admissible, the present work arises from the necessity to implement non-destructive methods to be applied in the chemical analysis of artifacts for which sampling or cleaning the superficial area is not allowed, such in the museum objects.

Following previous theoretical research [1-3], in this work a Monte Carlo simulation using the XRMC code package combined with EDXRF has been improved with the aim to characterize a collection of restored non-ferrous metals dated to the Islamic period (XII/XIII cent. AD) found at Mértola, Southern Portugal.

The analyzed artifacts were modeled as a two-layered structure formed by the corrosion layer and the bulk alloy. The Paraloid resin covering all the artifacts to protect their surface from corrosion does not contribute with characteristic peaks to the XRF spectrum, thus not having relevant influence in the simulation process.

The results proved that ED-XRF/MC protocol is able to reproduce the chemical composition of the deepest strata of the objects (i.e. bulk alloy), with no need of removing or cleaning the more superficial layers. The implementation of the ED-XRF/MC protocol used in this study, based on a commercial instrumentation such as an handheld XRF spectrometer for the spectra acquisition and a free available MC software package for processing the data, is undoubtedly a major advance in elemental analysis of archaeological artifacts, being able to establish itself as a versatile, fast and non-destructive quantification tool with a far-reaching applicability in the Cultural Heritage field.

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XRD, SEM/EDX and micro-Raman spectroscopy for mineralogical and chemical characterization of iron slags from the roman archaeological site of Forua (Biscay)

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This study deals with the mineralogical and chemical characterization of archaeometallurgical material from the Roman archaeological site of Forua (Biscay). The roman village of Forua corresponds to an iron production center of the 1st-4rd centuries AD and the distribution of the workshops, joint to the type of slags found there, indicates that correspond to a set of forging furnaces [1]. The Diputación Foral de Bizkaia funded the excavation of Forua site and the studied samples are stored in the Arkeologi Museoa at Bilbao (Spain).

Samples initially were analyzed by optical microscopy and X-ray powder diffraction in order to establish compositional groups of iron slags. The micro-textural, mineralogical and chemical features were analyzed using scanning electron microscopy coupled with electron-dispersive spectroscopy and Raman microspectroscopy. Three groups were differentiated; two of them correspond to forge slags, while the other group represents the ore materials that are composed by goethite and hematite. Iron slags are residues of the pirometallurgical process, varying in size, shape and chemical/mineralogical composition as a consequence of the technological process involved [2]. These two types of slags groups found in Forua, composed by iron-rich olivine and wüstite in a glassy matrix, indicate different stages in the production of iron from ferriferous sponge (Fig.1). The mineral and chemical association of the slags allows to determinate the different temperatures obtained during the metallurgical process [3].

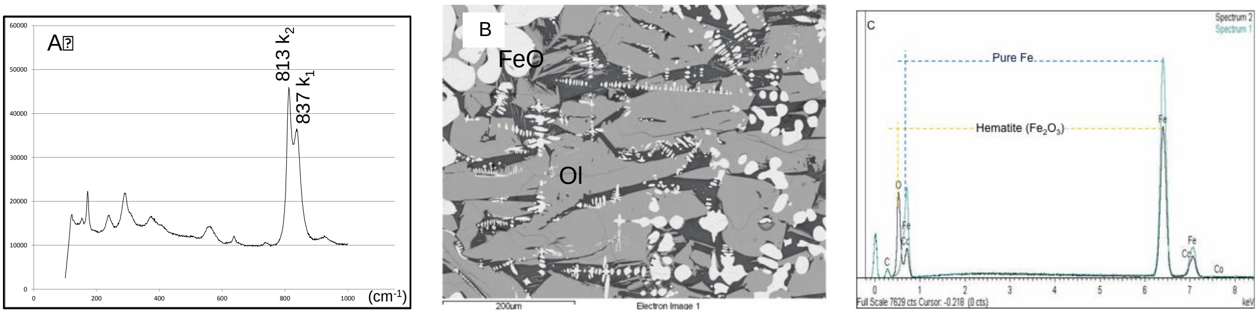

Figure 1. A: Raman spectra of olivine fayalite. B: Wuestite droplets (white colour) within olivine crystals (grey colour). C: SEM-EDX spectra.

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FTIR microscopy for analysis of treated archaeological wood samples

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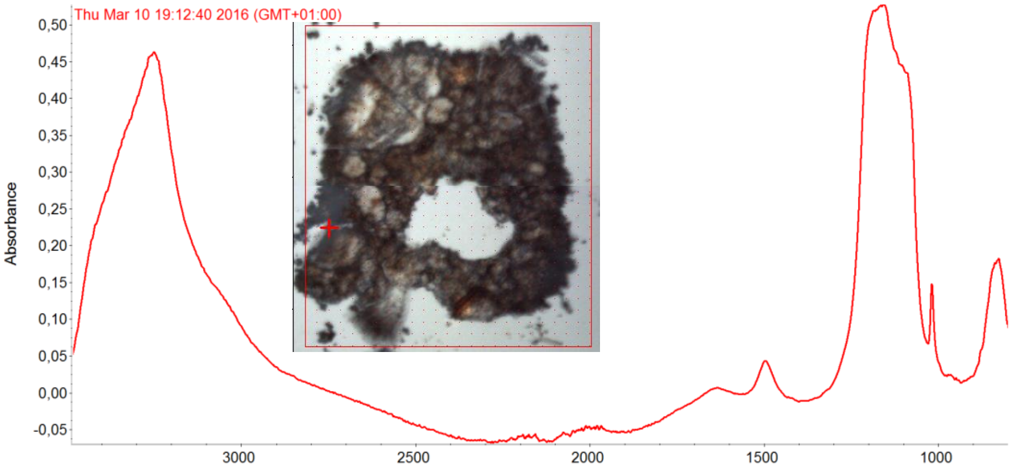
Artefacts from the Oseberg burial represent one of the most comprehensive collections of Viking Age wooden objects in the world. Upon excavation in the early 1900s, the more deteriorated waterlogged wood were conserved with alum ($KAl(SO_4)_2.12H_2O$), and then restored using various materials such as metal pins and screws, linseed oil and varnish. The resulting objects comprise a heterogeneous mixture of materials. Today, many of the objects are in alarming but variable states of decay. In order to elucidate decay mechanisms and to develop suitable preservation strategies, we are thoroughly characterising organic and inorganic components in a range of object samples [1,2].

Though acknowledged as a valuable tool in the characterisation of cultural heritage materials, FTIR microscopy has had limited application to archaeological wood to date. However, the spatial resolution achievable with FTIR microscopy, enhanced by the use of synchrotron radiation, proved particularly useful for analysis of these heterogeneous wood samples. In particular, we were able to identify compounds present as very small particles. Detailed mapping was used on small grains of sample to differentiate between particles of degraded wood, linseed oil and various inorganic salts present due to treatment and reconstruction. The identification of several inorganic salts was supported by complementary analyses using XRD and SEM-EDX.



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Dose-dependent effects of gamma irradiation on vegetable leather physical-chemical properties and structure

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The use of gamma irradiation as a method for mass decontamination of organic historical and archaeological items is highly desirable since ionizing radiation is universal biocide and assure large-scale and volume decontamination due to almost unlimited penetration. No residues, no induced radioactivity, no chemical and heat dependence are further advantages. The main drawback concerns with the possibility of irreversible effects on materials properties, i.e. colour, opacity, transparency, mechanical properties, chemical alterations, i.e. depolymerization, hydrolysis, crosslinking. The gamma radiation effect on vegetable leather is yet to be established. The aim of our study was to evaluate the dose-dependent effects of gamma irradiation on the structure, thermal stability and physical-chemical properties of vegetable leather at 6- and 12-month after the treatment. New leather samples prepared from calf, sheep and goat hides using mimosa-bark, chestnut-wood and quebracho-wood tannins were exposed to increasing doses of ^{60}Co gamma rays: 10, 25, 50 and 100 kGy. The doses were high so that the changes taking place could be more readily detected. Since alterations can be observed throughout the collagen's hierarchical structure we used a multi technique investigation [1-3] targeting the molecular (ATR-FTIR), nanoscopic (NMR MOUSE) mesoscopic (SEM and DSC), microscopic (imageMHT method) and macroscopic (contact angle measurement) levels of collagen. This approach has allowed us to integrate the data from different techniques and overcome the intrinsic limitation of each single technique.

