



The twelfth Biennial IRUG Conference

May 23-25, 2016

Book of Abstracts

ORMYLIA FOUNDATION

Art Diagnosis Centre

Ormylia, Greece



The twelfth Biennial Infrared & Raman Users Group Conference

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Organised by

**ORMYLIA FOUNDATION Art Diagnosis Centre,
Ormylia, Greece**

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Conference Program

Monday 23rd May

Conference Opening

Chair: Sophia Sotiropoulou

08:30 – 09:30	<i>Registration – Coffee</i>
09:30 - 10:00	Welcome addresses <ul style="list-style-type: none">• Priest Monk Serapion, President of the Ormylia Foundation Board of Directors• Georgios Karagiannis, Head of the Ormylia Foundation Art Diagnosis Centre• Beth Price, IRUG Regional Chair, Americas

Session 1: Non-invasive Spectroscopic Analysis of Artworks

Chair: Francesca Rosi, David Thickett

10:00 – 10:20	Characterization of materials in illuminated parchment manuscripts by r-FTIR, Raman and XRF <u>Wilfried Vetter</u> , Bernadette Frühmann, Federica Cappa and Manfred Schreiner
10:20 – 10:40	TR-FTIR techniques to support the conservation of metal surfaces: application to Renaissance gilded artefacts Andrea Cagnini, <u>Monica Galeotti</u> , Simone Porcinai, Barbara Salvadori
10:40 - 11:00	Non-invasive FTIR characterisation of varnishes of ancient brass scientific instruments belonging to the “Physic Cabinet” of the “Fondazione Scienza e Tecnica” in Florence Anna Giatti, Monica Galeotti, <u>Giancarlo Lanterna</u>
11:00 – 11:30	<i>Coffee break</i>
11:30 – 11:50	Thermal quasi-reflectography (TQR), handheld Raman spectroscopy, and optical profilometry: multi-technique mapping of decay in wall paintings Claudia Daffara, <u>Giacomo Marchioro</u> and Elisabetta Zendri
11:50 – 12:10	In-situ Raman spectroscopy as a key tool to study the nature of the soluble salts formed on mortars from the House of the Gilded Cupids (Pompeii) Nagore Prieto-Taboada, M. Veneranda, H. Morillas, I. Marcaida, S. Fdez-Ortiz de Vallejuelo, M. Maguregui, K. Castro, D. Rau, <u>Dawn Yang</u> , E. De Carolis, M. Osanna and Juan-Manuel Madariaga
12:10 – 12:30	Raman spectroscopic examination of mixed-phase pigments in Byzantine illuminated manuscripts <u>Catherine Schmidt Patterson</u> and Nancy Turner
12:30 – 12:50	Tracing the Ottoman palette of stone sculptures on the island of Crete <u>Zoi Eirini Papiiaka</u> , Aggelos Philippidis, Panagiotis Siozos, Maria Vakondiou, Kristalia Melessanaki, Demetrios Anglos
13:00 – 14:30	<i>Lunch break</i>

Session 2: Database and Methodological Developments on Raman Spectroscopy

Chair: Manfred Schreiner, Lynn Brostoff

14:30 – 14:50	Improved methodologies for the identification of inks in works of art by Raman spectroscopy <u>Silvia Centeno</u> , Maddalena Bronzato, M. Lorena Roldán, Adriana Rizzo, Alfonso Zoleo, Polonca Ropret, Barbara Biondi, Alfonso Venzo, Sara Bogialli
14:50 – 15:10	Distinguishing manufacturing practices for titanium white pigments: new Raman markers for dating commercial oil-based paints <u>Corina Rogge</u> and Julie Arslanoglu
15:10 – 15:30	Raman spectroscopy identification of red pigments on Upper Paleolithic ornaments from Grotta di Pozzo (Abruzzo, Italy) <u>Eliana Catelli</u> , Delia Gazzoli, Margherita Mussi
15:30 – 15:50	Introduction to the Infrared and Raman Users Group (IRUG) web-based Raman spectral database <u>Beth Price</u> , Haddon Dine, Andrew Lins, Charles Davis, Suzanne Quillen Lomax, Boris Pretzel, Marcello Picollo, Gabriel Richards
15:50 – 16:20	<i>Coffee break</i>

Session 3: Instrumental Developments - Novelties in commercial instruments.

Chair: Georgios Karagiannis

16:20 – 16:40	Presentation of “ORMYLIA” Foundation development actions focused on work that has been carried out with marketplace devices. Georgios Karagiannis, Ormylia Foundation Art Diagnosis Centre
16:40 – 17:10	Daniel Barchewitz, B&W Tek: Portable Raman for On-site Analysis Jan Wülfken, Agilent Technologies: Newest Developments in FTIR Spectroscopy for art and historical object conservation: Truly mobile and non-destructive FTIR tools and the highest spatial resolution true Imaging FTIR Vasiliki Chalepli, InterActive S.A: New generation FT-IR spectrometers: The precious tool from Research to Routine analysis

Session 4: Posters very short introduction

Chair: Beth Price, Stamatis Boyatzis

17:15 – 18:30	Very short introduction to the posters, 3 min per paper.
	μ-FTIR spectroscopy and other methods in technological expertise of golden paint <u>Irina Burtseva</u> , G.Gorohova, A.Mazina
	Contribution of Attenuated Total Reflection Fourier Transform Infrared spectroscopy (ATR-FTIR) in the investigation of historical parchment documents <u>Cristina Carșote</u> , Irina Petroviciu, Elena Badea and Lucreția Miu
	FTIR Spectroscopy study on wooden materials consolidated with acrylic based resins <u>Silvana Vasilca</u> , Thomas Guiblain, Ioana Stanculescu, Laurent Cortella, Quoc-Khoi Tran
	Tissue preservation of 16-18th Century mummies of Roccapelago (Modena, Italy): a SEM and FTIR study <u>Maria Grazia Bridelli</u> , Chiaramaria Stani, Victor Erokhin, Mirko Traversari, Elisabetta Cilli
	Physical and histological investigation of the embalmed skin: application to some Egyptian mummy heads from the Marro collection (Turin) <u>Maria Grazia Bridelli</u> , Chiaramaria Stani, Andrea Baraldi, Rosa Boano, Emma Rabino Massa
	On the rocks – unveiling the richness and specificities of the Guadameci from the Portuguese Templar Charola of the Convent of Christ in Tomar, Portugal <u>Catarina Miguel</u> , L. Falcão, Sara Valadas and Antonio Candeias
	Technological Survey of Rock Crystal Object <u>Klara Drabkova</u> , Zuzana Zlámálová Cílová
	Spectroscopic non-destructive characterization of gamma irradiated paintings Maria-Mihaela Manea, Daniel Negut, Ioana Stanculescu, Rares Suvaila, Marian Virgolici, Valentin Moise
	“PigmentX” application for pigment identification <u>Olimpia – Hinamatsuri Barbu</u> , Cătălin Dima, Adrian Stefănică and Horia Nicolau
	Complex methods of fine-art objects research Anna Litvinova
	Analysis of Lucerne auction paintings by mobile Raman and complementary analytical and imaging techniques Catherine Defeyt and <u>David Strivay</u>

Tuesday 24th May

Session 5: Methodological Developments on Vibrational Spectroscopy

Chair: Silvia Centeno, Sophia Sotiropoulou

08:45 - 09:30	Invited lecture Spectroscopic imaging: new trends and emerging applications to the objects of cultural heritage <u>Prof. Sergei Kazarian</u> , Professor of Physical Chemistry at Imperial College London.
09:30 - 09:50	Studying natural organic substances from cultural heritage through multivariate analysis of Raman and infrared signatures <u>Ludovic Bellot-Gurlet</u> , Céline Daher and Céline Paris
09:50 - 10:10	Gilt leather varnish analysis by infrared spectroscopy <u>Laurianne Robinet</u> , Marie Radepont, Sylvie Thao-Heu and Céline Bonnot-Diconne
10:10 - 10:30	Far infrared selectivity evaluation for reds and black pigments and lead degradation products P. Giménez, A. Linares, C. Sessa, E. Marín, H. Bagán, E. Boix, C. Clusella, Anna Vila, Birgit Vinther Hansen, Niels Borring, David Buti, Andreas Swane, Johanne M. Nielsen, Morten Ryhl-Svendsen and <u>José Francisco García</u>
10:30 - 11:00	<i>Coffee break</i>

Session 6: Damage Assessment and Degradation Analysis through Vibrational Spectroscopy

Chair: Laurianne Robinet, José Francisco García

11:00 – 11:20	FTIR spectroscopy of zinc carboxylates in model samples and modern paintings: the macro and micro-scale infrared properties <u>Francesca Rosi</u> , Francesca Gabrieli, Laura Cartechini, Alessandra Vichi, Sergei G. Kazarian, Costanza Miliani
11:20 - 11:40	Investigation of parchment degradation by nanoscale infrared spectroscopy Alexandre Dazzi, <u>Ariane Deniset-Besseau</u> , Laurianne Robinet, Gaël Latour, Marie-Claire Schanne-Klein, Curtis Marcott, Peter de Peinder and Kevin Kjoller
11:40 - 12:00	Raman and FTIR spectroscopy-based damage assessment of protein cultural heritage materials, artificially aged in urban gaseous pollutant atmospheres <u>Stamatis Boyatzis</u> , Soghomon Boghosian, Angelos Kalampounias, Ekaterini Malea, Stavroula Rapti, Efrosini Karantoni, Clio Vossou and George Panagiaris
12:00 - 12:20	Ageing processes in diterpenic resins used in artwork coatings <u>Victoria Beltran</u> , Gianfelice Cinque, Natividad Salvadó, Salvador Butí and Trinitat Pradell
12:20 - 12:40	Weathering of polyester and epoxy resins: degradation studies by in-situ time-lapse IRRAS, QCM and ex-situ MeV-SIMS Rita Wiesinger, D. Jembrih-Simbürger, I. Bogdanović-Radović, Z. Siketić, <u>Manfred Schreiner</u>
12:40 - 13:00	Fluorination technique to investigate photooxidative ageing products in bioorganic resin materials using infrared spectroscopy <u>Stefan Zumbühl</u> , Andreas Hochuli and Walter Caseri
13:00 - 14:30	<i>Lunch break</i>
14:30 - 14:50	Influence of the soft and strong artificial ageing on the photo-stability of artists' paints containing alkyd binder and phthalocyanine pigments <u>Marta Anghelone</u> , D. Jembrih-Simbürger and Manfred Schreiner
14:50 - 15:10	Effectiveness of protection, damage assessment and novel nano-particle based conservation treatment <u>Marianne Odlyha</u> , Sabina Rutkowska, Laurent Bozec, Angelica Bartoletti, Manfred Anders, Adrian Hawley, David Chelazzi, Rodorico Giorgi, Piero Baglioni
15:10 - 15:30	On site detection of cleaning system residues: a feasibility study for the application of reflection FTIR spectroscopy <u>Patrizia Moretti</u> , Laura Cartechini, Bruno Brunetti and Costanza Miliani
15:30 - 15:50	In situ measurement of damage with vibrational spectroscopy David Thickett
15:50 – 16:10	Analytical investigation of 20th century coatings on outdoor bronze sculptures from the JPGM <u>Herant Khanjian</u> , Julie Wolf, Arlen Heginbotham, Lynn Lee, Alessa Gambardella
16:10 – 16:40	<i>Coffee break</i>

Session 7: Materials characterization through Vibrational Spectroscopy

Chair: Ludovic Bellot-Gurlet, Monica Galeotti

16:40 – 17:00	Raman spectroscopic analysis and light fastness of specimens from Wilhelm Ostwald's colour system Alexandra Bridarolli, Thomas Prestel and <u>Christoph Herm</u>
17:00 – 17:20	Spectroscopic characterization of cobalt violet pigments in multi-layered structures: analysis and detection limits <u>Maria Kokkori</u> , Francesca Casadio and Lindsay Oakley
17:20 – 17:40	Combined Raman, X-ray Diffraction and UV-Vis spectroscopy characterization of natural and artificially aged neutral verdigris pigment <u>Lynn Brostoff</u> , Cynthia Connelly Ryan and Isabella Black

Wednesday 25th May

Session 8: Raman and FTIR Spectroscopy for the Study of synthetic polymers and modern materials

Chair: Maria Kokkori, Herant Khanjian

09:00 - 09:20	Die Kunststoffschule – a Unique Collection Identification of Plastics and their Ageing Phenomena <u>Susanne Brunner</u> , Thorsten Allscher
09:20 – 09:40	The colour of plastics: the identification of colourants in plastics <u>Suzan de Groot</u> , Henk van Keulen, Andrea Otte
09:40 – 10:00	A FTIR analytical study of 1960s synthetic polymer paintings and their artist repaints <u>Paula Dredge</u> , Raymonde Rajkowski, Céline de Courlon, Simon Ives and Nicole Tse
10:00 – 10:20	Polyurethane coatings in 20th century outdoor painted sculptures: discrimination of major subgroups by means of ATR-FTIR spectroscopy <u>Catherine Defeyt</u> , Julia Langenbacher and Rachel Rivenc
10:20 – 10:40	ATR study of dispersed nanosilica in carbonate and borate solutions <u>Eirini-Chrysanthi Tsardaka</u> , Maria Stefanidou, Georgios Apostolidis and Georgios Karagiannis
10:40 – 11:10	<i>Coffee break</i>
11:10 – 11:30	Closing remarks
11:30 – 13:00	<ul style="list-style-type: none">• Visit to the Ormylia Foundation's laboratories Meeting of the IRUG board
13:00 – 14:30	<i>Lunch</i>
14:30 – 16:00	<i>Visit to the Ormylia Monastery (Sacred Convent of the Annunciation)</i>

Oral presentations’ ABSTRACTS

Session 1 - Non-invasive Spectroscopic Analysis of Artworks

Characterization of Materials in Illuminated Parchment Manuscripts by r-FTIR, Raman and XRF

Wilfried Vetter, Bernadette Frühmann, Federica Cappa and Manfred Schreiner

Institute of Science and Technology in Art, Academy of Fine Arts Vienna, Schillerplatz 3, 1010 Vienna, Austria

Illuminated manuscripts on parchment are important sources for the study of cultural development of humanity from antiquity towards the end of the middle ages. In this respect, material analysis has the potential to provide knowledge about manufacturing techniques or traces of use; modern analytical methods such as r-FTIR, Raman and XRF allow non-invasive investigation of these precious objects. In this paper we report on the application of the mentioned methods for the analysis of four manuscripts (9th-12th cent.; Glagolitic, Greek and Latin), as well as specific analytical problems encountered using our equipment. Raman (785 nm laser) was applied for the analysis of the two Glagolitic manuscripts only.

We used three complementary methods to obtain comprehensive results but the instruments differed strongly with regard to the analyzed volume. In the case of r-FTIR, the signal derived from a spot diameter of ca. 3 mm and mainly from surface materials, whereas the 1 mm - diameter spot of the XRF instrument penetrates much deeper and thus, also materials from the backside of the folios were detected. In contrary, the Raman laser spot was much smaller (50 µm) and therefore, material inhomogeneity had to be considered when measuring points were selected or findings were compared to other methods.

The results showed that r-FTIR was very useful for the characterization of the parchment supports as various amounts of calcium carbonate and silicates were detected, resulting from whitening or polishing with pumice during the manufacturing process. Furthermore, oxyanion pigments (lead white, azurite, gypsum), a chloride hydroxide pigment (atacamite), red iron (III) oxide-hydroxide, as well as alumino-silicates (lapis lazuli, kaolinite) could be identified in the illuminations. These findings were supported by the XRF results. In several cases, glue and natural gum were detected as binding media, which could not be proved by other methods. r-FTIR analysis of black and brown inks frequently indicated contents of calcium oxalate, arguing for fungal degradation of ink components, whereas the ink materials could not be determined. In contrary, iron gall ink could be detected by Raman, and various contents of Fe, Cu and Zn allowed a characterization of differing iron gall inks by XRF. Raman further was useful to characterize sulfide and oxide pigments (vermillion, orpiment, red lead) which do not absorb MIR, and XRF results would not allow to differentiate between the modifications of orpiment (As₂S₃) and realgar (As₄S₄), or to determine whether Pb contents derive from red or white lead in mixtures (Fig.2). An identification of the pigments used for light color tones mainly was not possible, indicating lack of sensitivity, especially in case of r-FTIR.