The results indicated that effects depend on the radiation dose and are influenced by the collagen-tannin complex (e.g. tannin type and collagen species). In particular, a trend change was observed at 25 kGy for most measured physical parameters such as shrinkage T_s and denaturation T_d temperature, proton spin-lattice relaxation times T_1 and effective spin-spin relaxation times T_{2ef}. Surface properties, i.e. collagen fibers morphology and average contact angle values, showed significant variations at 50 kGy, while variations of both the amide I and amide II ratio and amide bands relative position were observed at 100 kGy dose only. Quebracho-tanned sheep leather shows to be the less resistant to the deterioration effect of gamma radiations, while mimosa-tanned goat leather was the most resistant. These results are of great importance for choosing safe parameters for future conservation applications of archival collections, upholstered furniture, ethnographic collections, etc. as well as for clinical and tissue engineering applications.

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A non-invasive in situ methodology to characterize the lacquers and metals from the *Edo period* Japanese armour

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Japanese armour is thought to have evolved from the armour used in ancient China and Korea. Cuirasses and helmets were manufactured in Japan as early as the 4th century and, centuries later, the complete Japanese armour was used for the battle. In the peaceful *Edo period* (1603-1869), the armour use was relegated to a symbol of the owner status. Armour continued to be worn and used in Japan until the end of the samurai era (*Meiji period*) in the 1860s, when the interest of the world collectors for these appreciate objects burst into. Few are the works dealing with the characterization of the materials used to create Japanese armours. Most of them are focused on the characterization of the helmet (*kabuto*) [1]. In this work we present the application of different portable instruments based on non-invasive spectroscopic techniques (Raman spectroscopy, infrared spectroscopy and energy dispersive X-ray fluorescence spectroscopy) to characterize the composition of the lacquers and metals/alloys used to create a Japanese armour from the *Edo period* property of the Armoury Museum of Alava (Basque Country, Spain). The armour was in situ investigated, for its later conservation, in the Restoration Service from the Provincial Council of Alava.

The *kabuto* and the cuirass (***d***) were made of at least 7 different materials. Regarding the metallic composition, both are made of iron, but the last one shows also a low percentage of copper in its composition. Among decorations, the greyish ones on the ***d*** and *kabuto* were achieved using tin, and the golden ones of the ***d*** were made of gold in some cases, and brass (3-4 parts of copper:1 part of zinc) in others. The decorations of the metallic strip (*kogai kanamono)* of the spaulders (*sode*) were achieved using copper, with a lower percentage of gold and other elements at minor/trace levels. The internal facing of the visor (*mabizashi)* of the helmet was made of iron with a red coloured lacquer, which includes cinnabar in its composition (*shu urushi nuri*). The direct analysis of the lacquered areas using Raman and infrared spectroscopy showed the presence of nitrocellulose lacquer, which was developed in the early 1920s. Thus, its presence can be attributed to a later intervention of the armour. Therefore, some lacquered areas were cleaned (around 1 cm) in order to remove the nitrocellulose layer. After that, and thanks to the infrared spectroscopy, it was possible to identify the black *urushi* lacquer. The elemental results also agree with the *urushi* use, since elements related with aluminosilicates (substrate of the *urushi* lacquer, *shitaji*) and iron (used as powder, to give the dark colour to the *urushi* paste) were identified.

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Canada's National Historic Sites and their contribution to Material Research and Cultural Heritage studies

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National Historic Sites of Canada are a great source of samples that bear information on the materials and technology of manufacture of the artefact/historic building which the samples are derived from. They correspond to a variety of materials that represent Canada's diverse past. The samples include architectural paints, organic residues, metals, indigenous artefacts, mortars which have been analyzed in order to collect the appropriate information for the cultural heritage professionals concerning the technology of manufacture, treatment, restoration, or historical documentation of the artefact studied.

The Conservation Science/Preventive Conservation laboratory at Parks Canada studies the artefacts' unique microstructure and composition with means of microscopic techniques, spectroscopic techniques (FTIR-ATR, Raman spectroscopy) and X-ray analysis (pXRF, SEM/EDX). The demanding analysis of the complete range of samples requires the knowledge of the analytical potentials of the techniques offered as well as the material science behind every object that is studied. In this way, conclusions on an artefact's materials, state of preservation or suitability of a technique could be reached.

Examples of analyses of artefacts that point out the aforementioned diversity of the collected results include the application of both FTIR-ATR and Raman spectroscopy as complementary techniques for the study of architectural paints. The results showed the former's limitation as a mixture analysis technique and the latter's powerful capabilities in the identification of both the inorganic and organic constituents of old paints. This may in turn cause a re-consideration on the popularity of FTIR in the identification of the paint's binder [1], [2] as well as characterize Raman spectroscopy as an indispensable tool in cultural heritage laboratories.

The 2015 discovery of HMS *Erebus* from Parks Canada Underwater Archaeology team, resulted in the exposure of objects that their study could shed light on the mystery behind the lost Franklin Expedition. Until now, the study of a glass medicinal bottle marked in embossed lettering "SAMUEL OXLEY" unveiled two of its components: arabic gum and potassium bicarbonate. Arabic gum was used as an emulsifier in a variety of products in the nineteenth century, including paint, food, ointments and creams. It was also part of every standard Royal Navy medicine chest together with potassium bicarbonate [3].

The use of spectroscopic techniques in the analysis of indigenous artefacts made of organic materials (baleen, sinew etc.) showed the difficulty in their identification. However, the use of more sophisticated instrumentation like GC/MS is not always possible, bearing in mind the complexity of the technique and the specialized knowledge that requires. Combined use of relative simple techniques widely used in Conservation Science laboratories may lead to the desirable result.

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Sourcing manganese-rich lumps from Middle and Upper Palaeolithic sites in South West France by external PIXE

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Lumps of mineral pigments are the more widespread archaeological remains found at Mousterian sites that may have been used by Neanderthals for symbolic activities. The analysis of their chemical composition is essential to identify behavioural consistencies in their selection, transformation and use, to reconstruct changes through time in these cultural practices, and discuss the emergence of symbolic cultures [1, 2]. In the Dordogne region of France, hundreds of black lumps, often bearing traces of intentional modification, were recovered at Middle and Upper Palaeolithic sites. A representative number of these lumps and samples from possible geological sources were analysed through external PIXE to precisely characterise their major, minor, and trace elements content. Preliminary multivariate statistical analyses, conducted by following methods proposed by Aitchison [3], identify trends in the geochemistry of both the manganese-rich geological samples and archaeological lumps. Once fully understood, the geochemistry of these lumps could allow us to make inferences on the cultural processes involved in the transmission of knowledge necessary for a long term exploitation of the outcrops where black lumps were collected by Neanderthal and modern humans, the criteria that influenced their choices, the manner and the aim the pigments were modified for, and the significance of these activities for those human societies. We also wish to investigate to what extent observed differences in behaviour may point to differences in landscape use, learning practices, social structure, and cognition. Gaining a better insight into the use of these materials will also be instrumental for comparing sites and reach a better understanding of how pigment exploitation may have changed at the Middle - Upper Palaeolithic transition [4-8].

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Potentiality of Raman spectroscopy for pearls characterization and authentication

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Pearls, with corals and shells, are "organic gemstones" often used for artworks and are by themselves objects exposed in museum collections. Red to pink corals, shells and pearls consist mainly of calcium carbonate in calcite, aragonite and vaterite forms. The pigments responsible for the colors are mixtures of methylated (carotenoids) or non-methylated polyenes with different UV-VIS absorption spectra and chain lengths [1]. The knowledge of the nature of the pigments in biogenic carbonates is of primary importance for a better conservation and for authentication purposes.

Raman microscopy is a powerful technique to identify both the inorganic phases and to define the nature of the organic pigments in corals, shells and pearls, especially when Raman resonance conditions are attained.

Here we report on an extensive Raman characterization performed on commercial natural and cultured (including freshwater and saltwater) aragonitic pearls from different geographic provenance (Japan, China, Australia, Tahiti) and with different shapes and colors.

Colored species show Raman frequencies typical of polyenic methylated or unmethylated chains. The nature of the pigments and the structure of the carbonate skeleton allow discriminating between freshwater and saltwater species and to recognize artificial or dyed pearls.