We conclude from our results that r-FTIR, Raman and XRF allowed the identification of several inorganic and organic materials frequently used for manuscripts, but an increased sensitivity (r-FTIR, Raman) and spatial resolution (r-FTIR, XRF) would be highly desirable.



Fig. 1: Raman analysis of a Greek manuscript in the Austrian National Library in Vienna, Austria.

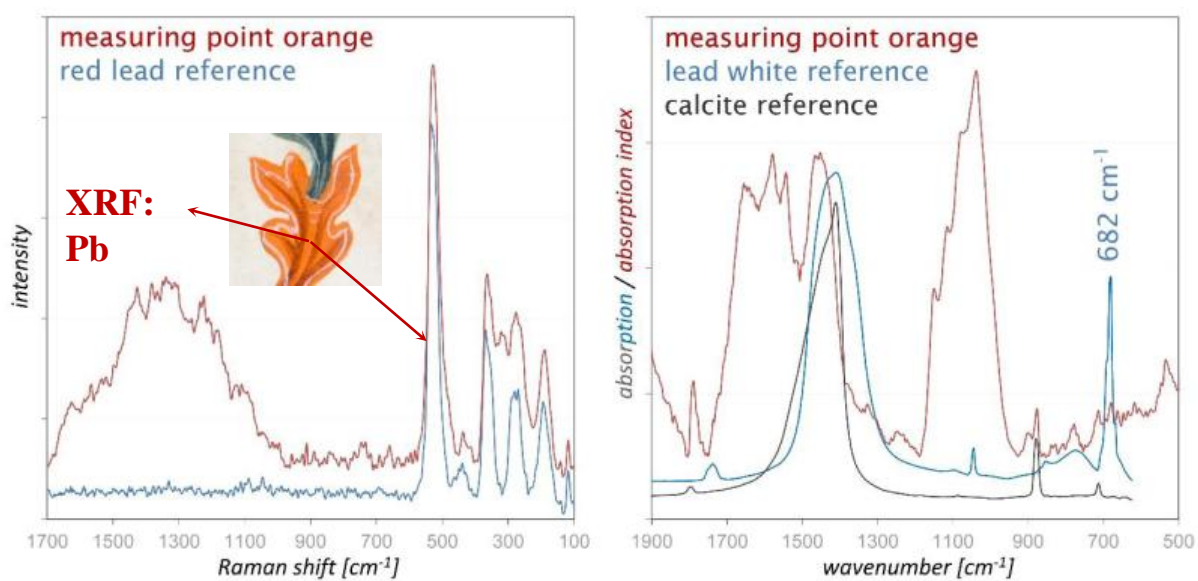


Fig. 2: Raman (left) and r-FTIR (right) results showed that mainly red lead was used, as the characteristic infrared band of lead white at 682 cm^{-1} was only very weak. Moreover, calcite, calcium stearate (doublet at 1578 and 1542 cm^{-1}) and a natural gum (broad band with maximum at 1040 cm^{-1}) were detected from the r-FTIR spectrum.

TR-FTIR techniques to support the conservation of metal surfaces: application to Renaissance gilded artefacts

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Non-invasive Fourier transform infrared spectroscopy (FTIR) methodologies in the field of conservation science have been of great interest in recent years, particularly those based on total reflectance (TR), both *in situ* TR-FTIR and TR-FTIR microscopy. Portable instruments offer the advantage of in-situ investigation, but there are some limitations due to both the probe head size and the investigated area width. Indeed, the probe diameter is about 5 mm with no possibility of assessing restricted areas of interest on the object. However, a FTIR microscope allows working on very small areas (down to a few hundreds of μm^2) of the surface of art objects or parts of them, if they are small enough to be placed on the microscope stage. Both methodologies are particularly suitable to investigate thin films on metal surfaces where the reflection-absorption phenomenon of the radiation may take place: the IR beam passes through a thin layer of the sample (coating or patina of corrosion products) and is reflected from the non-absorbing metal substrate. The method is essentially a double-pass transmission experiment, and the collected spectra resemble those obtained in transmission.

This paper presents case studies where the presence of a gold layer (amalgam or foil gilding) over bronze, silver or iron enabled the application of the non-destructive methods described above. The studies include a gilt element taken from a silver reliquary of the 15th century and a gilt iron panel of the 16th century, that were placed on the FTIR microscope stage; and Donatello's bronze sculpture of San Ludovico and bronze Pulpito della Passione, both investigated *in situ* with the portable instrument. The FTIR analysis on the artefacts shown in this work were carried out as part of conservation processes, which included cleaning and application of protective coatings.

The information resulting from the analysis proved to be very useful to underpin the restorers' work. The alteration products coming from the metal under the gold layer and/or the remains of coatings laid in the past were identified and, in some cases, their distribution on the surface was mapped. That helped to make an informed choice of the best conservation process to adopt. Based on the compounds detected, some cleaning methods were selected and applied on test areas. The different conservation procedures were evaluated by monitoring their effectiveness with TR-FTIR measurements.

Non-invasive FTIR characterisation of varnishes of ancient brass scientific instruments belonging to the “Physic Cabinet” of the “Fondazione Scienza e Tecnica” in Florence

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A series of over 40 scientific instruments belonging to the collection of “Fondazione Scienza e Tecnica” in Florence were submitted to scientific investigation by means of a portable Fourier transform infrared spectroscopy (FTIR) instrument (Bruker Alpha) in order to characterise the varnishes applied on the brass parts and surfaces. Brass is one of the most used materials for scientific instruments, with wood and glass, and the issue of its protection was taken into account since the earliest manufacturers. The literature reports various recipes of so-called “lacquers”, most of them based on alcohol and mixtures of several natural resins, gums and dyes.

In a previous work [1] the authors did search these recipes and replicate a series of brass historical lacquers; they were applied in thin film on a polished brass plate, then aged and examined by means of reflection FTIR. The quality of the spectra collected was very high because the phenomena of “transflection” in which the flat metal surface reflects the whole incident radiation doubling the beam path and straightening the peaks.

In this work the authors have chosen a large selection of scientific instruments used for research and didactics in physics and manufactured in Europe in the nineteenth century, with the aim to characterise the brass varnishes, to detect the ingredients formulation and to organize a comparison among the various instruments, according to the geographical provenience, the time and the workshop of production. The use of a portable FTIR equipment, working in total reflection mode, enabled us to analyse in a non-invasive way a large number of brass containing scientific instruments and, in some cases, the possibility to disassemble some parts or details offered a great help to the investigation of the surface. The results are organised in “families of lacquers” according to the spectra similitudes, and each family related to the geographical area of provenance. The importance of this work is also in the well-known geographical production of the scientific instruments belonging to the FST collection: this could be of great importance as a reference base of the instrument provenance, in case of unknown manufacture.

The final aim of this work is to start the building up of a freely available database of brass scientific instruments varnishes, useful for conservation scientists and collection curators, in order to catalogue and compare the lacquers composition. It represents also a guide for restorers and conservators to make informed decisions on the processes to adopt to preserve and restore the original varnishes.

[1] Anna Giatti, Giancarlo Lanterna, The non-invasive FTIR characterisation of brass varnishes of historical scientific instruments. *Proceedings of the conference Technart 2015, Catania 27-30 april 2015, O - 88*

Thermal quasi-reflectography (TQR), handheld Raman spectroscopy, and optical profilometry: multi-technique mapping of decay in wall paintings

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The combination of full-field imaging techniques with techniques that can analyze only a very limited portion of the artwork is very important to guarantee an effective sampling over the surface and hence collect reliable information about the work of art. Besides such guided sampling, the integration of imaging and spectroscopy, if properly based on ground-truth data and information processing, enables non-destructive identification and mapping of materials over the target surface. The effective use of a multi-technique analysis and its integration level is related to the knowledge of the performance of the employed methods as well as of their complementarity.

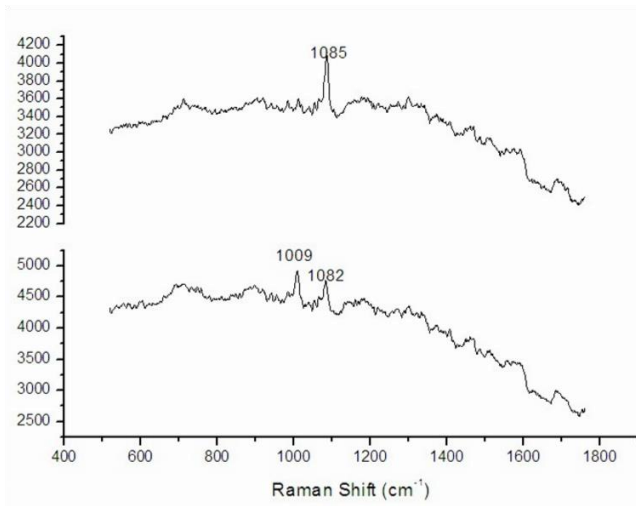
In this work, Thermal Quasi-Reflectography (TQR), handheld Raman spectroscopy, and optical laser micro-profilometry have been tested. These three techniques have been chosen to overcome specific limitations related to them, allowing a more accurate characterization of the sample under investigation directly in-situ. TQR is a recent imaging technique [1] based on the acquisition of the thermal mid-IR (3-5 μm) in (quasi-)reflectance modality, which has been shown to gain information where other optical methods are not effective. TQR response is determined by factors related to the material composition, to the density and microstructure, and to the surface roughness. As such, TQR has the potential to detect the presence of different materials and binders, and to discriminate the response of different surface layers. Combination of TQR with the above techniques is unexplored.

Multi-technique analysis has been applied on mock-up samples of fresco plaster. The high sensitivity of TQR permits to detect and to map changes in the composition of the surface materials, handheld Raman spectroscopy is then used to understand the composition of the areas mapped with the TQR, optical micro-profilometry is used to model the surface morphology and to understand any changes induced in the roughness structure at micron scale, [2].

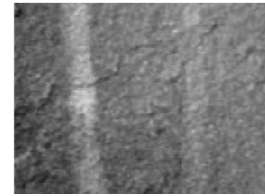
The results are discussed and the pro and cons of the above techniques are evaluated, with the aim of assessing their complementarity and thus performing an effective integration. Finally, the joint use of TQR imaging and Raman spectroscopy has been tested as a potential tool for mapping in-situ, full-field and non-destructively, the areas affected by sulphate decay in wall paintings (Fig. 1)

[1] C. Daffara, D. Ambrosini, L. Pezzati, D. Paoletti, *Optics Express* 20(13), 2012, 14746-14753.

[2] C. Colombo, C. Daffara, R. Fontana, M.C. Gambino et al, *Lasers in the Conservation of Artworks: LACONA VI*, 2005, 522-526.



VIS



TQR

Fig. 1: Analysis of plaster decay in fresco test-beds (example). Left: Raman spectrum of sound (top) area and sulphate decay (bottom); Right: VIS image and TQR response (sulphated areas are the vertical lines).

In-situ Raman spectroscopy as a key tool to study the nature of the soluble salts formed on mortars from the House of the Gilded Cupids (Pompeii)

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Pompeii is one of the most important archaeological sites all over the world and also a good example of how different environmental factors can have influence on the conservation state of the materials employed in its construction. The ancient aggressive atmosphere (e.g. volcanic emissions), the more modern and polluted one and natural factors (infiltration of waters, biological colonization, etc.) which surround the item under study are some of the causes that can promote the decaying of the building materials used to create the magnificent Pompeian houses. Due to this fact, it is very important to select a proper analytical methodology to characterize the original composition and possible deterioration products formed on the building materials, in order to carry out a correct and complete evaluation of the conservation state of these materials and to extract information about the chemistry behind the cultural heritage deterioration. In order to preserve the integrity of the cultural heritage content of the excavation, the possibility of sampling any material from the Pompeian houses is extremely restricted. Notwithstanding the foregoing, the use of portable and non-invasive analytical instrumentation is the only possible alternative to study the decaying processes that can take place on these materials. Among all these kinds of techniques, Raman spectroscopy is one of the most suitable ones, because it can offer the molecular information of the building materials under study without the necessity of sampling.

In this sense, in the present work in-situ analysis has been carried out within the framework of APUV project (Analytica Pompeiana Universitatis Vasconicae) in the House of the Gilded Cupids (Casa degli Amorini Dorati, Regio VI, Insula 16), one of the most important houses of Pompeii. The analyses were conducted on the main pathology visually noticeable in the mortars used to cover the walls at some areas of this house: the formation of salts crystallized on the mortars (efflorescences). For that purpose two portable Raman spectrometers from B&WTEK_{INC.}, both providing a 785 nm excitation laser were used. The first one is the innoRaman spectrometer (USA) and the second one belongs to the i-Raman Pro, an improved version of the i-Raman spectrometer which is powered with a high quantum efficiency CCD array detector with ultra-deep cooling, see Fig. 1. The acquisition of the data was done using the B&WSpec software (B&WTEK_{INC.}, USA).

Thanks to this in-situ analyses, a complex mixture of salts were observed on the efflorescences: calcite (CaCO₃), syngenite (K₂Ca(SO₄)₂·H₂O), gypsum (CaSO₄·2H₂O), apthitalite ((K,Na)₃Na(SO₄)₂), thenardite (NaSO₄), sodium nitrate (NaNO₃) and other nitrates. Some of them are usually complicated to identify due to their similarities in the spectra or due to the low intensity of their secondary bands.

However, both Raman spectrometers used in this work allowed their complete identification thanks to the detection of the medium and weak bands associated to the mentioned salts. Therefore, this work evidences that these kind of portable Raman spectrometers can be used successfully to perform a conclusive identification of the nature of the salts formed on ancient Roman mortars and thus on other kind of building materials.



Fig. 1: A detail of the iRaman Pro spectrometer use in the House of the Gilded Cupids (Casa degli Amorini Dorati).

Raman spectroscopic examination of mixed-phase pigments in Byzantine illuminated manuscripts

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When Byzantine art is considered, it is often thought that the highest quality materials or widest selection of pigments were reserved for the most important artisans in the major production centers, while a lesser quality and variety of materials was available in the outlying regions. An extensive technical study tests this hypothesis by examining manuscripts produced throughout the Byzantine Empire, dating from c. 1000 to c. 1300. By examining a large number of objects to look for trends in material and pigment use, this on-going study can better contextualize the results, providing greater insight into cultural aspects such as material trade, artistic practice and workshop organization, than is possible from single-object studies. Selected initial findings from two Byzantine manuscripts, one dated to the early twelfth century and one to the middle of the thirteenth century, will be presented.

All manuscript illuminations in the study were analyzed using only non-invasive techniques, including Raman microspectroscopy. Raman spectroscopy using 785 nm excitation has identified the use of multiple inorganic yellow and red pigments in these two manuscripts. Orpiment (As_2S_3), realgar (As_4S_4), pararealgar (As_4S_4) and related arsenic sulfide pigments have been found on both manuscripts. Interestingly, a second inorganic yellow pigment – lead tin yellow – was identified on the twelfth century manuscript (on five different folios), though not on the later manuscript.

Although in most cases identification of these pigments was relatively straightforward, in a surprising number of instances the Raman spectra did not correlate exactly to the expected spectra from pure examples of the known forms of arsenic sulfide or lead-tin yellow. Rather, the spectra were found to contain features (primarily in the low-frequency range) indicative of the presence of either multiple pigments or mixed-phase species. For example, in some arsenic sulfide-containing areas, some spectra seem to indicate the presence of a mixture of orpiment and realgar (or of realgar and pararealgar). While it is well known that arsenic sulfide species undergo conversion, the consistency of the spectra obtained from these manuscripts raises the question as to whether discrete, mixed-phase, species, might be present, rather than a mixture of pure components. Similarly, in the case of lead tin yellows, spectra containing features consistent with both lead tin yellow type I (Pb_2SnO_4) and lead tin yellow type II ($\text{PbSn}_{1-x}\text{Si}_x\text{O}_3$) were found. The interpretation of these possible mixed-phase spectra will be considered through examination of representative reference materials and the use of data processing methodologies that provide a means of identifying correlations and trends within the data-set. The possible significance of these findings for enhancing our understanding of the techniques and materials of Byzantine illuminators will also be discussed.

Tracing the Ottoman palette of stone sculptures on the island of Crete

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A versatile analytical methodology, that combines the use of two mobile laser-based analytical techniques, (a) Raman microscopy and (b) laser-induced breakdown spectroscopy (LIBS), has been applied for the integrated investigation of sculptures, dating from Ottoman period (17th-19thc.), kept in the Historical Museum of Crete and in the conservation laboratory of the Ephorate of Antiquities at Heraklion (Greece). In a typical investigation, Raman analysis is carried out first. Raman microscopy provides direct molecular information, with high spatial resolution (typically 10-15 μ m) and the analysis is non-invasive. Given that Raman signals may be in some cases weak or masked by fluorescence emission, complementary analysis is carried out by LIBS, which affords strong emission signals that provide qualitative and semi-quantitative elemental analysis at nearly microscopic spatial resolution (typically 100-200 μ m) and is classified as micro-destructive (Fig. 1).

The study of pigments on Ottoman sculptures is the first attempt to construct the Ottoman palette in the Greek territory. According to the results obtained so far, this palette consists of the pigments: red lead and more scarcely cinnabar or vermilion for red hue, chrome yellow, ultramarine, a Cu-based green pigment and a blend of Prussian blue and chrome yellow for light green hues. Moreover, a gold-silver-copper alloy was possibly applied as a decoration on the surface of several Ottoman stone sculptures.

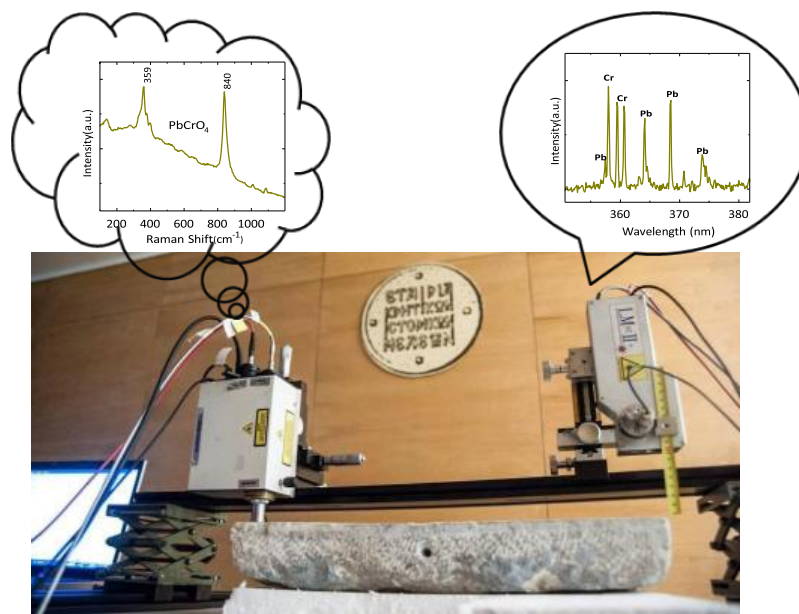


Fig. 1: Image taken during the campaign at the Historical Museum of Crete. The LIBS and Raman probes are mounted on a rail permitting parallel work over the sculpture surface.

Session 2 - Database and Methodological Developments on Raman Spectroscopy

Improved Methodologies for the Identification of Inks in Works of Art by Raman Spectroscopy

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The firm identification by Raman spectroscopy of colorants in inks such as those based on logwood, sepia, and bistre is often challenging because the spectra depend on the recipe and/or on the natural source of the materials, and are also affected by aging and interferences from the binding media [1-3]. The talk will highlight recent advances in the characterization and identification of Fe, Fe/Cu, and Cr logwoods, bistre, and sepia in works of art by Raman spectroscopy, complemented by other microanalytical techniques.

Logwood inks based on Cr, Fe, Fe/Cu and Al, respectively, were synthesized following different nineteenth century procedures and were characterized by Raman spectroscopy, FTIR, electron paramagnetic resonance (EPR), electrospray ionization mass spectrometry (ESI-MS), and liquid chromatography-quadrupole time-of-flight mass spectrometry (LC-QTOF-MS) to investigate how the different inorganic salts employed to obtain different hues, as well as other additives, affect the ink composition and the Raman spectra. Natural bistre, a variety of natural sepia pigments, including one extracted in the laboratory from the cuttlefish, some natural commercial samples, and a pure commercial melanin, along with a synthetic eumelanin, were studied by conventional microRaman, SERS, FTIR, Py-GC/MS, and XRF techniques. The compositions of these pigments were found to be strongly influenced by their sources, and/or the purification procedures used [4-6].

Examples of the successful application of the improved Raman methodologies proposed to identify the materials in nineteenth century works of art will be presented. The results highlight how the in-depth chemical characterization of artistic materials prepared following as close as possible recipes from a variety of historic sources and using different raw materials is indispensable to correctly assign the vibrational features and to build comprehensive databases.

- [1] Centeno, S. A., Identification of artistic materials in paintings and drawings by Raman spectroscopy: some challenges and future outlook (Review) *Journal of Raman Spectroscopy*, (2016), **47**, 9.
- [2] Centeno, S. A.; Ropret, P.; Federico, E. D.; Shamir, J.; Itin, B.; Jerschow, A., Characterization of Al(III) complexes with hematein in artistic alum logwood inks, *Journal of Raman Spectroscopy*, (2010) **41**, 445.
- [3] Centeno, S. A.; Shamir, J., Surface enhanced Raman scattering (SERS) and FTIR characterization of the sepia melanin pigment used in works of art, *Journal of Molecular Structure*, (2008) **873**, 149.
- [4] Bronzato, M.; Zoleo, A.; Biondi, B.; Centeno, S. A., An insight into the metal coordination and spectroscopic properties of artistic Fe and Fe/Cu logwood inks, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, (2016) **153**, 522–529.
- [5] Roldán, M. L.; Centeno, S. A.; Rizzo, A., An improved methodology for the characterization and identification of sepia in works of art by normal Raman and SERS, complemented by FTIR, Py-GC/MS, and XRF, *Journal of Raman Spectroscopy*, (2014) **45**, 1160.

- [6] Roldán, M. L.; Centeno, S. A.; Rizzo, A., Characterization of Bistre Pigment Samples by FTIR, SERS, Py-GC/MS and XRF, In *Materials Issues in Art and Archaeology X, MRS Fall Meeting 2013 Symp. Proc.*, P.B. Vandiver, W. L., P. Sciau and C. Maines Ed. Warrendale, PA (2013).

Distinguishing Manufacturing Practices for Titanium White Pigments: New Raman markers for dating commercial oil-based paints

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Titanium white pigment revolutionized the paint industry in the 20th century. Nontoxic, relatively inexpensive, and with high covering power, it was everything that zinc and lead white pigments were not. Although initially slow to be adopted as an artists' material, it was ubiquitous by the latter half of the century, so the identification of titanium dioxide in a modern painting seems to provide little dating or material information. However, changes in pigment production resulted in several shifts in the nature of the pigments used. The first titanium white pigment produced in the United States was the anatase form co-precipitated onto barium sulfate (1916), a type of pigment also termed 'composite'. The anatase form co-precipitated onto calcium sulfate was introduced by 1925 and production continued until the 1970's. Pure anatase itself was widely available by 1927. The rutile form, with a higher refractive index and greater coloring power, was more difficult to manufacture and the co-precipitated forms of this species weren't introduced until 1941 and the pure species in 1957. The rutile barium sulfate co-precipitate was phased out in the late 1940's while production of the calcium sulfate co-precipitate continued until the 1970's. Therefore, determination of the crystal form of the titanium dioxide, easily accomplished by Raman spectroscopy, provides some dating information. However, simple co-detection of titanium dioxide and calcium sulfate or barium sulfate does not provide sufficient information to determine if a co-precipitated pigment is present because both calcium sulfate and barium sulfate are commonly used fillers and can be added mechanically to titanium dioxide. SEM-EDX analysis of individual pigment grains may provide some evidence for co-precipitates rather than mixtures, but this approach is time-consuming and laborious.

Recent technical studies on paintings by abstract expressionists, including Franz Kline and Barnett Newman from the collections of the Museum of Fine Arts Houston, the Menil Collection and the Metropolitan Museum of Art, dating from the 1950's-60's revealed a unique Raman fluorescence signature in certain white paints that can provide evidence of a co-precipitate. Detected only when using a 785 nm laser, a series of broad peaks at ~1195, 1280, 1370, 1475, 1575 and 1660 cm⁻¹ (Fig. 1) is assigned to fluorescence due to the presence of trace amounts of iron present in the pigment, and occurs only in spectra of co-precipitated pigments produced by the sulfate process [1]. Thus, detection of this fluorescence along with characteristic peaks of rutile, anatase, calcium sulfate and barium sulfate allow precise identification of the type of titanium white pigment present and permit a narrowing of the date range of manufacture. To date co-precipitated pigments have only been detected in oil paints, not in samples of historic solution or solvent acrylics, and furthermore, they were not found in any samples of historic artists' oil paints held in the Art Materials Research and Study Center at the National Gallery of Art, Washington, DC, which date from the 1950's onward. Further research is planned to determine if the detection of co-precipitated pigments in later artworks is a marker of commercial oil paints.

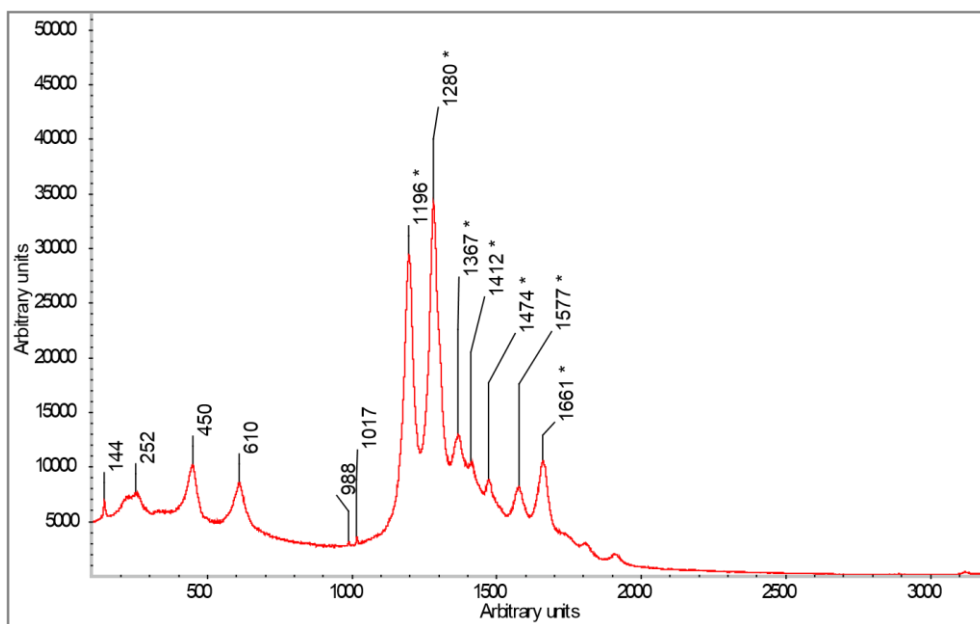


Fig. 1: Raman spectrum of a paint containing the co-precipitated rutile form of titanium dioxide, the fluorescence peaks are indicated with an asterisk.

- [1] L.E. Smith, *Analysis of pigments and complex pigmented media using non-destructive analytical methodologies and chemometrics*, Ph.D. thesis, Rutgers University, 2006, 174.

Raman spectroscopy identification of red pigments on Upper Paleolithic ornaments from Grotta di Pozzo (Abruzzo, Italy).

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Perforated marine shells, stained by red pigments, have been discovered at Grotta di Pozzo, a rock-shelter of Abruzzo, central Italy, at 720 m a.s.l. in the Appennine range of mountains. Specimens of *Glycimeris sp.*, *Cyclope neritea*, *Cyclope donovani*, *Columbella rustica* and *Dentalium dentalis* were found in Late Glacial (15.000-14.000 cal BP) and early Holocene (10.500-9.000 cal BP) layers, in association with Epigravettian and Sauveterrian artifacts and with faunal remains. Microscopic analysis allows identifying a red substance interpreted as a pigment, partially coating the inside and the outside surfaces of the shells. Raman analysis, performed with micro-Raman Renishaw in Via, also allowed identifying iron oxide and oxihydroxide ores, which are the primary constituents of ochres. Hematite (Fe_2O_3) is the main component. Goethite ($\text{FeO}(\text{OH})$) and some traces of lepidocrocite ($\gamma\text{-FeO}(\text{OH})$) were also detected. Calcite (CaCO_3 , trigonal structure) and aragonite (CaCO_3 , orthorhombic structure) phases were present in some spectra and recognized as mineral carbonates that form part of the shells. In addition, 140 fragments of ochre (max. size: 2.33 - 43.47 mm) were also collected from some layers of Grotta di Pozzo. Hematite and goethite are the main chromophores, with a wide range in colour from deep red, red, reddish-brown to brownish yellow and yellow, and with fine particles size. Microscopic observations and Raman spectroscopy confirmed that the color shades depend from the presence of iron oxide and oxihydroxide ores. The physical characteristics and chemical composition of the red pigments support the hypothesis that the marine shells were colored with red ochre. We assume that the shells were personal ornaments and a component of the symbolic sphere of the hunter-gatherer groups peopling central peninsular Italy during the late Upper Paleolithic and early Mesolithic. For a more comprehensive study, techniques such as XRF, SEM-EDS and FT-IR will be used in the next future.

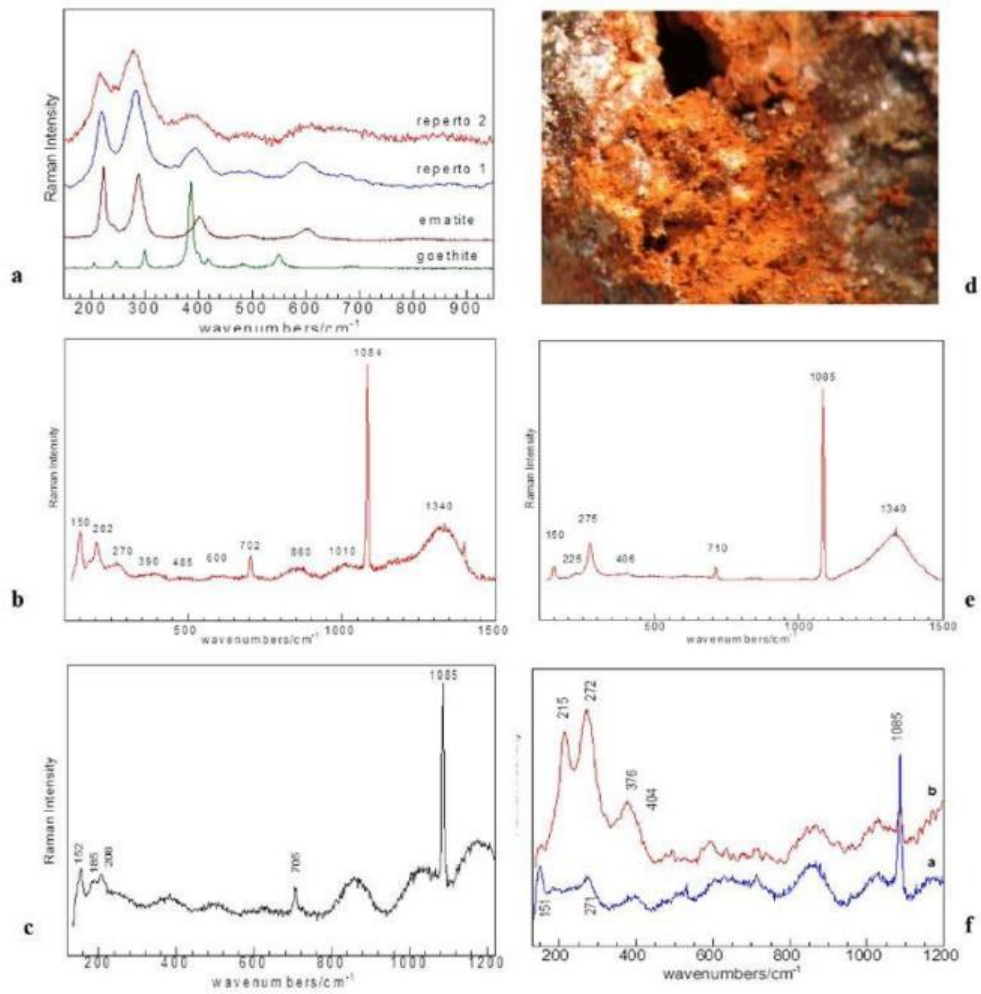


Fig.8: Raman spectra of: archaeological ocher sample (a-d) *Glycimeris* sp. (b); *Columbella rustica* (c); *Dentalium dentalis* (e); *Cyclope neritea* (f).