In this study particular attention is devoted to the comparison between the results obtained on pearls by portable and laboratory Raman equipments and on the resonance effects observed at different excitation lines (785, 632.8, 532, 473.1 nm).

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Protective effect of linseed oil varnish on archaeological wood treated with alum

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The Viking Age wood artifacts recovered in the early 1900s from the Oseberg mound and treated with alum, are today highly degraded, a condition attributed to the effects of the alum-treatment and of the reactivity of alum and derived salts [1]. Some of the artefacts from Oseberg collection which were treated with alum, were also coated by linseed oil. Although the linseed oil did not fully penetrate the wood in many cases, these artifacts appear to be better preserved with respect to those not treated with linseed oil regarding their visual condition.

In order to assess the effect of the presence of linseed oil on wood preservation, alum treated woods coated with linseed oil were investigated. Fragments were sampled at different depths from the surface. Three analytical techniques, giving relevant information about the molecular composition and state of preservation of both archaeological wood and aged linseed oil, were adopted: gas chromatography coupled with mass spectrometry (GC-MS), pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and high-performance liquid chromatography coupled to electrospray ionisation and quadrupole time-of-flight mass spectrometry (HPLC-ESI-Q-ToF).

Specifically, Py(HMDS)-GC/MS was applied in order to assess the state of preservation of the main wood components in the presence of linseed oil and the alum treatment, while GC-MS and HPLC-ESI-Q-ToF were used to perform the lipid characterization and to investigate the lipid degradation and oxidation processes.

The results showed that although the wood was highly depleted of carbohydrates [2], it was better preserved with respect to those artefacts not coated with linseed oil. Results from GC-MS and HPLC-ESI-Q-ToF together with those from Py-GC/MS suggested that the linseed oil played a mitigating role towards wood degradation. The behavior of the lipid material, more oxidized on the wood surface respect to the depth section, suggested that the selective oxidation of the oil instead of the wood components in the aerobic environment leaded to a better preservation of the material.

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A micro XRF study of the bronze statue of Poseidon of Livadostra at the National Archaeological Museum in Athens

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The bronze statue of Poseidon of Livadostra (fig.1) was recently reconserved in order to be exhibited at the jubilee exhibition "Odysseys" of the National Archaeological Museum in Athens [1]. The statue dates back approximately to 480 BC and is an indicative example of the transitional period from the late archaic years to the early classical ones. The statue was recovered from the sea at the end of the 19th century and had been conserved three times before the analysis. Prior to its recent conservation treatment, it was covered with corrosion products which can be attributed to both the museum environment and the past conservation treatments.

The micro-XRF study was carried out in view of the new exhibition of the statue using a customized model of the ARTAX portable micro-XRF spectrometer (Bruker Nano GmbH). The analytical investigation aimed to determine the composition of the original alloy used for the production of the statue and for the inlaid facial parts (eyebrows and lips), and if possible to identify the type of corrosion products.

The analysis of different clean and corroded areas on the surface of the statue helped to further advance and validate a global quantitative criterion proposed in [2] for the suitability of a bronze alloy surface to offer reliable compositional results. The results of the present micro-XRF investigation of Poseidon of Livadostra are discussed and compared with those obtained from other studies [3,4].

Figure 1. The bronze statue of Poseidon of Livadostra, National Archaeological Museum of Athens. © Archaeological Receipts Fund Photo by Galanopoulos, 2016

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2 step algorithm for the segmentation of varnish layers in OCT images of cultural heritage

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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.

In this study we present a methodology to segment OCT images of varnish layers of cultural heritage. These images contain information about layer thickness and stratigraphy. Manual segmentation of such image data is subjective and time consuming, therefore automated image processing is of great value. We developed a 2 stage algorithm, to this effect.

During the first stage, we apply graph cut based segmentation on the obtained OCT images. This segmentation method is adaptable and is applicable to different layer-substrate structures, but is prone to local errors when the object contains either delaminations, indentations or other damages. In stage 2 we correct for this artefact, by determining the attenuation coefficient (AC) of every pixel within the image. The AC is a material property and for a unique varnish layer the corresponding pixels have the same AC. Using this characteristic we resegment the image.

We analysed OCT images of different works of art such as; Paintings, furniture, photographic paper and lithographic prints. We established that the algorithm is capable of semi-automatically segmenting an arbitrary number of varnish layers, and it successfully deals with discontinuities in the objects. Our work shows the value of segmented OCT images for the preservation, conservation, and restauration of works of art.

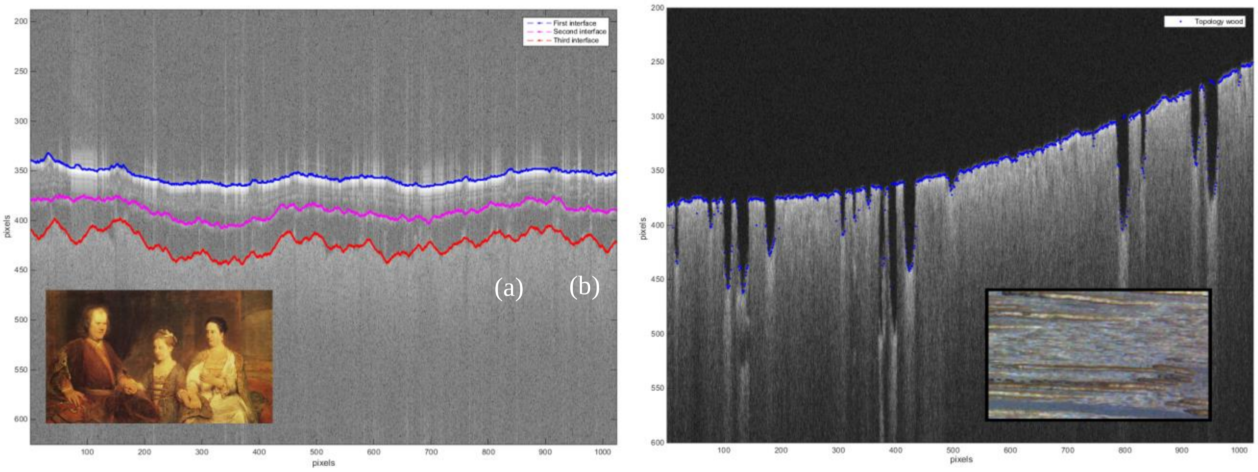

Figure 1. (a) 3 segmented interfaces in an OCT image. Dataset originating from Hermanus Boerhaave, Aert de Gelder. (b) Segmenting the topology of a wooden panel (historical cabinet backside)

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Research of Photographic Materials

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National Technical Museum holds a large collection of historical photographs, photographic apparatus and accessories. Photography is a relatively young art. In the past, the photographs were valued mainly for their informational potential, such as personal, family or social documents, rather than as an art worthy of protection. Currently, with the pictures dominated by digital technology, the classic photography became history and the subject of collecting of private collectors and museums. Physical and chemical analytical methods contribute to the identification of historical photographic methods and to the study of degradation processes running on historical photo materials.

Research focus of photographic materials has mainly the description of physical condition of photographs, their mechanical damages and the specification of photographic techniques. The studied photo materials on different type of underlays (glass, metal, paper and plastics) have been observed at first visually and then using a stereomicroscope. Observation gives a lot of information on the surface morphology, on the stratigraphy of layers, on the details of damage (for example cracks) and on corrosion products (e.g. efflorescence). Also, under the microscope, different types of prints can be distinguished. Elemental analysis of sensitive layers and their pads was done by using XRF analysis. Micro FTIR spectroscopy has been used for precise identification of material composition of pads, photo-sensitive layers and some of the colours used for picture colouring. This method can detect the presence of wax or other protective layers. FTIR and Raman micro-spectroscopy were also used successfully in the identification of degradation products on the photographs, for example after the damage caused by the floods in Prague in 2002.

To determine the historical photographic techniques, in many cases we combine several research methods mentioned above.

One of the tested collection items had been a herbarium, created in Prague in the second half of the 19th century by F. Fridrich, publisher and court photographer. The herbarium consists of 70 sheets – hand painted photographs of trees and flowers or groups of flowers, affixed on cardboards. This herbarium is in a good condition and some of its sheets are part of the permanent exhibition of the museum.