Introduction to the Infrared and Raman Users Group (IRUG) Web-based Raman Spectral Database

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Infrared and Raman spectroscopies are well-known, powerful techniques for the study of cultural heritage materials. The number of Raman systems installed in museum and academic laboratories has grown over the past decade, driving the demand for readily accessible, peer-reviewed, Raman reference data on known substances to serve as comparisons for samples taken from works of art and archaeological artifacts.

To meet this need, the Infrared and Raman Users Group (IRUG) has created a new Raman spectral database on the redesigned IRUG website at www.irug.org. The project was supported by an Institute of Museum and Library Services (IMLS) National Leadership Grant for Advancing Digital Resources awarded to the Philadelphia Museum of Art (PMA) [1]. IRUG is pleased to report that the web-enabled database recently was completed and now serves as a secure repository for the archiving and exchange of spectra within the international community.

The new database software enables users to create personal accounts for online submission, peer-review, and download of spectral data. As with IR spectra, Raman spectra are submitted in a non-proprietary raw JCAMP-DX (ASCII text) format, along with supporting information regarding the sample, sampling and data acquisition (see Figure 1). Submissions then are peer-reviewed and edited, formatted into the IRUG JCAMP-DX format and distributed via user download as discrete data records [2]. Public keyword and spectral searches of the database have been enabled. Match results provide an 'Interactive IRUG Spectrum' with zoom and cross-hair features, 'Details' table and 'Chemical Structure(s)' display for spectra. The searchable bibliography containing open-source PDF papers and glossary have been retained.

Prior to the development of the Raman web-enabled database, IRUG exclusively distributed infrared compilations. The latest contained over 2,100 peer-reviewed spectra of carbohydrates, minerals and pigments, oils and fats, natural and synthetic resins, and waxes. These IR spectra have been migrated to the new database to which 1400 new Raman spectra of synthetic organic colorants, mineral pigments and polymers have been submitted. Recent contributions have come from the Academy of Fine Arts, Vienna; Bern University of the Arts; Cultural Heritage Agency of the Netherlands; Indianapolis Museum of Art; Metropolitan Museum of Art, NY; US Naval Academy; National Gallery of Art, Washington; Museum of Fine Arts, Boston; National Taiwan Normal University; Philadelphia Museum of Art; Victoria and Albert Museum; and Winterthur Museum.

IRUG engaged Endertech web design and software development company to develop the Raman database and associated functionalities using MySQL® open-source database management system. This paper will cover the development and functionality of the new web-based database and software. Individuals interested in submitting or reviewing spectra should contact their respective IRUG

Regional Chair: Beth Price, Americas; Marcello Picollo, Asia and Australia; Boris Pretzel, Europe and Africa; or the IRUG Raman Committee Chair, Suzanne Lomax [3].

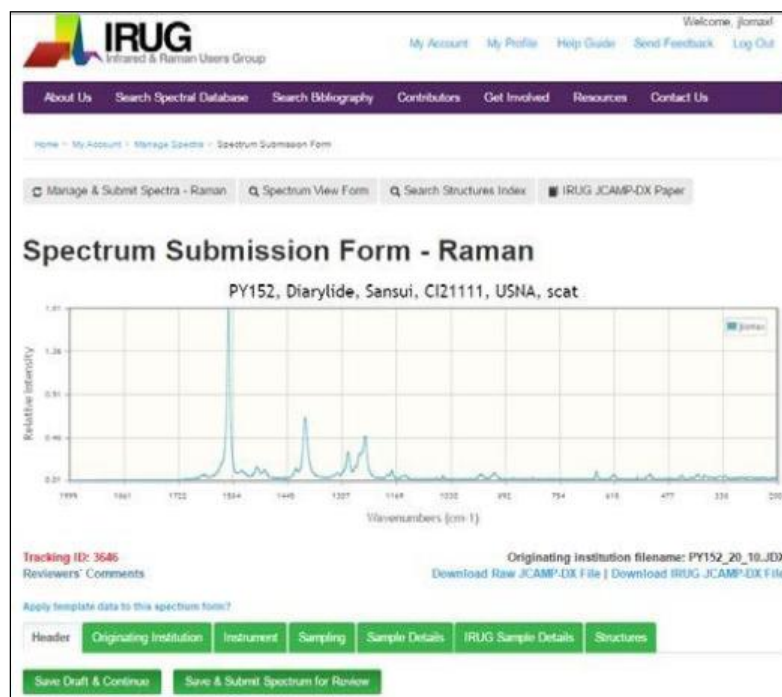


Fig. 1: Redesigned IRUG website screenshot showing online Raman spectrum submission form and interactive spectrum accessed from a user's personal account.

- [1] The IMLS is the primary source of federal support in the United States for libraries and museums. Its mission is to create strong libraries and museums that connect people to information and ideas; to sustain heritage, culture, and knowledge; to enhance learning and innovation; and to support professional development. See <http://www.imls.gov> (accessed 15/12/2015).
- [2] JCAMP-DX (Joint Committee on Atomic and Molecular Physical Data Exchange) is a file specification. For full information on the IRUG JCAMP-DX protocol, see B. A. Price, B. Pretzel, S. Q. Lomax, C. Davis, J. Carlson, Revised JCAMP-DX Spectral File Format for Submissions to the Infrared & Raman Users Group (IRUG) Spectral Database, irug.org/uploads/documentation/irugjcamp.pdf (accessed 15/12/2015).
- [3] The following individuals and institutions are acknowledged for their support: Soon Kai Poh; Jacob Zhang; Kate Duffy; Peter Marchetti; Institute of Museum and Library Services; National Center for Preservation Training & Technology; The Dow Chemical Company, Advanced Materials and Corporate Information Technology Divisions; Philadelphia Museum of Art; National Gallery of Art, Washington; Victoria and Albert Museum; and Institute of Applied Physics "Nello Carrara", CNR.

Session 3 - Instrumental Developments and novelties in commercial instruments

B&W Tek: Portable Raman for On-site Analysis

Daniel Barchewitz

B&W Tek Europe GmbH, Newark, DE 19713, e-mail: danielb@bwtek.com

B&W Tek is an advanced instrumentation company producing optical spectroscopy and laser instrumentation, as well as laboratory, portable and handheld Raman systems. It provides spectroscopy and laser solutions for the pharmaceutical, biomedical, physical, chemical, LED lighting and research communities. Originally established as a producer of green lasers in 1997, it has grown into an industry-leading, total solutions provider; coupling our core technologies with custom design and manufacturing capabilities.

Newest Developments in FTIR Spectroscopy for art and historical object conservation: Truly mobile and non-destructive FTIR tools and the highest spatial resolution true Imaging FTIR

Jan Wuelfken

AGILENT Technologies

This talk will cover all the main areas of significant improvements in FTIR spectroscopy techniques for the analysis of art and historical objects, in support of efforts to conserve, restore and validate authenticity of these rare objects. The first part refers to a new and truly mobile, light, ultra-robust and versatile FTIR Systems giving unparalleled and non-destructive analysis results, wherever the objects reside. The second part covers a truly unique FTIR Imaging system with the highest spatial resolution available, the biggest field of view to measure large areas of the sample and even for microscopy ATR measurement with a unique sample-contact feedback function we eliminate main pain point of sample damage/deformation that traditional systems easily do. This allows the same and often very precious sample, to be re-analyzed via other analytical techniques, providing for better correlation between different techniques.

New generation FT-IR spectrometers: The precious tool from Research to Routine analysis

Vasiliki Chalepli

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InterActive S.A. is distributor of scientific instruments & advanced materials. It specializes in the promotion of quality control lab equipment for the industrial laboratories, chemistry & physics University departments, technological institutes and research centers. It supplies high quality scientific instruments such as FT-IR, NIR & RAMAN spectrometers, microscopes & imaging systems by BRUKER, Portable XRF spectrometers for elemental analysis & positive material identification in alloys by NITON, high vacuum pumps and systems by EDWARDS.

Session 5 - Methodological Developments on Vibrational Spectroscopy

Spectroscopic imaging: new trends and emerging applications to the objects of cultural heritage

Invited lecture by Prof. Sergei G. Kazarian

Department of Chemical Engineering, Imperial College London, United Kingdom

Analysis of materials of cultural heritage collections has a vital role in a responsible modern approach to conservation. Recent advances in spectroscopy, such as the development of FTIR spectroscopic imaging using infrared array detectors, have opened up a window of opportunities for the characterisation of materials in art and archaeology. We develop applications of FTIR spectroscopic imaging to cross-sections from cultural heritage paintings and objects to reveal the chemical composition and to understand the degradation processes in paintings from the National Gallery, London [1] and other museums.

This talk will outline the research we are developing in this area with focus on ATR (Attenuated Total Reflection)-FTIR spectroscopic imaging using both macro and micro modes, [2]. Recent developments in macro ATR imaging with the use of inverted prismatic diamond without the use of an infrared microscope, show great potential with applications to a broad range of samples of cultural heritage. Micro ATR-FTIR imaging has the potential for greatly improved spatial resolution compared to conventional transmission FTIR microscopy, without recourse to a synchrotron, [1, 2]. This methodology opened up many new areas of study, which were previously ruled out by inadequate spatial resolution. For example, using micro ATR-FTIR imaging now allows more precise analysis of the very small pigment particles or multiple thin layers often encountered in samples from paintings, so that a far wider range of samples to be explored. An opportunity exists of obtaining images from layers of sample with different thickness by changing the angle of incidence and thus the depth of the evanescent wave by placing special apertures in the optical path of a microscope objective in micro ATR-FTIR imaging, [3]. This approach could provide information on the degradation of a sample as a function of depth. These advances demonstrate that micro ATR-FTIR spectroscopic imaging can be a powerful tool for the study of paint cross-sections and other samples for chemical visualisation with enhanced spatial resolution and obtaining valuable chemical information about the samples of cultural heritage. This information is crucial for conservation practices and our ability to preserve our cultural collections for future generations.

[1] M. Spring, C. Ricci, D. Peggie, S. G. Kazarian, *Anal. Bioanal. Chem.* (2008) **392**, 37.

[2] S. G. Kazarian, K. L. A. Chan, *Applied Spectroscopy* (2010) **64**, 135A.

[3] T. P. Wrobel, A. Vichi, M. Baranska, S. G. Kazarian, *Applied Spectroscopy* (2015) **69**, 1170.

Studying natural organic substances from Cultural Heritage through multivariate analysis of Raman and infrared signatures

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Natural organic substances are widely used in History and constitute a precious testimony of human exploitation strategies, exchange networks and techniques for their implementation in numerous ancient objects. These materials have been for a long time neglected because of their poor conservation and challenging characterisation. With the re-evaluation of vibrational spectroscopies (Raman and infrared) potentialities through spectral treatment procedures, alternatives or complements to the current analytical strategies based on separation methods can be proposed. The use of FT-Raman (excitation at 1064 nm) is needed to avoid fluorescence, and infrared measurements are performed using a micro-ATR or specular reflectance configuration to eliminate the sample preparation step, both allowing non-destructive analyses.

The first part of the study deals with the differentiation of a broad range of natural organic substances: proteins (animal glues), triglycerides (oils), polysaccharides (gums) and terpenoids (resins from different geographical provenances). This requires specific strategies to differentiate between vibrational signatures with similar features. A methodology is here proposed, based on spectral decomposition of CH stretching massifs followed by Principal Component Analyses of the extracted decomposition parameters. Applying PCA on the raw data, as commonly done, was tried and appeared to be indiscriminative. However, PCA of the fitting parameters becomes an efficient and powerful tool to cluster the different materials. Indeed, it is highly related to their vibrational features and thus to their molecular characteristics. This approach proved the possibility of identifying the natural organic substances, sometime at the scale of the tree species, and an application on archaeological samples and museum varnished objects showed that some alteration or ageing is not an issue to their recognition.

The second part concerns the quantification of identified organic substances in mixtures. Starting from pure products, a methodology was developed by combining these pure products spectra in order to fit the mixture spectra to provide an evaluation of their proportions. This approach proved its ability to quantify resin/oil proportions first on experimental varnishes, with the aim to quantify museum varnished objects.

These developed approaches can find applications in various contexts (archaeology, museum context, conservation purpose) and for a wide range of natural organic materials as varnishes, binders or adhesives, with the advantage of being non-destructive and even sometimes non-invasive.

Gilt leather varnish analysis by infrared spectroscopy

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(3) Centre de Conservation et Restauration du Cuir, Moirans, France.

Gilt leathers are luxurious decorations that have been used all over Europe from the 16th to the end of the 18th century, to embellish the interiors of the richest residences. Despite its name, it is not defined by the presence of gold. According to historical texts it was made by attaching to the leather a silver foil which took the aspect of gold after being covered with a yellow varnish. Nowadays it is still difficult to date and to classify gilt leathers as they are not signed and assumptions concerning their provenance are generally made from stylistic studies, [1]. An analytical methodology was developed recently to characterize the different components within gilt leather, [2]. This methodology is currently being applied to a corpus of historical gilt leather samples to learn about the manufacturing technique of these decors and try to identify physico-chemical markers that would permit to trace back their provenance.

Historical texts depending on the country or the period provides different recipes for the preparation of the “gold” varnish, [3]. All the recipes are based on a mixture of a siccative oil and a pinaceae resin but differ by the presence of additional components and by their oil-resin ratio. Gas chromatography/mass spectrometry and Fourier transform infrared spectroscopy have been applied to try to reveal these discriminating elements from the analysis of varnishes on historic and facsimile gilt leather samples. The first results show that the siccative oil and the pine resin are clearly visible but the markers of the other components are not detectable most likely because these components have reacted during preparation of the varnish.

The present paper will examine the potential of infrared spectroscopies from the far to the near infrared region to extract discriminating information in gilt leather varnishes. This will include the use of spectral deconvolution to try to extract quantitative information from the data. Thanks to the presence of the silver foil in the stratigraphy, trans-reflectance measurements, which are non-invasive and contactless, can be carried out by mid-infrared spectroscopy on these decors. However the quality of the spectra obtained will be strongly dependent on the thickness of the varnish analysed, Fig. 1.

Thus, the distortion and band shift induced in the infrared spectra by the varnish thickness will be discussed. The ultimate goal being to analyse in-situ gilt leather collections that cannot be moved nor sampled, these results we help define the optimum conditions to carry out measurements in reflectance with portable instruments.

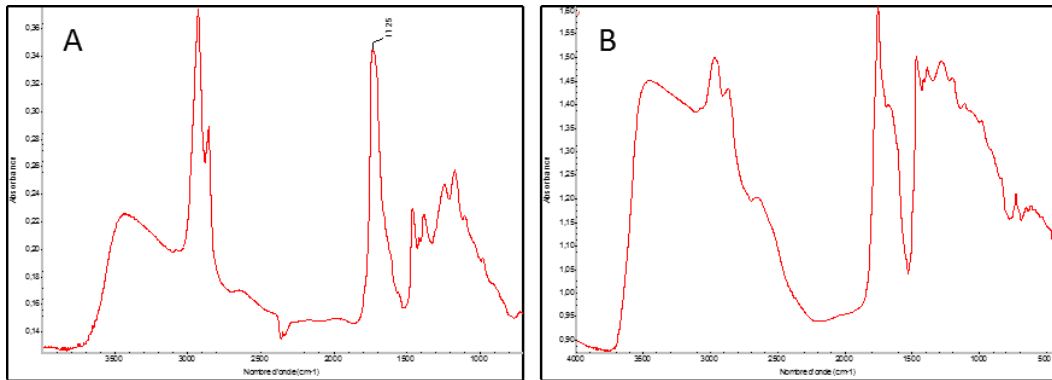


Fig. 2: Comparison of the mid-infrared spectra of a 2 μm (A) and a 20 μm (B) thick varnish in gilt leather samples measured by transreflectance with a portable infrared spectrometer.

- [1] J.-P. Fournet, Mémoire de recherche approfondie, *PhD dissertation*, Ecole du Louvre, Paris, 2004.
- [2] C. Bonnot-Diconne, L. Robinet, C. Pacheco, M. Ioele, and M. Paris, *ICOM-CC 17th Triennial Conference Preprints*, 2014, art. 0701, 8 pp.
- [3] A. Schulze, Goldleder zwischen 1500 und 1800 – *Herstellung und Erhaltung*, *Arbeitsheft 17 des Landesamtes für Denkmalpflege Sachsen*, Ed. Sax-Verlag, Dresden, 2011.

Far infrared selectivity evaluation for reds and black pigments and lead degradation products.

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(4) *Museu d'Art Girona, Pujada de la Catedral, 12, 17004 Girona.*

Far infrared radiation induces vibrations on bonds with high reduced-mass. This is the case of many pigments that are oxides. Thus, taking into account that no many other constituent materials included on artworks absorb in this range, it is interesting to explore the capability of far infrared spectroscopy to improve the determination of pigments in mixtures. An additional advantage for implementation of this potential capability is the extension of the detection range of some commercial equipment available up to 200 cm⁻¹.

In this study, the considered challenges are mixtures of red pigments (Hematites, Red lead, Vermillion and Lead white); black pigments (Carbon black, Ivory black, Iron black and Manganese black) and lead degradation products. These are three cases with problems of identification following other analytical techniques, as XRF, or due to the uncertainty associated to the degradation process.

The study includes, first, the determination of the reference spectra of the different compounds. Next, the detection capability of the equipment used (Frontier from Perkin Elmer) by analyzing mixtures in oil with decreasing amount of pigments from 10 – 0.1%. After this, several mock ups painted by using the same materials were analysed and finally red samples from an actual artwork Retaule de Montagut from Pere Mates (s. XVI century) as well as lead white from graphic art was also studied.

The results show that all red pigments can be detected down to 1% concentration; Iron and Manganese black can be observed down to 1% in mixtures including Carbon black and Ivory black and that lead degradation products are difficult to be observed in presence of Lead white and/or Vermillion.

An additional observation in the mock ups samples, which requires further investigation, is the shift on the position of the absorption bands of the pigments in mixtures with binding media with regard to the values found for the pure pigments.

Session 6 - Damage Assessment and Degradation Analysis through Vibrational Spectroscopy

FTIR spectroscopy of zinc carboxylates in model samples and modern paintings: the macro and micro-scale infrared properties

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The occurrence of Zn-carboxylate species, characterized by sharp and broad infrared bands at 1540 and 1580-90 cm^{-1} , respectively, is often observed when investigating modern oil paintings by both transmission and non-invasive reflection FTIR spectroscopy [1], [2].

One of the aims of this work was to reproduce in laboratory the different species of Zn-carboxylates and to perform a vibrational study aimed at explaining the nature of the broad infrared band. Firstly, the comparison of the FTIR spectral evolution of binary mixtures based on linseed oil and ZnO, and alternatively ZnS and ZnCO₃ demonstrated that the peculiar broad band is strictly connected with the presence of zinc oxide. Both the lower and higher soluble Zn-compounds (the sulfide and carbonate, respectively) show only the sharp band at 1540 cm^{-1} (generally assigned to zinc stearate and/or palmitate) and no evidence for the blue-shifted broad infrared band has been observed. Secondly, the polymerization and ageing processes of binary mixtures made of ZnO with linseed oil, or the corresponding triglyceride (trilinolein) and alcohol (γ -linolenyl alcohol) were investigated in order to deeper investigate the ZnO-oil interaction.

The other focus of this work was to study at a micro-scale level the formation and evolution of both broad and sharp features of Zn-carboxylates on model samples simulating the XX century oil paintings containing aluminum monostearate as one of the most common jellifying agent. Micro-ATR-FTIR spectroscopic imaging allows spatially resolved chemical images showing distribution of specific substances to be obtained [3] and it was performed on unaged and artificially aged samples prepared as cross sections. The results of the spectroscopic imaging study were supported by SEM-EDS and micro-Raman.

The knowledge gained in the laboratory models was then integrated and improved with vibrational data acquired in modern and contemporary paintings that were comprehensively investigated by the same micro-ATR-FTIR imaging and macro FTIR spectroscopy approaches.

[1] J.J. Hermans, K.Keune A. Van Loon, P. D. Ideam, *J. Anal. At. Spectrom.* **30**, (2015), 1600.

[2] C. Clementi, F. Rosi, A.Romani, R. Vivani, B. G. Brunetti, C. Miliani, *Appl. Spectr.* **66**(10), (2012), 1233.

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Investigation of parchment degradation by nanoscale infrared spectroscopy

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(4) Laboratoire d'Optique et Biosciences, Ecole Polytechnique, CNRS, INSERM, Palaiseau, France

(5) Light Light Solutions, LLC Athens, Georgia, USA

(6) Anasys Instruments, Inc. Santa Barbara, California, USA

Parchment was the main writing material in the Middle Ages in Western Europe up to the growth of paper production in the 14-15th centuries. Made from an untanned animal skin it was preserved by liming, scraping and drying the skin under tension. Parchment is sensitive to water, causing in extreme case the denaturation of collagen, its main constituent, to gelatin. Our study has allowed us to demonstrate the interest of correlating two complementary nondestructive techniques, nonlinear optical microscopy and nanoscale IR spectroscopy. Here we will focus on the results obtained by nanoscale infrared spectroscopy that give a better understanding of the mechanisms of degradation.

Infrared spectroscopy provides information on collagen secondary structure and is used to characterize the parchment gelatinization process that is associated with a change in the molecule from a triple helix to a random structure (gelatin). To have a better insight into the local collagen modifications, analysis have to be performed at the fibers (~1-5 μm) or fibrils (~100 nm) scale, therefore infrared technique with a high spatial resolution is required. For this purpose we use a technique called AFMIR. It is a cutting-edge near-field technique using a setup in which an atomic force microscope (AFM) is coupled with a tunable pulsed infrared laser to record spatially resolved absorption measurements. This IR nanoscopy allows acquiring chemical mapping and local infrared spectra to characterize and image samples at nanoscale and has been largely applied in polymer science and microbiology. Here we report the first results obtained on parchment fibers analysis at the nanometer scale using AFM-IR technique. To conclude we will discuss the potential of coupling AFM-IR with other microscopy imaging techniques (especially nonlinear optical microscopy) to obtain new insight into the degradation of the collagen structure from nanometer to millimeter scale.

Raman and FTIR spectroscopy-based damage assessment of protein cultural heritage materials, artificially aged in urban gaseous pollutant atmospheres

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(2) *Department of Chemical Engineering, University of Patras*

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(4) *Department of Chemistry, University of Ioannina*

(5) *Technological Educational Institute of Piraeus (TEI-P), Department of Electronics*

Protein-containing materials constitute significant components of cultural heritage (CH) artefacts and related objects of various types. When exposed to environmental conditions in closed spaces (museums, collections, etc.) they may suffer damages, among others, through exposure to atmospheric pollutants. With this in mind, a comprehensive study has been designed aiming at assessing damage levels on these materials exposed to urban environmental factors such as gaseous pollutants and humidity (typically, nitrogen and sulfur oxides) through a wide range of analytical/testing methodologies. So far, detailed damage assessment on related materials, involving environmental factors and incorporating a wide range of analytical techniques, has only been done for parchment [1-3] and has been valuable in providing information and guidelines for conservation and additional study methodologies. This specific presentation focuses on the vibrational spectroscopy results on artificially aged specimens of bone, parchment and wool textile.

Aiming at the molecular integrity of these materials, the condition of collagen (bone, parchment) and keratin (wool) is the main target of this Raman and FTIR-based investigation which provides information through the molecular and inter-molecular bonding within these materials. According to specifically focused experimental design [4], a room temperature artificial ageing scheme was employed, aiming at simulating typical urban environments involving two different levels of NO₂ and SO₂ (10 and 25 ppm, correspondingly) and moisture (45% and 70% RH) with overall exposure times set to 14 and 28 days. In the comprehensive analytical part of this design, vibrational spectroscopy is a vital part aiming at supporting the overall study with the necessary molecular information.

Raman spectra were recorded (resolution 4 cm⁻¹) in backscattering geometry using the 1064 nm laser line of a Nd:YAG laser, with a notch filter (>50 cm⁻¹) and an LN₂-cooled CCD detector. Peaks at ~1000 and 1045 cm⁻¹ were detected in a number of cases indicative of the incorporation of sulfate and nitrate groups into the materials. Evaluation of Raman features allowed the development of specific markers, indicative of peptide bond hydrolysis, involvement of hydrogen bonding and transformations into random chains; furthermore, newly formed nitrate and sulfate-containing features were detected (Fig. 1a).

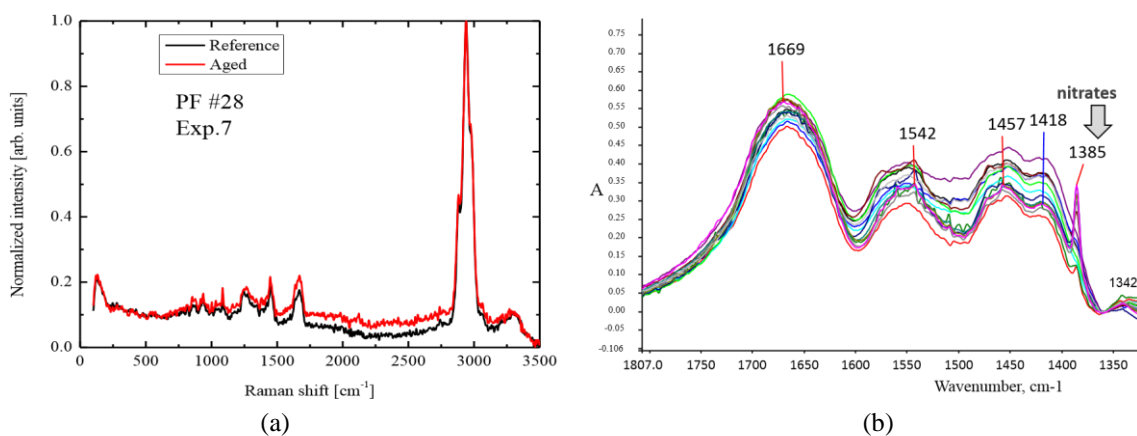


Fig. 1: (a) Right angle Stokes-side Raman spectra of reference (black) and aged (red curve) parchment samples after artificial ageing at 70% RH, exposed to NO_2 atmosphere (10ppm) followed by SO_2 (10ppm), (b) FTIR spectral region containing amide I, II bands and carbonates, recorded from powder samples of artificially aged bone specimens.

Attenuated Total Reflection-Fourier Transform Infrared spectroscopy (ATR-FTIR) was applied on parchment and wool textile specimens, while bone was investigated through detached powder samples (KBr-FTIR). In all specimens, protein materials resulted in the typically broad amide I and II bands, the envelope of which is sensitive to the chemical environment of protein amide links. Further analysis of these using a deconvolution/peak fitting routine revealed a trend for less ordered peptide chains in the aged materials, which were especially evident in parchment and wool. Additionally, newly-formed peaks due to nitrate-containing products were detected (Fig. 1b), which were generally in accordance with Raman investigations.

In the case of bone, specifically, the attention in both Raman and FTIR spectroscopy was additionally focused on carbonate/phosphate, phosphate/amide I and carbonate/amide I ratios, which are markers for the mechanical condition of the samples. A small reduction of the inorganic fraction is indicative of reduced skeletal fragility and decrease of the corresponding Young's modulus.

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Ageing processes in diterpenic resins used in artwork coatings

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Coating and varnishing cultural heritage objects has been a constant practice throughout history. The study of those coatings can provide information about the materials themselves but also about the artworks and for determine their optimal conservation and, if necessary, their restoration.

Among the large variety of materials used as coatings, resins are one of the most used, in particular, diterpenic resins have been traditionally used in Europe. This category includes resins based in abietic acid (*Pinaceae* sp. resins) and also resins based in communic acid (like sandarac). All they show a complex chemical composition because they contain different molecules of high molecular weight and a similar structure, some of them are stable but others evolve with ageing, [1]. It is essential to identify the main molecules because the stable ones can be used as specific markers of each resin while the unstable ones can help establishing its degradation degree.

A wide range of techniques have been used to study diterpenic resins. Among them Gas Chromatography coupled to Mass Spectrometry (GC/MS) and Pyrolysis coupled to GC/MS allow the identification of the fresh and aged molecules but imply the dissolution of the samples and use derivatization procedures so intermolecular interactions and macromolecules cannot be observed, also samples are spoiled and cannot be analyzed by means of other techniques [2]. Other analytical techniques are Infrared (FTIR) and Raman Spectroscopies, but until now the related studies have been mainly focused on the identification of the *Pinus* resin fingerprint [3, 4]. However, they can detect macromolecules and do not require the dissolution and derivatization of samples so, consequently, they can give information of the intermolecular interactions. The main disadvantage is that the interpretation of the spectra can be very complex, especially for identifying the specific markers of the molecules with a similar structure.

A systematic study by FTIR and Raman spectroscopies complemented with GC/MS of diterpenic resins ageing, using resin samples and pure reagent compounds is carried out. The changes observed during ageing have been corroborated studying resin samples from different epochs and also kept in different storage conditions. The specific sample preparation and optimal analytical conditions for FTIR and Raman analysis will be discussed with particular emphasis in the Raman as the thermal sensitivity of the thermally treated resins makes those analysis particularly difficult. Moreover, band assignment of the FTIR and Raman spectra is proposed. The data is of particular value for the analysis of artworks resins, as it helps establishing the type of material and, in some cases, its degradation degree.

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Weathering of polyester and epoxy resins: degradation studies by in-situ time-lapse IRRAS, QCM and ex-situ MeV-SIMS

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Synthetic polymers such as polyester and epoxy resins play an important role as modern artists' materials but also in the field of conservation of cultural heritage objects. Its applications are widespread ranging from stabilizing and coating composites, metal, wood, plastics, photographs, paints, inkjet prints, canvas, ink, paper, spraypaint and many more. As those materials are exposed to different ambient indoor or outdoor atmospheres their stability is of crucial importance as already small chemical changes may cause visible ones which spoil the aesthetics of the artistic object. Conventional atmospheric parameters that may affect material degradation comprise weathering factors (temperature, moisture, solar radiation, etc.), air pollutants (H₂S, SO₂, CO₂, NO_x, O₃, etc.) and aerosols. The increasing concentration of anthropogenic caused corrosive gases mainly present in urban environments is challenging scientists and conservators dealing with art objects in museums or outdoors, private collections or archaeological sites. As our cultural heritage is inherited from past generations, unique and irreplaceable, it is our responsibility to preserve and protect this cultural property for future generations. For this reason it is of special interest to study the occurring reactions in-situ and in a time-resolved way in order to develop methods and strategies to reduce or even stop and prevent those atmospheric attacks. Due to their various applications in works of art synthetic polymers such as polyester and epoxy resins are of special interest for such investigations.