Albumen process has been confirmed in all photographs. Deep red colour (for example red roses) had been created by dragon's blood (a natural red resin produced by the rattan palm tree); green mineral pigments consisting of copper pigment and Prussian blue (or in a mixture with yellows) have been discovered in green and blue tones; also zinc white has been identified in a lot of hand painted photographs. The distribution of chemical elements from inorganic pigments and scattering of bonds characteristics for specific organic pigments or dyes have been documented by XRF and FTIR mapping in the area.

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Composition analysis of writing materials in Geniza fragments

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The Cairo Geniza is an "archive" discovered in the 19th century in Ben Ezra Synagogue in Fustat, a district in Old Cairo (Egypt), located south of the center of modern Cairo. The giant collection of mostly Jewish documents that vary in genres, languages and writing supports contains a large number of early medieval Hebrew manuscripts, mostly in fragmentary form. The larger part of the Cairo Geniza is stored today in the Cambridge University Library.

The Geniza provides sources for the literary, linguistic, historical studies of the various aspects Jewish life. As the documents attest, at least two Jewish communities co-existed in Fustat up to 11th century: a so-called Babylonian and Palestinian. These communities had different leaders, different traditions and lived independently. The differences seem to manifest themselves also in the paleographical, codicological and some material properties of the manuscripts produced by each community.

My work addresses the ink composition in the documents attributed to the members of these communities. For the determination of the inks type and composition I employ reflectography and μ-XRF spectrometry, respectively. The preliminary typological studies indicate that iron-gall inks were found predominantly in the manuscripts attributed to the Palestinian community.

FUTURAHMA: an online non invasive spectroscopic database of modern art materials by Lefranc

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The study here presented deals with an early 20th Century *nuancier* from the renowned French paint manufacturers Lefranc: a catalogue containing 144 handmade coats of oil colors on paper. This unique collection of organic and inorganic pigments covers a wide range of colors from greens, reds, yellows, blues, blacks, browns, oranges, to violets, with the only exception of whites.

The *nuancier* was accessible to the Italian Project FUTURAHMA (Futurism: Research Art History and Material Analysis) for performing non invasive analysis by complementary spectroscopic techniques.

The 144 colors within the *nuancier*, which can be considered an ideal, naturally aged sample, were non invasively investigated in the wide spectral range from X-ray to medium infrared. Atomic composition by X-ray fluorescence was complemented by molecular FTIR and UV-vis-NIR spectroscopies revealing not only the nature of the pigment composition, but also the presence of supplementary additives and/or residues of the commercialized paint formulations. The study of the binder performed by FTIR indicated essentially the use of a lipidic medium, substituted or improved by other organic compounds for some pigment formulations.

The whole dataset is a unique collection of spectroscopic data on historical reference materials available on the Futurahma website (http://www.futurahma.it). The website, proposed and created within the project, aims to present and disseminate the most relevant results of the research. A high-resolution viewer (powered by IIPMooViewer and IIPImage server), developed with open source technology, which uses tiled pyramidal TIFF images allows the visualization of high quality images with an extremely rich detail, even with normal speed connections, through the assemblage of high-resolution files. The high resolution images of the Lefranc *nuancier* are enclosed with the spectroscopic data that are freely consultable and downloadable as text files.

Silver coins from the Spain Independence's War minted in Catalonia Region: Legal and counterfeit coinage

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We studied, by means of energy dispersive X-ray fluorescence (EDXRF), silver coins minted during the War of Spanish Independence in Catalonia region (NE, Spain). In a previous work [1] a collection of 130 coins of this period existing at the Catalonian Numismatic Department (GNC) of the National Museum of Fine Arts of Catalonia (MNAC) were examined and the main compositional features of the each minting factory were established. Now, complementary research for the characterization of counterfeit coinage has been carried out.

Energy dispersive X-ray fluorescence (EDXRF) has been extensively applied in Numismatics since the relationship between the chemistry of the alloys, the economic situation of the mintage period and the differences between minting factories are subjects of interest for archaeologists, conservators and historians. The possibility of furnishing data to distinguish original and counterfeit alloys of coinage is another useful application. Likewise, using the adequate software [2] in the spectral data treatment, it is possible to determine both the layer thickness and its composition and the composition of the alloy in the substrate, in a simultaneous way.

Two different counterfeiting manufactures have been recognized: a) the reduction in the silver content in massive coins, and b) coins of low cost alloys with silver coatings to simulate the legal ones. Three main different alloys have been identified (bronze, brass and Sn-Sb alloy). Silver-based coating thicknesses are in the range from some tenths of nanometers up to 7 microns. Coatings are mainly produced by amalgamation and mercury can be found in some coins with a very high content.

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PXRF for the characterization of metals used in the Fountain of the New Waterfall. La Granja de San Ildefonso Royal Palace, Segovia (Spain)

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Non-destructive and portable analytical techniques are gaining great importance on artistic and cultural heritage research [1]. The use of portable X-ray fluorescence (PFRX) has allowed the elemental quantification of the metals of the New Waterfall Fountain located in *La Granja de San Ildefonso* Royal Palace, Segovia (Spain), which belongs to the National Heritage.

The Fountain of the Waterfall was completed in the 18th century and occupies an important place in the layout of the palace gardens. It is formed by 10 pylons aligned to different levels that constitute the waterfall itself and that pour the water to the larger pylon pond located in the bottom part. Which has in its center a statue that represents the goddess Amphitrite, sitting on a cart pulled by four dolphins designed to be water spouts. Each pylon is lined with ornamental stone slabs anchored with metal elements.

This fountain has suffered different interventions throughout its history. The first restoration finished in 1872. Small maintenance works were carried out at the end of the 19th century. Further repairs were necessary in 1922 and small maintenance interventions continued in subsequent years. Therefore, the current New Waterfall Fountain is not a work of the 18th century or a creation *ex novo* of the 19th, but a mixed work that brings together components of different interventions, which makes difficult its restoration.

Previous studies for the Fountain restoration were initiated in 2016. A NITON SERIES XL3t portable x-ray fluorescence detector has been used to identify metals. This technique of elemental analysis is non-destructive and fast [2]. It has allowed to identify and to semi-quantify the metallic elements and also to establish their evolution in the different epochs.

Copper cramps and dowels, which were then anchored with molten lead, were used in the restoration completed in 1872. In the restorations of the 20th century, dowels are composed of a Cu and Zn alloy, there are also dowels of Fe; and in the most recent restorations, dowels of stainless steel (SS 316) have been used.

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Use of Metal Nanoinks for Surface Enhanced Raman Spectroscopy (SERS) Investigation of Dyes in Felt-tip Pens

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Since their initial fabrication, felt-tip pens have been increasingly used for original and creative artworks. Their low cost, novelty, easy availability and use as artistic medium have attracted numerous artists and, currently, a varied range of markers-based works of art on different substrates (as paper or wood) is displayed in museums or private collections [1]. However, there is an increasing concern about the preservation of these artworks because they present challenging conservation issues since felt-tip pen inks can fade, show severe deterioration and changes in appearance in a few years [2]. Moreover, dyes and pigments in inks can be difficult to identify because their heterogeneous formulation, often protected by patent, include also other components in the mixture such as solvents, stabilizers, plasticizers, surfactants and other additives. Still few research works have been carried out in order to address these issues and identify inks components, and most of them include chromatographic methods often coupled with standard spectroscopic techniques. In this frame, Surface Enhanced Raman Spectroscopy (SERS) can represent a valuable alternative when mass-limited samples, in situ applications and locally selective dyes identification are required [3, 4]. In particular, SERS can be very efficient if the emerging use of plasmonic nanostructured inks is considered [5].

In this work we present the use of gold nanorods and silver nanoparticles based nanoinks as metal substrates for the SERS analysis of felt-tip pens on paper samples. Marker pens of different color and brand have been applied on commercial A4 paper and analyzed at 514 nm wavelength. Microscopically amounts of metal nanoinks have been put on the colored samples in order to get the SERS effect, allowing the collection of useful information on dyes identification. Comparison between Normal Raman and SERS spectra showed high enhancement factors attributed to an electromagnetic effect generated by the use of metal nanostructures. Gold and silver nanoinks resulted differently effective in the identification of specific dyes. Phthalocyanine-based dyes have been identified in blue and green markers while Rhodamine-based dye in red and pink ones.

Moreover, original markers used by the famous movie director Federico Fellini, who realized in his life numerous drawings between 1960 and 1990, have been analyzed. The analysis of the brand-new reference marker pens helped in the identification of dyes in Fellini's original markers and gave some indications on their conservation state.

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A micro-invasive study of a 15th century Armenian manuscript from Matenadaran Museum

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This contribution presents preliminary results from the diagnostic study of a 15th century Armenian illuminated manuscript held in the collection of Matenadaran ancient manuscripts Museum, in Yerevan (Armenia). The manuscript was produced in a scriptorium at Aghtamar Island, in the Vaspurakan region of historic Armenia. Fifteen small fragments (mostly < 1 mm) were taken from the manuscript, selecting them in order to cover all hues present. The fragments were analyzed by means of microscopic techniques in order to characterize the overall palette used by the artist for the miniatures and to have diagnostic information on the history of the manuscript itself. Considering the extremely limited size of the samples, it was mandatory the use of techniques able to work under the microscopic scale in order to obtain reliable information. The techniques used were therefore Raman spectroscopy, Surface Enhanced Raman Spectroscopy (SERS), Scanning Electron Microscopy - Energy-dispersive X-ray spectroscopy (SEM-EDX) and HPLC-mass spectrometry. In addition, UV-Visible diffuse reflectance spectrophotometry with optic fibres (FORS) was used on the samples to have a preliminary identification of the colourants.

The combination of molecular (Raman, SERS, FORS, HPLC-MS) and elemental (SEM-EDX) techniques allowed the characterization and identification of hues used in miniatures. Natural ultramarine blue, indigo, cinnabar, minium and orpiment were the main pigments identified. Green hues were obtained with a mixture of indigo and orpiment, the so-called *vergaut*. Particularly relevant was the identification in black areas of irongall ink, a colourant mostly used as an ink but in this case used as a pigment for black, as it was typical of early medieval artists. In addition, FORS analysis highlighted in the brilliant red samples the presence of a dye from scale insects, which could be attributed to one between kermes, Armenian or Polish cochineal and lac dye. Work is in progress in order to identify the right colourant by means of SERS analysis and HPLC-MS analysis.

Interesting information was obtained from the restoration point of view also. In fact, Raman analysis highlighted the presence of 20th century pigments such as phthalocyanine blue and Naphthol Red, clear indications of a contemporary restoration intervention.

Despite the very limited size of the samples, it was possible to obtain a large amount of information useful for the artistic, historical and conservative overview of the manuscript.

The Francisco Pizarro's Banner of Arms: a multi-analytical approach contributing to Latin America history

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The authenticity of the so-called Francisco Pizarro's Banner of arms stored at the National Museum of Colombia in Bogotá has been the subject of intense debate amongst historians and conservators for the last two centuries (Fig.1). The banner was transferred from the cathedral of Cuzco in Perù to Bogotá in 1825 by General Antonio Jose de Sucre during the military campaigns against Spanish rule. General de Sucre was the first person to associate the banner with the arrival of Francisco Pizarro in the New World. In order to provide for the first time analytical evidence on the material used for the making of the banner and to support its authenticity, a set of 25 micro samples from different areas were collected and characterized by Optical and Scanning Electron Microscopy and Energy Dispersive microanalysis (OM, SEM-EDS), High Performance Liquid and Chromatography Mass Spectrometry (HPLC-MS), Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC-MS) and Raman Spectroscopy. Seven samples were also analyzed by Accelerator Mass Spectroscopy (AMS) for radiocarbon dating. Results obtained allowed to identify as silk the textile used in the elaboration of the Banner's fabric, as well as the use of natural dyes for dyeing the fibers used on the emblem: use of cochineal and brazil wood as a source of red, luteolin plant-based for yellow color, indigotine plant-based for blue, and a mixture of yellow and blue dyes for green were identified. Similarly, animal glue and rag paper were also used in the manufacturing process. The metal threads study from the Banner confirmed the use of a silver core wire gilded with a thin gold sheet, being flattened and entwined with silk threads (Fig. 2). The AMS results indicated a Banner manufacturing date between the XV-XVI century with restoration interventions with the addition of new textile materials in modern times. The analytical results are consistent with the hypothesis of a European manufacture at the time of the conquest process of the New World by the Spanish Crown.

Figure 1.

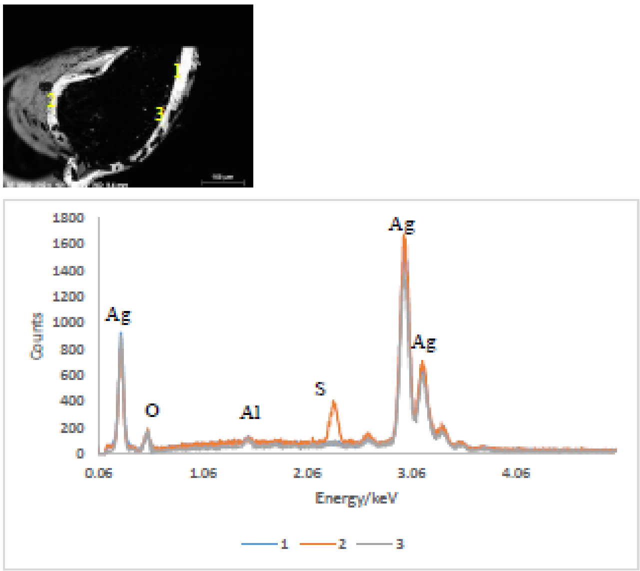

Figure 2.

The “Bacile della Nereide”. Non invasive P-XRF and XRD investigate an outstanding paleo-byzantine silver basin

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The “Bacile della Nereide” from Gualino collection (Galleria Sabauda, Torino) holds a relevant role within paleo-byzantine jewelry. This particular basin - carrying a number of four control stamps on the back, which allowed to collocated its production in Chartage around 541 AD [1] - is considered one of the few examples of the north-African roman production under the Vandal control [2].

The diagnostic campaign, based on portable X-Ray Fluorescence (p-XRF) and X-ray Powder Diffraction (XRPD) was carried out in parallel with a delicate conservative intervention performed in 2011-2012. The front of the basin was in effect covered in heterogeneous patinas partly hiding the delicate details of the Nereid image, while on the back a wide area showed evidence of a past integrative intervention and a thick crust recovered the majority of the plate.

The analyses addressed the characterization of a) the degradation and alteration products and b) the materials constituting the original alloy and the past restoration, i.e. the soldering and integration alloy. PXRF and XRPD were performed directly on the basin and on samples of the alteration materials provided at the end of the cleaning process. Compositional results obtained on the basin were compared with data produced on analogous artifacts, that is the “Plate of Gelimer” and the “Plate of Venus and Adonis” from the Cabinet des Medailles (Bibliothèque Nationale, Paris) [3]. Attention was given to the silver enrichment issue [4, 5] according both to literature and experimental research.

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Surface silver-enriched layer of ancient silver coins studied by means of micro-PIXE

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The analysis of ancient silver coins has been carried out by our group since few years using non-invasive techniques, analysing their chemical composition in correlation to their chronology and provenance [1,2]. In objects like coins made of a silver-copper alloy, the presence of surface silver-enriched layer is quite common (papers in literature have already discussed the topic [3,4]) and, for this reason, some coins have been sectioned to study their microstructure and especially to assess the presence or absence of corrosion layers, enriched layers and inhomogeneity between surface and bulk. Coins presented here are victoriati and quinarii minted by the Roman Republic between II and I century B.C. and Illyrian drachmas.

Micro-PIXE measurements were carried out on cross-sections at the AN2000 microbeam facility of INFN-LNL, using 2 MeV protons. The beam was focused to a spot size of ~5 m and raster-scanned over the samples both on parts close to the surface and in several areas of the bulk. Quantitative analysis has been carried out by means of the Gupixwin software.