In this study surface sensitive analytical methods have been applied to investigate the degradation behavior of polyester and epoxy resins exposed to controlled atmospheres containing synthetic air, 70% relative humidity (RH), SO₂ and H₂S in the ppm range, as well as O₃ in the ppb range. For these investigations a self-constructed in-situ weathering chamber [1] was used which allows time-lapse InfraRed Reflection Absorption Spectroscopy (IRRAS) and Quartz Crystal Microbalance (QCM) measurements to track chemical reactions and gravimetric changes during weathering. Furthermore, MeV Secondary Ion Mass Spectrometry (MeV-SIMS) was performed before and after weathering to obtain information on molecular changes due to weathering.

Fig. 1 (upper graph) shows the time-lapse IRRAS measurements of polyester resin exposed to synthetic air, 70% RH and 2.4 ppm H₂S for 90 hours. To better estimate small changes of absorbance bands over time the time-lapse spectra were all divided by the spectrum obtained at time 0 (reference). By evaluating the increase or decrease of the absorbance bands which are related to certain chemical species, conclusions can be drawn on the degradation behavior of these resins under different atmospheric conditions. These fundamental deterioration studies are indispensable for developing strategies and methods to reduce such environmental attacks.

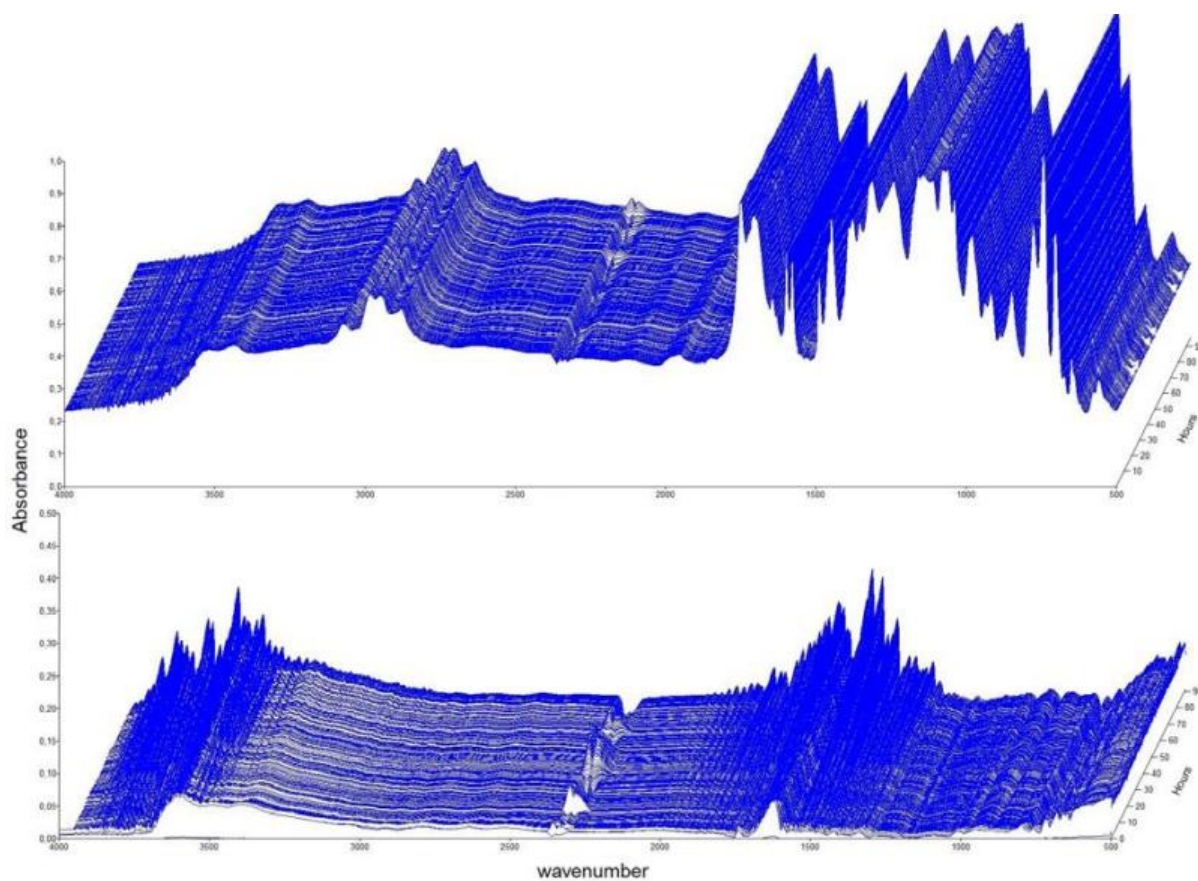


Fig. 1: Timelapse IRRAS measurements of polyester resin exposed to synthetic air, 70% RH and 2,4 ppm H₂S for 90 hours (upper graph). Lower graph shows the time-lapse spectra after calculation the ratio by using the measurement at time 0 as a reference.

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Fluorination technique to investigate photooxidative ageing products in bioorganic resin materials using infrared spectroscopy

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Infrared spectroscopy (FTIR) is a long established standard technique to characterise organic materials in conservation science. There are, however, limitations to the technique when analysing chemically complex multi-component materials with interfering functional groups. This is particularly the case with aged terpenous resins. Due to the ease of these raw materials to oxidise, the ability to correctly assign the functional groups is critical for their identification and characterisation of their oxidation state. The distinction of oxidised di- and triterpenes, for example, is hindered by the interference of similar absorption bands of characteristic carbonyl functional groups, summing up to a broad, non-distinctive signal. Various attempts have been published on the statistical peak deconvolution of different IR signals in terpenous resins. While these allow isolation of distinctive carbonyl bands, they do not deliver unconditional characterisation of the functional groups. Thus, it is of interest to discriminate overlapping signals in a chemical way, using a selective chemical group transformation method.

To increase the spectral selectivity of the infrared spectroscopic technique to characterise oxidative ageing products, a derivatisation technique applying gaseous sulfur tetrafluoride SF₄ is able to selectively fluorinate various acids. Derivatisation of the functional groups leads to characteristic band shifting, allowing the separation of otherwise overlapping bands. It achieves the splitting of primary acids, α,β -unsaturated acids, tertiary acids, peroxy acids, esters, ketones, and α,β -unsaturated ketones, into spectrally distinct absorption bands. The method enables to detect and identify all mentioned carbonyl compounds, using infrared spectroscopy, even in complex mixtures of terpenes. Using this technique the ageing behaviour of triterpen (Dammar and Masic) and diterpene varnishes (Colophony and Sandarac) was investigated. The functional groups are formed during light ageing was characterised sequentially over ageing time.

The high sensitivity and selectivity of this method characterising functional groups provides infrared spectroscopy with a higher level of specificity, which is of particular interest to structural studies on oxidised organic compounds. Peak separation is such that in combination with chemometric methods, quantification of the compounds is feasible. Thus, this is of specific interest to characterise the oxidation state of a material. Furthermore, new perspectives are given by this method with respect to research on oxidative degradation reactions of organic materials in artwork, since the formation of the various reaction products may shed new light on the respective reaction pathways.

Influence of the soft and strong artificial ageing on the photo-stability of artists' paints containing alkyd binder and phthalocyanine pigments

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Alkyd paints are widely used in modern and contemporary art objects kept in museums as well as exposed to outdoor environment. For the works of art exposed to outdoor conditions, one of the main causes of paint layer degradation is the exposure to solar radiation. Wavelength in the UV-A range (400-315 nm, near UV) and in the UV-B range (315-280 nm, middle UV) are not absorbed by the atmosphere, and their energy fall within the bond dissociation energy range of many polymers (240-400 nm). Photo-degradation is a surface phenomenon, caused by the combination of electromagnetic radiation and oxygen diffusion within the uppermost layer of the paints [1]. In alkyd resins, photo-degradation process results in cross-linking, chain-scission and Norrish reactions, taking place on the oil as well as on the polyester component of the resin [2], [3]. When alkyd is used as binder in artist's paints, the presence of pigments can influence such degradation processes, acting as light stabilizer or as catalyser, depending on the paint system.

In this study the influence of blue and green phthalocyanine pigments (PB15:x, PB16, PG7 and PG36) on the stability of alkyd paints exposed to outdoor radiation conditions is investigated. Thus, self-made and commercial paints samples were artificially aged by exposure to accelerated solar radiation, including UV-B range. The ageing was performed with Xenon Arc lamp at soft (177 W/m², comparable to natural ageing) and at strong (910 W/m²) irradiance values.

The behaviour of alkyd paints exposed to such conditions was investigated by microRaman Spectroscopy (μ -RS), Attenuated Total Reflection Infrared Spectroscopy (FTIR-ATR) and Thermally assisted Hydrolysis and Methylation Gas Chromatography/Mass Spectrometry (THM-GC/MS). μ -RS was used to study the behaviour of the pigments; FTIR-ATR gave useful information about the whole paint systems and allowed semi-quantitative considerations about the influence of each single pigment on the ageing process [4]. Finally, THM-GC/MS analyses were used to better characterize the degradation products formed during ageing [5].

The results showed that no changes occurred on the pigments with ageing, indeed phthalocyanines are well-known for their light fastness [6]. Already after one month ageing at soft conditions the photo-degradation products of the alkyd binder were detected. Further, the degradation products found in samples aged under both conditions were comparable, but a higher amount of them was obtained in samples exposed to strong conditions. Thus, the photo-oxidation pathways started already at low irradiance value (177 W/m²) and the high irradiance value (910 W/m²) had influence only on the extent of such reactions. Independently from the ageing conditions, the ester bond of the polyester portion of the alkyd binder was affected by photo-cleavage (Norrish type I), and free phthalic acid was formed. The presence of phthalocyanine pigments was stabilizing the paint systems against this process. Nevertheless, among the tested samples, the paints containing chlorinated and brominated copper phthalocyanine green (PG36) showed higher extent of degradation. Due to the decomposition of the binder by chain-scission and Norrish reactions volatile species were formed. Therefore, a relative enrichment of pigments and of fillers was observed on the surface of the self-made and of the commercial paints, respectively.

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Effectiveness of protection, damage assessment, and novel nano-particle based conservation treatment of vegetable tanned leather

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The EU funded MEMORI project brought awareness to conservators of the problem of volatile organic acids in enclosures and demonstrated their damaging effects particularly on organic-based cultural objects [1]. For collagen-based materials (parchment, leather) improper storage conditions with elevated levels of volatile organic acids contributes to collagen denaturation with lowering of pH resulting in surface gelatinization. For preservation of these objects this can be a problem as fluctuations in RH and temperature can lead to damage of this surface layer resulting in cracking. Within the EU project NANOFORART, one of the aims was to protect collagen-based artefacts with novel nanoparticle formulations. The basic idea is to adjust pH and prevent the collagen from being exposed to low or high pH values at which damage occurs. Some preliminary results on collagen-based objects, in particular vegetable tanned leather (sumac), will be presented.

In this paper it will be demonstrated that ATR/FTIR can be used to monitor the effectiveness of nanoparticle treatment on vegetable tanned leather. When vegetable tanned leather (sumac) is aged, it shows changes to the Amide I and Amide II peaks which represent the collagen structure. The shape of the Amide I peak, in particular, is representative of the collagen secondary structure, [1]. There is a broadening of the Amide I peak to higher wavenumbers. The changes can be quantified by measuring the ratio of absorbances at selected wavenumbers within the Amide I peak. The 1660:1630 ratio within the Amide I peak has been selected in previous work for assessment of damage to collagen, [2]. The higher this ratio, the more damaged the collagen. This approach was also used in the EU funded IDAP project for damage assessment in parchment, [3]. In addition there is a shift of the Amide II peak to lower wavenumbers indicative of changes in the hydrogen bonding in collagen (crosslinking) and that some denaturation has occurred. Additional complementary information from small angle X-ray scattering (SAXA) on aged sumac tanned leather demonstrated that the D-banding values for collagen have been reduced from 65nm to 56nm in these samples. There are also changes in the peak at 1231 cm⁻¹, which include contributions from the amide III and tannin (sumac) peaks.

Treatment was performed on both unaged, historical, and then accelerated aged leathers using formulations which included calcium carbonate nanoparticles with and without Klucel, calcium lactate nanoparticles with microemulsion and gel. ATR/FTIR spectra of modern leather indicated that the addition of calcium carbonate Klucel did not cause any denaturation of the collagen in leather. On ageing, however, it showed beneficial protective effect as there were minimal changes in the treated sample compared to the untreated aged sample. This was also the case for the calcium lactate treated

samples. Both treatments still maintained a protective effect even after the second step of ageing. This was also observed in tested historical leathers.

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On site detection of cleaning system residues: a feasibility study for the application of reflection FTIR spectroscopy

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During the last fifteen years, several new formulations and procedures for painting cleaning have been developed [1]-[3] in order to selectively remove deposits and deteriorated coatings without affecting integrity of the underlying paint layers. These innovative methodologies, in fact, provide the use of specific active substances like surfactants, chelating agents and enzymes able to solubilize in a targeted way the components to be removed. Generally, the surfactants perform a detergent function, the chelating agents are metalcomplexing agents, while enzymes catalyze chemical reactions of proper substrates rendering them more soluble. In addition, to minimize the penetration of cleaning solvents and to localize their action into the painting matrix, reducing negative side effects of swelling and/or leaching, gelling materials are usually employed. Unfortunately, the total control of the cleaning action is extremely difficult and residues of these cleaning products, as reported from the reference literature [3], [4], can remain on the painted surface. The presence of cleaning residues has been investigated by micro-destructive techniques [5]-[7], which allow to optimize the cleaning formulations through laboratory tests. However, these formulations must be applied on real paintings which are very complex physico-chemical systems characterized by a specific conservative history, therefore the development of a non-invasive spectro-analytical method for *in situ* real-time monitoring of cleaning procedures is mandatory [8].

In the present study, the selectivity and sensitivity of reflection FTIR for the detection of nonvolatile cleaning residues have been evaluated. This analytical technique has been chosen for its high specificity for identification of organic, inorganic and organometallic materials and sensitivity for surface molecular properties. Furthermore, the used instrumentation is non-invasive, portable, fast, reliable and, therefore, recommended to perform *in situ* investigations. More than ten nonvolatile compounds, frequently reported in cleaning formulations, have been selected. The infrared spectral features of a series of surfactants (*Ethomeen C-12/C-25*, *Tween 20*, *sodium lauryl sulphate*, *mucin*, *coconutcollagen*), chelating agents (*EDTA*, *TEA*, *TAC* and *citric acid*), enzymes (*lipase*) and gelling materials (*Klucel G* and *Carbopol Ultrez 21*) have been analyzed in transmission and reflection mode to elaborate a complete infrared database. The study included also the evaluation of the matrix effect leading to spectral distortions caused by specular and diffuse reflection phenomena at the surface, as well as the issue of spectral overlapping of surface/cleaning compounds infrared bands. For this purpose, several solutions of the selected cleaning agents were prepared in different concentrations, applied on painting mock-ups and analyzed by reflection FTIR spectroscopy.

The results from the performed experimentation provided significant information to assess limits and potentials of this technique for *in situ* on-line monitoring of cleaning treatments of painting surfaces in order to provide a ready detection of possible cleaning residues.

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In situ measurement of damage with vibrational spectroscopy

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There is a current debate about safe relative humidity and temperature bands for objects. A portion of the disagreement revolves around the use of surrogates to undertake destructive scientific testing. The properties of many naturally aged materials are difficult to replicate and this brings doubt about the representative nature of otherwise exhaustive studies. An alternative approach is to measure damage in situ on actual objects kept under different environments. Advances in instrumentation allow routine, non-invasive and portable measurements with vibrational spectroscopy. This paper will discuss the advantages and limitations of such techniques through a series of case studies.

DRIFTS FTIR was used to follow corrosion on small archaeological lead plaques stored in wooden drawers. The corrosion rate was determined as a function of RH and acetic acid concentration. The measurements were limited by the topography of the plaque surfaces. When possible they proved far easier than conventional corrosion product stripping.

Portable Raman spectroscopy has been used to rapidly survey corrosion observed on archaeological copper alloy. Previous research has shown the high potential for misidentifying stable corrosion products as bronze disease with visual examination. The results were incorporated into a criteria anchored survey of objects displayed in different RH and acetic acid environments.

ATR FTIR has been used to follow the oxidation of natural rubber gas masks presented in situ in a world war two tunnel complex. Autocatalytic degradation was observed. A survey of curatorial attitudes developed an acceptable oxidative change that measured values could be compared to. The same technique has been used to assess the degradation rate of cellulose acetate folders on display and in store.

Infra-red microscopy has been applied to vulnerable Limoges enamel plaques to measure glass deterioration over 12 years. Instrument stability over such a period requires checking with suitable stable standard materials. This study has initiated and validated improvements in the display environment. The precise repositioning of analysis is necessary to achieve sufficient accuracy. Fortunately the degradation is generally slow, hence the requirement for accuracy. Holes cut in Melinex masks aligned with the enamel design allowed accurate repositioning. Sample area and depth are important. Whilst micro sample areas are advantageous for some conservation science, a larger area is more representative of the often very heterogeneous surfaces of interest. A thorough understanding of depth is required for the often overlapping enamel layers.

Near infra-red spectroscopy can determine degree of polymerization and pH of paper with correct calibration. The rate of degradation of notebooks used by Charles Darwin during his voyage on the Beagle has been determined in store and on display under different environmental conditions.

Non-contact reflectance FTIR has been used to analyze the state of collagen in archaeological bone, its crystallinity index and likelihood of DNA retrieval.

Vibrational spectroscopy has been shown to be a powerful tool to measure chemical degradation in situ on objects. Sufficient targeted studies combined with monitoring of different environments can provide vital evidence to inform preventive conservation.

Analytical Investigation of 20th Century Coatings on Outdoor Bronze Sculptures from the JPGM

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An analytical study was conducted of original patinas and restoration coatings from a group of 20th century outdoor bronze objects, donated in 2005 to the J. Paul Getty Museum from the Ray Stark Revocable Trust. The investigation was prompted as part of a five-year plan to restore acrylic coatings on a collection of outdoor bronzes, including works by notable artists such as Barbara Hepworth and Aristide Maillol. FTIR, Raman, Py-GC/MS and X-ray fluorescence analysis of the conservation treatment was initiated to better understand the coating removal process and inherent difficulties posed by intractable layers applied during previous restoration work. Oxidized microcrystalline and ester containing waxes, along with Incralac, basic copper chlorides, sulfates, carbonates and organic metal complexes were identified. The analysis results helped clarify the aging influences on the formation of certain degradation products.

The investigation was complemented by a parallel evaluation of artificial and natural aging of conservation grade waxes and acrylic coatings applied on metal coupons and glass slides. The testing was intended to provide coherent assessment of coatings used for outdoor sculpture maintenance, including their efficacy and long-term working properties. Various physical and chemical properties of the coatings were evaluated during the aging period, as the processes helped highlight the chemical and inherent solubility changes of treatment coatings.

Session 7 - Materials characterization through Vibrational Spectroscopy

Raman spectroscopic analysis and light fastness of specimens from Wilhelm Ostwald's colour system

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The chemist and Nobel Prize winner Wilhelm Ostwald (1853 – 1932) has developed a specific colour system from the year 1914 on. A great deal of Ostwald's heritage is still being kept at his former house "Energy Estate" at Grossbothen near Leipzig, Germany. At first, the "Colour Circle" was developed and realized by stained paper strips and published in the "Colour Reader" (1917). A more comprehensive issue of the colour system from 1919 consisted of painted colour strips. Later, collections of coloured powders were developed as well, called „Colour Organ“. Although the theoretical background of the colour system is well understood, only little is known about the chemical composition of the material representing it. A few details were published by Ostwald himself, but no analysis has been undertaken so far. The coloured paper sheets are said to generally be prepared using synthetic organic dyes. Presumably synthetic organic pigments (SOP) have been used for the powders although no indication is given in the literature. Knowledge of the composition of these historic scientific materials is not only important to understand how the colour system was realized, but is also essential to estimate their light fastness. The light fastness of the paper specimens already has been criticized by contemporary researchers and artists.

Specimens of the colour systems mentioned above were investigated for their composition and light fastness. Each sample was measured with dispersive Raman microspectroscopy at 785 and 532 nm excitation wavelength. The samples were measured directly as well as using alternative techniques such as KBr pellets. Samples with high fluorescence were additionally measured with a dispersive NIR-FT-Raman spectrometer (1064 nm). In order to achieve more differentiated Raman spectra thin layer chromatography (TLC) was carried out on silica plates, where Raman spectroscopy was directly applied to the stains. Light fastness was measured using a Micro Fading Tester (MFT) with an illuminance of 9 Mlux at a spot of 0.2 mm diameter. The fading is expressed as a change in colour distance (CIEDE00) to the initial CIE L*a*b* values. The colour change was compared to the change of Blue Wool Standards (BW) under the same conditions.

For the stained paper samples some of the synthetic dyes mentioned in the literature could be identified by Raman spectroscopy. In the powders, barium sulphate and lithopone were identified together with binary or ternary combinations of six different synthetic organic dyes and pigments (monoazo, β -naphthol, phenylxanthene, and triarylcarbonium). The light fastness of the different samples showed great differences. Some of the powders from the "Scientific Colour Organ" showed a light fastness even less than BW1.

Raman microspectroscopy has shown its great potential for identifying synthetic organic dyes and pigments, although triarylcarbonium pigments could not be clearly identified. Thin layer chromatography proved a complementary technique for identification of organic pigments. The analytical results suggest that obviously Wilhelm Ostwald has switched to more light stable synthetic organic pigments for the later developments of his colour system.

Spectroscopic characterization of cobalt violet pigments in multi-layered structures: analysis and detection limits

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Cobalt phosphate, a type of cobalt violet, is reported in most books on artists' materials as a semi-opaque, 'delicate violet' pigment made in a variety of shades ranging from violet-pink to deep violet, [1]-[3]. Although cobalt violet was known since 1880s, its occurrence in artworks has not been well documented to date, [4].

While examining Kazimir Malevich's *Painterly Realism of a Football Player - Color Masses in the 4th Dimension* of 1915, using non-invasive techniques at the Art Institute of Chicago, the purple paint used by the artist was found to contain mainly cobalt violet. In the examined purple areas of this work, XRF detection of Co and P, and a complex convolution of bands between 710 and 1171 cm^{-1} by reflectance FTIR was consistent with cobalt phosphates mixed with an ultramarine underlayer. Point areas analyzed with FORS, highlighted the presence of cobalt blue, possibly used to darken the hue or being present in adulteration with ultramarine blue. The detection of ultramarine blue by R-FTIR and cobalt blue by FORS in the examined purple areas of the painting, led to the creation of mockups demonstrating that a layered system with ultramarine blue below and cobalt violet above would give spectra consistent to the ones recorded in situ on the painting.

This paper reports on the systematic testing of reference paint mixtures composed of cobalt violet, ultramarine blue and cobalt blue with reflectance spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), FT-Raman and X-ray Fluorescence spectrometry (XRF). The systematic evaluation of the reference paints allowed establishing limits of detections for cobalt violet when used alone or in mixtures with ultramarine blue and cobalt blue pigments in multi-layered paint systems. The research also confirmed that a combination of techniques is necessary for the positive identification of cobalt violet in an unknown mixture of violet and blue pigments.

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Combined Raman, X-ray Diffraction, and UV-Vis Spectroscopy Characterization of Natural and Artificially Aged Neutral Verdigris Pigment

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Artists have been aware at least since the Middle Ages that the pigment known as verdigris is subject to color change, especially in thin washes or glazes, turning greener and sometimes becoming muddy-brown over time, [1]-[6]. Nevertheless, verdigris remained an important pigment through the 18th century and found special popularity among map and book colorists, who could achieve transparent green color washes that would not obscure the printed lines. The fickleness of verdigris' color naturally relates to its chemistry, so that precise identification of the pigment in works of art is an often vexing problem for the analyst. This is due first of all to the fact that verdigris exists in two different chemical compositional groups based on either the neutral or basic copper acetate salt. For example, commercial distributors who do not assay their verdigris pigment, normally supplied as copper acetate monohydrate (Cu(II) (CH₃COO)₂·H₂O), often misidentify the product as basic verdigris. Second of all, verdigris has a propensity to alter into phases with subtle differences in composition. Verdigris may also become completely amorphous during aging in paint films, possibly forming organo-copper complexes, [7], [8]. Therefore, verdigris is often identified in historical works solely by the presence of substrate degradation in the vicinity of a green pigment and the presence of copper, although this is not a sufficient means of attribution.

This paper expands on the preliminary results presented by poster at IRUG11 and details research to date entailing combined X-ray diffraction, Raman, and UV-Vis spectroscopic characterization of model paint-outs of neutral and basic verdigris, with and without natural and artificial aging. Distinguishing spectral features between aged neutral and basic verdigris highlight differences in stability of the two types, where the former is far more reactive, converting readily to variations of basic copper salts under different conditions. Our results thus aid in the identification of verdigris in cultural heritage, as well as advance our understanding of verdigris aging paths. Results also suggest that the importance of neutral verdigris as a pigment has been underestimated, since it is the more commercially viable type.

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Session 8 - Raman and FTIR Spectroscopy for the Study of synthetic polymers and modern materials

Die Kunststoffschule – a Unique Collection

Identification of Plastics and their Ageing Phenomena

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Literature dealing with FTIR measurements in the conservation field of plastics concentrates on single materials or practical questions. This work provides on one spot the main plastic groups, their ageing mechanisms, their identification via FTIR spectroscopy and the markers for deterioration in the spectra.

The oldest of the more than 170 samples date back to the 1950s and are taken from a unique collection, *Die Kunststoffschule*, edited by AG Dt. Kunststoff Industrie [1], [2]. For consistent measurements, samples were taken from the subsequent editions of the Kunststoffschule (1960s), the *Probensammlung zur Kunststoffkunde* (1985) and the *Kunststoff Probensammlung* (2004 and 2015) as well as further samples. All samples were photographed and catalogued providing information about texture, colour, signs of deterioration, date, FTIR Measurement and plastic species and a database of spectra for naturally aged plastics and polymers of different ages and structures was established using the Bruker Alpha FTIR Spectrometer (equipped with either an attenuated total reflection (ATR, Diamond cell) or an diffuse reflection module (DR)).

Measurements were mainly taken with the ATR unit, if the samples could be clamped taut. Fragile and degraded objects from the Cellulose derivatives were measured with the reflection module, which barely touches the sample.

The chemical composition of some samples was unknown, but could be identified by comparing their spectra with reference databases, [3] - [5]. The assignment of peaks to their respective molecular unit in a polymer's spectrum was documented and resulted in an elaborate work of reference. DR revealed to be a useful technique to supplement ATR in the identification of plastics - Cellulose acetate and Cellulose acetobutyrate could be more easily distinguished using FTIR-DR.

FTIR spectra of the same plastic sort were grouped: Cellulose derivatives, phenolic plastic, aminoplast, polyacrylate, polyamide, polyester, polycarbonate, polyethylene, polypropylen, polystyrene, polyurethane, polyvinyl chloride, polytetrafluor ethylene and silicone. Spectra within the groups were compared referring to their ageing. Structural changes in the spectra of differently aged polymers were detected and designed to ageing processes within the chemical structure of the polymers.

In some plastic groups prominent markers were found for ageing. For instance, from the group of nine Polystyrene samples only one showed signs of ageing by view: a solid transparent sample from the 1990s shows yellowing, crazing and cracks. In the FTIR-ATR-spectrum this sample shows clear OH-markers around 3300 cm⁻¹. Ageing took place by oxidation: OH-groups were substituted to the chemical structure of polystyrene. One sample of evaporated Polystyrene (2.2 EPS) from 1985 shows no signs of ageing by view but again OH-markers around 3300 cm⁻¹ – in contrast to a solid sample of the same age and storage (2.1 PS), which has a smaller surface and therefore shows no signs of degradation in the spectra yet, (Fig.1).

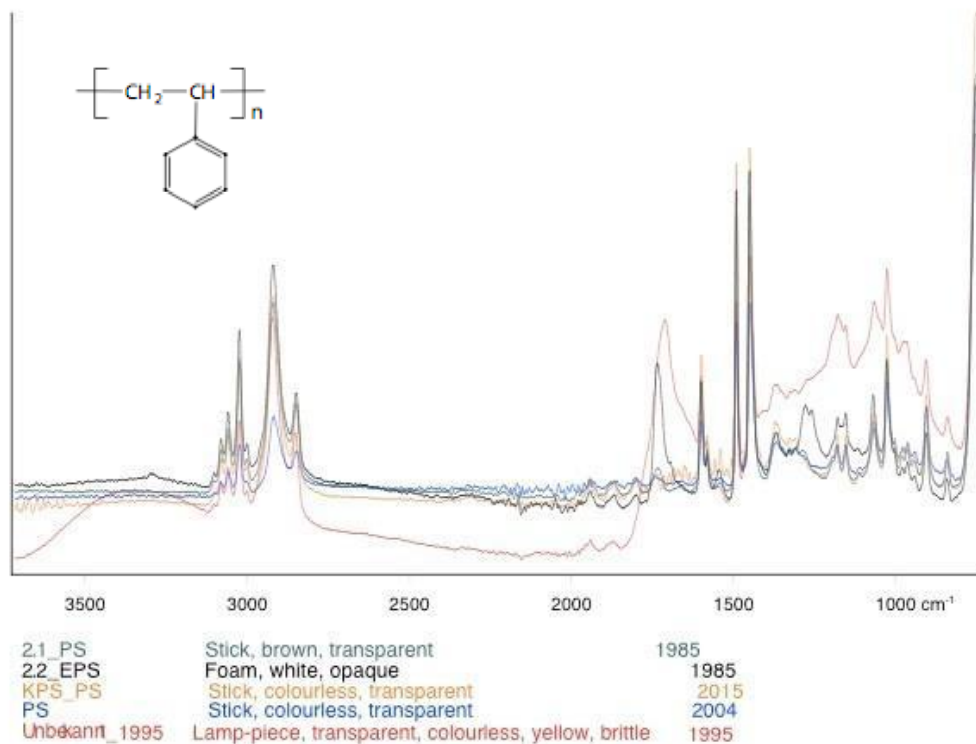


Fig. 1: Polystyrene samples in different stages of ageing. Markers for Oxidation of Polystyrene around 3300 cm^{-1} (black and red curves).

This project gives an overview over FTIR analysis and identification of polymers. Furthermore, the markers, which show significant changes in the signals due to ageing, were detected. This way, detailed records about the most common plastic groups, their chemical composition, their ageing reactions, identification using FTIR and their ageing phenomena in the spectra were kept.

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The colour of plastics: The identification of colourants in plastics

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Few would dispute that scientific research will continue to play a crucial role in the study, documentation and conservation of modern and contemporary art and design. There seems to be a never ending number of new materials and application techniques being used for works of art, each of which would presumably require the development of appropriate analytical methods for their identification.

Colourants (pigments and dyes) in plastics play an important role in the appearance and perception of an object. However, more and more plastic objects show colour change due to problems with colourants; colourants can fade and also the transfer of colourant to adjacent differently coloured plastics may take place.