The presence of a very thick surface silver-enriched layer (up to 250 m) has been detected on the Illyrian drachmas and victoriati, confirming recently published data [5], whereas quinarii do not appear to be affected by this phenomenon. Profile measurements carried out on victoriati show that silver content is clearly higher in the surface layer, suggesting an intentional depletion occurred with acid chemicals before minting operations [3]. The most interesting results, however, concern the distribution of minor elements along the section. Elements like chlorine and iron, commonly present in soil and water, are detected mainly in the silver enriched layer close to the surface and can be therefore linked to alteration phenomena due to the bury conditions. On the other hand, gold is clearly linked to silver, as it appears mostly present in the silvery layer. Nickel and zinc seem, on the contrary, to be correlated to copper, since their presence is concentrated in the bulk.

In conclusion, the strong different elemental distribution between surface and bulk implies that compositional analyses carried out with surface techniques on untreated surfaces on silver-copper alloys are not reliable to provide fineness of ancient coins.

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Evaluation of handheld X-ray fluorescence spectroscopy results of Roman copper alloy brooches by using archaeological typology

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As part of the Late Roman research project in Belgium and the Netherlands [1], 187 Roman copper alloy brooches were analyzed by means of handheld X-ray fluorescence (hXRF) spectroscopy in order to explore the relationship between composition, production organization and change over time.

The selected brooch type is called 'the crossbow brooch', which is an artifact that is closely associated with the Late Roman elite, frequently occurring in many portraits on mosaics, sculptures and fresco's from the 4th to the 6th century. The biography of the crossbow brooch, however, starts in the 3rd century as a simple military object and develops into one of the most significant symbols of Roman state authority in the 5th and 6th century.

The hXRF spectrometer provided a non-destructive, mobile, quick and inexpensive way of analyzing these brooches that were part of valued museum and archaeological collections. The samples were selected to cover the entire chronological, geographical and stylistic variation of these brooches in the study area. Each object was measured in three to five locations to compensate the heterogeneity of the copper alloy and the geometry of the object. The compositional results revealed a continuous variation that crosses copper alloy boundaries with no evident groups or trends, as is often the case for archaeological data sets.

To move beyond a black box approach that provides little insights, the typological information was added to interpret the compositional data. An archaeological typology is constructed based on observed variations that represent expressions of choices made by craftsmen and workshops. In other words, typology contains information that can help explain compositional variation caused by different manufacturing techniques or production centers, changes in consumer demands, as well as factor in aspects of chronology and regionality.

Consequently, the division of the compositional data in the six types of crossbow brooches allowed distinguishing patterns that indicated changes in production organization related to social context. The combination of typology and compositional data allowed to characterize the different phases in the crossbow brooches' life history, which in its turn contributed to the larger narrative of the rise to power of the military elite in the Late Roman period.

[1] N. Roymans, S. Heeren, W. De Clercq. Social Dynamics in the Northwest Frontiers of the late Roman Empire, 2017.

Advanced Codicological Studies of Codex germanicus 6

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The Codex germanicus 6 that contains twelve different texts is an excellent example for a manuscript with a complex history. It is a plain 614 pages long manuscript without illuminations, it was created around 1450. Most of the twelve different texts are composed in Middle High German. The whole manuscript has been written and rubricated by a scribe who names himself Jordan of whom little else is known - for his personal use as he conveys in two colophons on page 365 respectively 560. Combining classic codicology and material analysis we were able to reconstruct the production process of this codex.

In five measurements campaigns we used line µ-XRF scanner (Artax 800, Bruker Nano GmbH) and imaging µ-XRF (Jet Stream, Bruker Nano GmbH) to fingerprint the black iron-gall and red inks throughout the manuscript. Well defined composition of the iron gall inks allowed determining the text units copied by the scribe. The red inks, however, displayed a rather heterogeneous distribution that could be well understood with the help of high-resolution imaging XRF. The scribe used pure cinnabar and adulterated cinnabar inks during some 3-4 years required for copying the texts. Every time after finishing a text unit he would go through the manuscript making corrections in rubrications and over-colouring the initials. Since he always used red ink at hand the final ink composition resulted from a multiple correction process as shown in fig. 1.

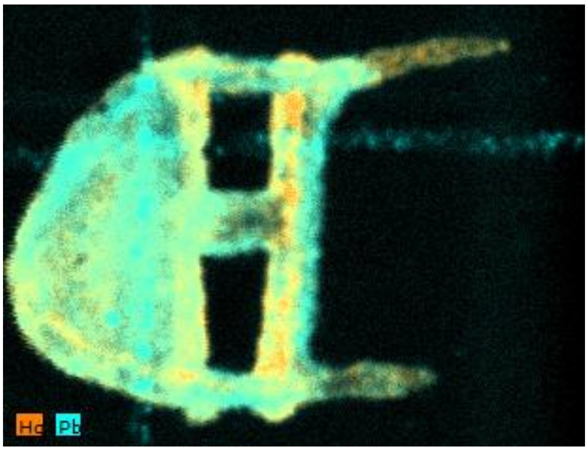

Figure1. Distribution of the elements mercury (Hg) and lead (Pb) in the initial from the page 2

[1] I. Rabin, O. Hahn, M. Geissbühler, manuscript cultures 7 (2015) 126-131.

Modern inks: investigation of felt-tip pens

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(3) Paper conservator, 11 rue de Bellefond, Paris (France).

Inks of felt-tip pens are used by modern artists for the realization of sketches, drawings, copies, architectural drawings and other technical designs. However, these inks are usually very sensitive to light and chemical agents and the exact knowledge of their composition may be important to define the optimal conservation treatment and/or storage conditions. So far, few studies have been addressed to the chemical characterisation of these materials [1] and often information on binders, fillers, dyes and pigments is lacking.

In this study felt tip pens (Faber-Castell) used by the French modern artist Anne Flore Cabanis (Fig. 1) and other artist pens (Stabilo) were investigated by using an integrated analytical approach. The inks have been analysed with Fourier transform infrared (FT-IR), μ-Raman and visible reflectance spectroscopy, and pyrolysis - gas chromatography - mass spectrometry (Py-GC-MS). The Raman spectra of the Faber-Castell inks clearly show the presence of phthalocyanine, dioxazine and azo pigments. The Stabilo inks, instead, contain mixtures of dyes as evidenced by thin layer chromatography (TLC). Surface-enhanced Raman spectroscopy on the TLC spots allowed to identify triarylmethane dyes [2], rhodamine B and tartrazine. (Py-) GC-MS and FTIR spectroscopy provided data on binders, solvents and additives and confirmed the identifications of the pigments and dyes.

Figure 1. Anne Flore Cabanis, *Couleurs*, Ink on paper, 2013

Since the photosensitivity of this type of inks is usually very high, a preliminary investigation on accelerated ageing on some ink samples was carried out. Spectroscopic techniques were used for the monitoring of photo-degradation.

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[2] Y. Cheng Ho, W. W. Y. Lee, S. E. J. Bell, Analyst 141, 2016, 5152.

SEM-EDX and optical microscope study of bronzes with high tin content: **characterization of ‘bell metal’**

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Bells are made of a particular bronze composition with relatively high tin contents, frequently in the range of 20-25 wt.% Sn. Other elements might be present in small amounts, such as Pb. This bronze composition has been named ‘bell metal’, and has particular characteristics which makes it advantageous for the bell production, such as superior sonorous qualities.

Bronzes with this composition are characterized by a microstructure with two main phases, the alpha (solid solution of tin in copper, <15 wt% Sn) and delta (~32 wt% Sn), being that the delta phase can be present in higher quantity (relative volume) than the alpha phase. Depending on the cooling rate and on subsequent events to solidification, such as thermal or mechanical actions, the microstructure can present specific features that allow the inference of these events. Also, objects that were subjected to adverse environments during long periods of time will be affected by corrosion.

In the present work we will explore the use of scanning electron microscopy with X-ray microanalysis (SEM-EDX) and optical microscopy for the microstructural and elemental characterization of various remains of ‘bell metal’. These include a bell from an historical shipwreck affected by a fire, a medieval bell, and the metallurgical remains of two foundry areas for bell production that were uncovered during archaeological works. All bells and fragments were recovered in the Portuguese territory, one underwater and the others on land, and were all affected by long-term corrosion which developed with particular features depending on the microstructure, besides the environmental conditions of exposure.

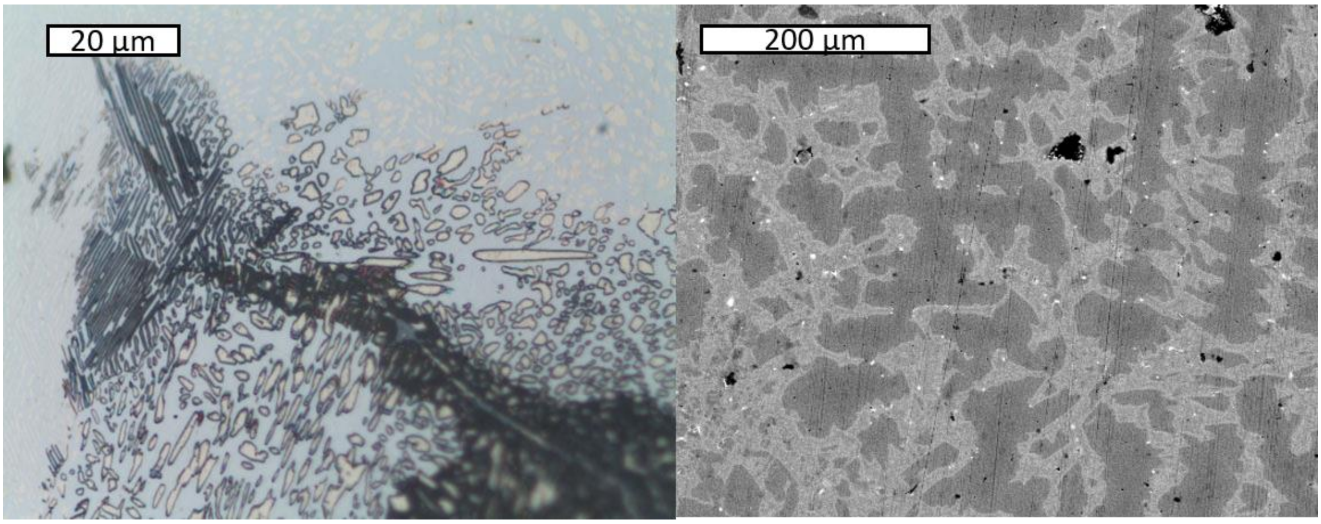

Figure 1. Details of the microstructure of studied ‘bell metal’ fragments with Sn contents in the 20-25 wt.% range. At left an optical microscope image showing intergranular corrosion (in black) that reveals the boundaries of alpha and delta phases. At right a backscattered electron image from SEM-EDX revealing the alpha phase coarse dendrites surrounded by the (alpha+delta) eutectoid and scattered small globules of Pb (in white color).

The new dynamic positioning system of the LABEC XRF scanner for the diagnostics of non-planar CH samples

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Diagnostics referred to Cultural Heritage (CH) is a well-established research field. Among all the techniques for CH diagnostics, X-Ray Fluorescence (XRF) imaging is one of the most used because it allows for non-invasive, non-destructive and *in situ* analyses, providing elemental distribution maps which can give crucial information on the composition of the whole analysed area. XRF analyses, both in single point and in imaging modes are normally constrained to flat, planar surfaces. This is particular relevant in the CH field, since most of the artworks do not have such structure, owing to artwork manufacturing, or aging, and/or degradation phenomena. In addition, should the scanned surface exhibit irregularities or deformations, while scanning the measuring head might scrape against the artwork, which might be irreparably damaged. To overcome this limitation, thanks to the collaboration with the NYU in Abu Dhabi, the LABEC XRF scanner was equipped with a dynamic positioning system, based on a laser telemetry sensor, to automatically keep the head-to-sample distance constant (~6mm) during the scan.

In order to evaluate how deviations from the proper working distance affect the elemental distribution maps, tests were carried out on two different typologies of CH non-flat-surfaces samples. The effectiveness of the tracking system has been successfully demonstrated by comparing results obtained with and without the tracking system. The first studied artwork is a *"Madonna con Bambino"*, a wood panel enriched with a three-dimensional application: the Virgin's head and halo are painted on a panel inclined up to 5.5 cm. The second artwork is an illuminated parchment (ca AD 1340), with uneven and undulated surface, with deformation up to 2 cm (in red Fig.1), a case by far more difficult to be properly coped with than the previous.

The tracking system actually extends the XRF scanner capabilities. Indeed, now analyses can be performed for a wider range of non-planar sample geometries, with improved data quality and no risks for the analyzed works.

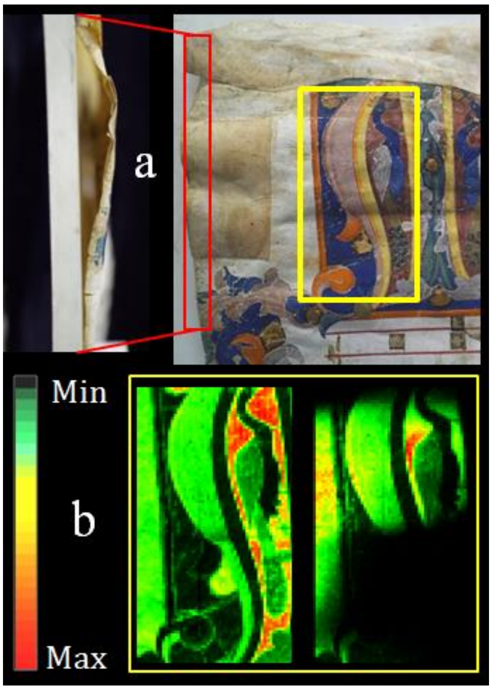

Figure 1. a) the lateral and frontal images of the parchment, highlighting the extent of the deformation; b) the Ca elemental maps of the same area of the illuminated letter, acquired with (left)

Villa de Noheda (Cuenca, Spain): a multi-analytical approach for mortar characterization

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The Roman architectural ensemble of Noheda, known by the fantastic dimensions of the tile panels have been classified as Cultural Heritage in 2012 and open to the public since 2015. Located at 500m of the homonymous village in Spain, corresponds to a roman *Villa*, dated from 4th to 5th century, which evidences an agricultural use trough a constructive complex with several functions.

Until now there are two exhumed areas of the rural complex: some structures belonging to the *pars rustica* and on the other hand, a sector of the *pars urbana*, composed of some balneary outbuildings and various rooms of the residential building. It is in this last one that stands out the so-called Triabsid Room, not only for its imposing dimensions of 290.64m^2, and its extraordinary pavements, but also for its complex architectural articulation and its careful walls decoration composed by marble plaques and mural painting.

Under the framework of a bilateral Iberian project, several mortar samples were analysed for their compositional and textural characterization. The studied mortars cover a wide spectrum of architecture contexts (*triclinium* and its access areas, octagonal room and baths), inside and outside walls, and also later added walls. The data acquisition techniques consisted of X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy coupled to energy dispersive X-ray spectrometry (SEM-EDS) and thin-section optical microscopy.

The mortars are mainly composed by quartz aggregates, with semi-angular to semi-rounded grains, and very small amounts of K-feldspars. A generalized feature is the presence of numerous lime nodules, sometimes of centimeter-size, with calcitic composition. Lithic, ceramic and coal were occasionally observed. According to XRD analyses, the raw materials are very similar between samples suggesting a similar provenance, probably a river sand. The binder is an aerial calcite lime that was used mainly with a binder:aggregate ratio of 1:2 as determined by TG-DTA. The mortar from the baths have a smaller amount of binder (1:4) as well as an external wall (1:3) interpreted as a late enlargement after abandonment of the *Villa*.

The results obtained point out to a considerable similarity not only at the level of the raw materials but also in the production technique used in the different areas of the residential building of the *pars urbana*, which would not have been altered in subsequent interventions. Differences were found only for the different functionalities; whether in the baths or when dealing with external walls.

SEM-EDS characterization of hard soldering with copper-tin alloy of Roman handle attachments from *Conimbriga* (Portugal)

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Hard soldering or brazing with Cu-Sn alloys applied to copper based artefacts has been used at least, since the Greek Period, although scarce studies have been made about their compositions. H. Lechtman and A. Steinberg [1] reported the rarity in finding hard soldering in ancient artefacts. Nevertheless, this kind of joining technique was important in Antiquity and should have been widely used during Roman times. Several solder vestiges were reported to be found in a collection of handle attachments of *situlae* from the archaeological site of *Conimbriga*, an important city in the Lusitania Province (Portugal) [2]. In the present work we are investigating the fusible metallic alloy present in 10 artefacts, which were cast in high leaded coppers and bronzes and previously studied [3].

Scanning Electron Microscopy with Energy Dispersive X-Ray (SEM-EDS) microanalysis and Optical Microscope observations were made along the solder vestiges. Results point out to a standard composition around 60:40 wt.% of Cu:Sn, with Sn contents close to ε phase composition. Also, two features have been found a) melting of the interdendritic Pb-rich chains with long range diffusion of the solder alloy into the substrate and b) the etched surface of the solder/substrate interface showed an intermetallic phase (δ phase) resulting from high temperature Sn diffusion into the substrate.

Hard soldering alloys analysed exhibited rather homogeneous compositions in the opposite to the observed for the artefacts. These present rather diverse alloy compositions, apparently resulting from a poor control in the artefacts production [3]. Further studies should be made to better understand this process.

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[2] Delgado, M. Conimbriga, IX, 1970. 15–43.

[3] F. Lopes, R. J. C. Silva, M. F. Araújo, and V. H. Correia, Materials and Manufacturing Processes, 2017, in press.

Lead provenance of Late Republican Roman artefacts from an archaeological military camp in Portugal

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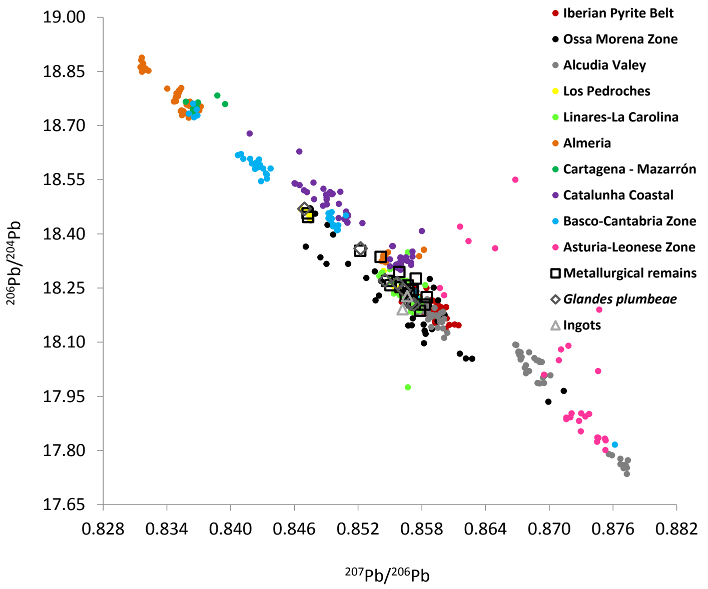
The interpretation of Pb isotope ratios is a very important tool to assess the provenance and trade routes of lead artefacts rather widespread over the roman world. As well-known, the mineral deposits have characteristic Pb isotope ratios distribution that do not change during the metallurgical processes and remaining identical on produced lead artefacts. Thus isotope ratios can be directly associated to a particular/distinct ores, being similar whenever submitted to identical geological processes.

In the present study 29 roman lead artefacts were analysed by ICP-MS to determine Pb isotope ratios. Artefacts collection include seven *glandes plumbeae*, two probable ingots and 20 other metallurgical remains recovered from a military camp related to the Late Republican Roman army located in Monte dos Castelinhos, in Tagus Valey, close to a Roman road, which connected Olisipo to Bracara Augusta. Pb isotope ratio distribution allowed the identification of different groups pointing to a lead manufacture from distinct ore provenance in the Iberian Peninsula.



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Studying the thermal transformation of lead carbonates involved in Antique Roman eye care medicine

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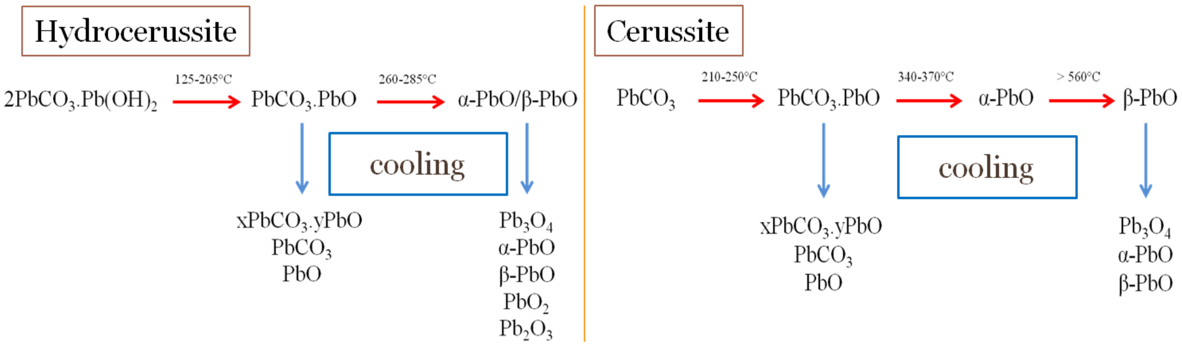
Medicine was widely developed during the ancient times as the Ancient Egyptians, Greeks and then Romans prioritized public health. Some physicians, named oculists, were specialists in eye care. They used medicines called collyria, a Greek term related to their small bread-like shape. These medicines mainly contain heavy metals, plants and gums. We aimed to reproduce the processes developed during collyria's synthesis for the inorganic compounds. As many metal components are "burned" in the ancient recipes, the thermodynamical studies of those phases are of main importance. Knowing their stability fields and behaviours during thermal treatments is, on the one hand, required to underline the processes related to compounds identified in artefacts and on the other, helps to attribute the terms and nouns of ancient texts to reliable chemical formulae.

We focused on the thermodynamical behaviour of the two main metallic salts used according to the recipes, the cerussite: $PbCO_3$ and the hydrocerussite: $2PbCO_3.Pb(OH)_2$. Even if the thermodynamical decomposition of these two lead salts has been widely studied (mostly using TGA, Raman spectroscopy or XRD) their evolution schemes are still controversial. Our study of lead salts thermal decomposition is based on two different approaches. The first one is the "static heating process": white leads are treated at fixed temperatures and the final compounds are identified by Raman spectroscopy and XRD. The second approach consists in a "dynamic heating process". The lead salts are submitted to temperature gradients and are analysed *in situ* by Raman spectroscopy to characterise the intermediates, even the transient ones. Thanks to the recording of the low frequency Raman features a high sensitivity is achieved for following the transformations of these heavy metal compounds.



We were thus able to characterize the different steps of the thermal decomposition of cerussite and hydrocerussite and identify the intermediates leading to the formation of lead oxides.

Analyses of 6 canvases from Osman Hamdi Bey's Paintings using PCA on FTIR-ATR data

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Being a non-destructive analysis method ATR-FTIR is one of the popular methods to study with materials in the field of conservation. In this study FTIR spectra of 6 individual canvas samples from paintings made by Osman Hamdi Bey and 3 control samples were recorded using FTIR-ATR. Then PCA was conducted on gathered data after preprocessing of the accumulated data using Python 3.6 with Numpy module. Samples were labelled as 00087, 00089, 00091, 00129, 00280, and 00352 while control samples were 1, 2, and 3.

All samples, except 00352, showed characteristic FTIR signals of cellulose which was the primary component in canvas with an extent of signals belonging to varnish. The only exception 00352 mainly showed signals related with amber resin due to a recent restoration [1, 2]As varnish was relatively fresh probably covered the surface of the canvas preventing the IR radiation to access to the cellulose chain.

The characteristic signals of cellulose could be summarized as O-H stretching as a broad signal with a peak position around 3500 cm^{-1}, various signals related with C-O stretchings and C-H, C-O bendings between 1800-800 cm^{-1}. Especially signals between 1500-900 cm^{-1} were highly sensitive to the structure of cellulose [3, 4], which was meaning that additives and side groups on the main chain would cause small changes in the pattern in this part. However, these changes would be very hard to determine without any further process. Thus PCA was conducted to find out the differences. Then maximum variance of the data is determined along which directions (PCs) via PCA. More than 95% change in the variance was due to first 3 PCs according to the cumulative variance versus PCs plot. Thus clustering was conducted using PCs 1 to 3.

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