At the Cultural Heritage Agency of the Netherlands (RCE) in Amsterdam research has been carried out into the conservation of plastics used for and applied to modern and contemporary art and modern design objects. For the conservation of these plastic art objects, the composition of their main components and additives should be known. A variety of analytical techniques exist for the identification of the composition of plastics, of which non-invasive techniques are preferred. Mostly, the main components of the plastics are identified, whilst additives and colourants have not been researched in detail.

Various synthetic organic pigments from the RCE Reference Collection were analysed with several analytical techniques: Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and X-ray diffraction (XRD). Using the resulting reference data, many synthetic organic pigments in reference plastics could be identified. After the identification of pigments in reference plastics, experience and confidence was built to identify pigments in objects of art.

One of the case studies for the research was ‘The Rimpfishhorn Handicap, part 1’, (1991) by Seymour Likely an artist collective from Amsterdam. This work is composed of orange coloured fins adhered to a circle made of wood (see Fig. 1). The plastic material was identified with FTIR as Isoprene – butadiene – styrene copolymer, a synthetic rubber. Using Raman pigment orange 16 was identified (see Fig. 2). Py-GC/MS analyses confirmed the presence of pigment orange 16 as well as the presence of the Isoprene – butadiene – styrene copolymer.

The identification of the organic pigments in plastics can contribute to formulating exhibition lighting guidelines for a particular object of art. When it is known which colourants are present in an object, the light-fastness can be derived from literature and the sensitivity class can be determined. Objects containing pigments with poor light fastness may only be exposed to a low illumination dose, whereas others may be exposed to a higher dose.



Fig. 3: 'The Rimpfishhorn Handicap, part 1', (1991) by Seymour Lively.

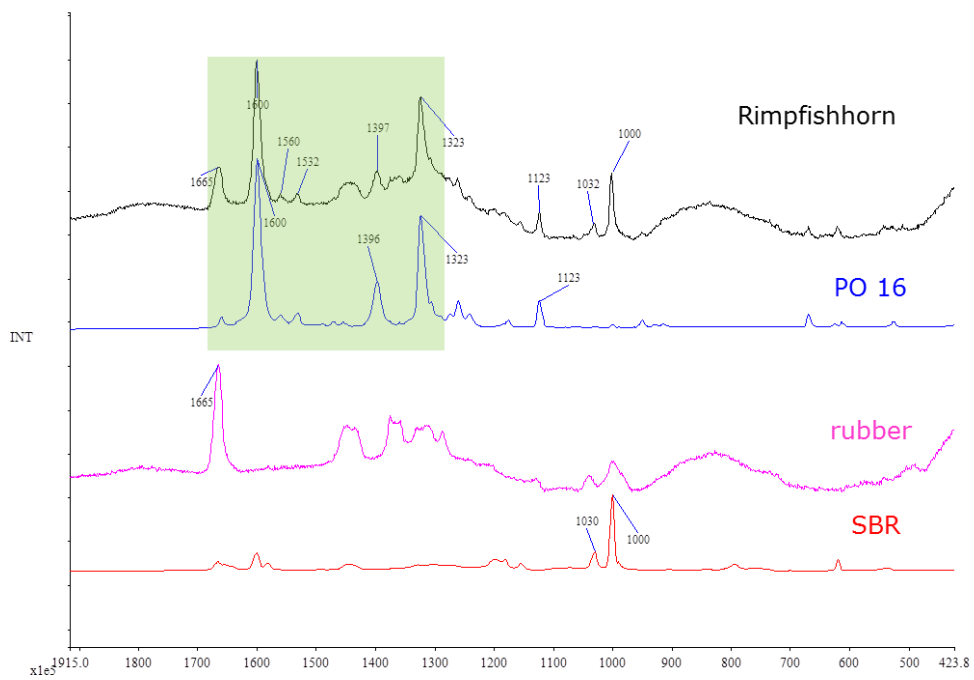


Fig. 2: Raman spectrum 'The Rimpfishhorn Handicap, part 1', (1991) by Seymour Lively and Raman reference spectra of pigment orange 16, rubber and styrene butadiene rubber (SBR).

A FTIR analytical study of 1960s synthetic polymer paintings and their artist repaints.

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Conservation researchers in Australia have been studying paintings dating from the mid to late 1960s with broad unmodulated high-keyed colour, often described as Colourfield paintings. Typically painted on cotton duck canvases stretched on shaped artist-made strainers, these works have been vulnerable to damage from handling, embedded stains and dust and both accidental and deliberate abrasions. These types of visual breaks in the matte and flat surfaces of the works have often been considered unacceptable by both artists and curators and many have been repainted by the artists prior to, and occasionally after, their entry into art gallery collections.

Recent research on this group of works has included interviews with the artists in which questions regarding repainting have been raised but it has been the analytical and technical examination of the paintings that has led to a significant shift in our understanding of how these paintings were first constructed. The Fourier transform infrared (FTIR) analysis of the paint and ground layers has revealed that most were not originally painted in acrylic, as had been presumed. Polyvinyl acetate (PVA) paints were far more commonly identified with FTIR analysis, and other mediums such as distemper and nitrocellulose have also been found. The surprise of these results is that acrylic emulsion paints were so little used by these artists in the mid to late 1960s, suggesting that local supplies of acrylic paints may have been limited.

FTIR has been successful in further characterising these 1960s PVA paints. Several paintings could be identified as homo-polymers of PVA, (externally plasticised) and in artist interviews it was revealed that PVA glue had indeed been used by at least one artist in 1967 mixed with dry pigments. Artists' repaints of damaged paintings were invariably identified as acrylic emulsion paint. Used over the original PVA and distemper paints, these newer layers are more lustrous and increase the overall thickness of the paint layers. Interviews have revealed that artists on occasion consider the repainted artwork to be better than the original. This is a challenge to the idea that artworks are necessarily embedded in their historical context through the limitations of available materials.

This research relates more broadly to the up-take and availability of synthetic polymer paint brands in the 1960s and their use in Australian Colourfield painting, currently being investigated in a PhD study at the Grimwade Centre for Cultural Materials Conservation. Conservation analysis and treatment of a number of paintings at the Art Gallery of NSW was funded by the Women in Arts Group.

Polyurethane coatings in 20th century outdoor painted sculptures: discrimination of major subgroups by means of ATR-FTIR spectroscopy

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Like acrylics and alkyds, polyurethanes (PUs) represent an important class of industrial paints adopted by 20th and 21st artists; primarily by those creating outdoor painted sculptures (OPS). Because PU coatings offer a compromise between aesthetic and performance expectations, unachievable with other types of paints, they are commonly recognized as the most appropriate option for painted artworks intended for an outdoor setting. However, the PU class includes various systems and subgroups possessing very different properties, for instance two package solvent-borne, two package water-borne, one package water-borne and fluoropolymer polyurethanes.

The present research aims to provide to the conservation professionals a better understanding of the versatility and diversity of PU coatings through compositional information and to outline markers helpful to differentiate the major PU subgroups from OPS by means of ATR-FTIR spectroscopy. The ATR-FTIR study conducted on a wide range of PU reference materials from the Getty Conservation Institute (GCI) reference collection highlights the relevance of this routine analytical method to discriminate certain subgroups of PU coatings. Indeed, by investigating well-known specimen it was possible to outline diagnostic FTIR features for three specific systems; fluoropolymer PU, one package water-borne PU made from acrylic latexes and two package water-borne PU prepared with PU dispersions. Furthermore, the FTIR measurements performed on various activators and co-reactants emphasized the significant contribution of the polyisocyanate absorptions in the spectra of the activated two package PU systems. However, the results obtained for various unmodified and water dispersible HDI polyisocyanate activators showed that the FTIR-ATR technique does not allow the discrimination within both types.

ATR study of dispersed nanosilica in carbonate and borate solutions

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It is a well-known fact that nanosilica suspensions are widely used in the area of construction materials and specifically in coatings, gels, polymer films and alloys, in order to improve specific properties such as hydrophobicity, porosity, hardness, thermal resistance and durability, [1]. The common methodology to introduce nanocomposites in construction and inorganic materials is the addition in water and ultrasonication. Although this methodology is accepted, researchers evaluate the parameters that affect the dispersion and form agglomerates that reduce the functional specific surface of the nanoparticles, [2]. Agglomeration also effects on the properties of each application of nanosilica and shows the need to find a suitable methodology for the precise use, depending on the matrix, [3].

In this paper, a suspension of nanosilica in carbonate and borate solutions is proposed and an ATR study of suspensions is performed in order to test the dissolution achieved. ATR contributes in a detailed way to record the bonds of Si-O-Si and carbonate and borate salts, in order to enlighten resulted dispersion of nanosilica in these solutions. According to the results, ATR contributes in researching the influence of the solution parameters (the concentration of salts and the pH) to the suspension and the behavior of nanosilica.

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Posters' ABSTRACTS

μ -FTIR spectroscopy and other methods in technological expertise of golden paint.

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Expert examination of art objects is rather difficult and complex task. Technico-technological research is only one part of it. But its role and value are rising. A great variety of analytical techniques are currently available to analyze the materials of art objects the results of which give objective information of them.

In this paper the combination of μ -FTIR spectroscopy and other methods such as XRF and XRD were used to investigate the paints of illuminated ancient manuscript from private collection. Almost all pictures were covered with golden paint and there were some artifacts that gave us prediction this document wasn't original.

Traditionally gold or mixture of gold and silver were used to illuminate ancient manuscripts. Also SnS₂-paint was applied to imitate gold. There were some other mixtures such as silver with saffron and different varnishes, pike bile with saffron and mica, gold and silver with copper and different varnishes, [1].

As it was found by XRF, the paint didn't contain either gold or silver but the large amount of titanium along with iron and silica. Microscopic observation, microchemical tests together with μ -FTIR spectroscopy showed the presence of a yellowish ochre, clay and oil as a binder of the paint and protein (animal) glue in the upper layer. The analytical results were consistent as the identified substances were used in painting from ancient times, however, the presence of titanium was strange. XRD analysis discovered titanium oxide in rutile phase and identified the type of silica mineral as hydromica. It is known, that titanium oxide in rutile phase began used as the component of painting in the middle of 20-th century. Hydromica the nature mineral vermiculite may be of different colours. They depend on the birthplace of the mineral and sometimes it has got golden colour, [2].

So the conclusion was made: this "golden" paint was modern and the manuscript was the imitation of the ancient book. For the first time in our practice we met such composition of golden paint. A combination of these methods is very useful in providing material expertise.

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Contribution of Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR) in the Investigation of Historical Parchment Documents

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A large number of historical parchment documents are preserved in public and private museums, libraries, archives and monasteries all over the world. Although stronger and with a higher ability to adapt to the environmental factors as compared with leather or textiles, parchment is still vulnerable and efforts are required in order to optimize its storage and exhibition conditions so that documents to last over centuries.

Based on the experience gathered in European and national research projects [1]-[3], an analytical protocol was set up to meet the requirements for the non-destructive investigation of historical parchment documents, from the macroscopic to the molecular level. The visual examination performed by the naked eye and with a microscope enables the animal origin identification, based on the hair follicles pattern, and the quality of the manufacturing process. The latter is assessed on the basis of a number of features such as hair remains and bleedings, sign of veins, calcium carbonates deposits, holes and/or translucent areas, surface flaking and indentations due to the unskilled use of knives, [4]. The microscopic evaluation was performed with a Dino-Lite digital handheld microscope (AnMo Electronics Corporation) at various magnification (20x – 200x), in visible and UV (375 nm and 400 nm) light.

Complementary to the microscopic evaluation, the infrared spectroscopy allows to determine the presence of materials added during manufacturing or formed due to ageing and deterioration, as well as to detect the degradation of collagen at the molecular level. Measurements were performed using the ALPHA model FTIR portable spectrometer equipped with a Platinum ATR module (Bruker Optics). The variations in the position and intensity of both the amide I and amide II bands indicate conformational changes of collagen triple helical structure, [5], while the polypeptide chain oxidation is indicated by the presence of carbonyl compounds and carboxylic acid bands visible at 1720 - 1740 cm^{-1} . Among the compounds we have most frequently observed on the parchment surface, there are aluminosilicates from dust and dirt (1025 cm^{-1}) and calcium carbonate (1447 cm^{-1} and 875 cm^{-1}). The presence of calcium carbonate is associated with two manufacturing steps, i.e. the hide dehairing process and parchment surface preparation for writing. Sometimes, stearic acid salts, formed as a result of the slow reaction between fats (endogenous or added, e.g as softening agents) and the residues of metal oxides from various steps of the manufacturing process, are also observed in the FTIR spectra at 1575 cm^{-1} , [6].

Due to its capability to identify materials present on the parchment surface and to evaluate damage at the molecular level without any sampling, ATR-FTIR has been proved to be a valuable tool in the non-destructive investigation of a number of historical parchment documents from Romanian and Italian libraries and archives [4], [6], [7].

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FTIR Spectroscopy study on wooden materials consolidated with acrylic based resins

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The conservation of highly degraded wood artefacts by gamma irradiation is a technique with perspective of expanded use. Extremely degraded wood is impregnated with a standard styrene-unsaturated polyester resin in liquid state which is then polymerized *in-situ* by gamma ray irradiation. The consolidation by radiation-curing monomers or resins has two welldefined phases: an impregnation and a polymerization step. The impregnation consists in the diffusion of the resin dissolved in a reactive monomer, into the pores of a deteriorated artefact. Afterwards, in the presence of gamma radiation, the styrene free radicals will interact with the free radicals on polyester, creating bridges between the linear polyester oligomers. The outcome of this radiation-crosslinking is the formation of a three-dimensional macromolecular structure that fills the pores of the artefact, ensuring increased mechanical resistance to the wooden artefact.

Recently, styrene's toxicity to humans was more and more questioned in the USA and Europe. The aim of this present work is an in depth styrene-free resins analysis, to understand their chemical and physical properties in comparison with the styrene-polyester resin used before, using FTIR spectroscopy. In order to see the behavior and the effectiveness of the resins, we have used for the impregnation different kinds of wood samples: an old painted wood, modern spruce wood and oak wood, but we also have performed accelerated ageing tests and thermogravimetric and scanning electron microscopy analysis.

Molecular structure characterization was performed by Nicolet FT-IR MicroSpectroscopy. Vibrational spectra ensured information about changes in the molecular structure of the artefact given by the presence of the polymer inside of the wood's structure, but also changes as respect the resin's structure after UV artificially induced degradation.

Our preliminary investigation shows that acrylic based resins could be an alternative to the styrene-polyester resin consolidation.

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Physical and histological investigation of the embalmed skin: application to some Egyptian mummy heads from the Marro collection (Turin)

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The work will discuss the materials employed in the mummification of some Egyptian Dynastic embalmed heads (VI – XI Dynasty) and is the summary of a lot of studies performed in this framework in the last two years. The samples are skin fragments removed from mummified heads belonging to the “Giovanni Marro” collection, developed by Professor G. Marro between 1907 and 1913, at the necropolises of Asiut (the old Lycopolis), 380 km south of Cairo, and of Gebelein 28 km south of Luxor (the ancient Thebes), during three of the archaeological campaigns of the Italian Archaeological Mission. The collection is curated at the Museum of Anthropology and Ethnography of the University of Turin. The present work takes part in the number of activities promoted by the Museum for management and conservation of the stored ancient remains [1].

Several physical techniques were employed to detect and analyze the traces of the embalming materials on the mummified remains. FTIR spectroscopy was applied on samples prepared as KBr pellets and allowed to gain information both on the embalming substances spread on the skin and on the preservation state of the skin from the analysis of the characteristic bands of the cutaneous tissue. Micro-FTIR spectroscopy (beam light area about $0.4 \times 0.4 \text{ mm}^2$) was employed to identify the chemical nature of the materials on the skin surface and to measure the embalming substance penetration in the skin by focusing the IR beam on tissue layers at different depth. The results were compared with the histological measurements. Skin fragments were Mayer’s hemalum and eosine stained and revealed some brownish-yellow bands inserted among the bluish collagen fibers which may be attributed to the embalming substances soaked through the skin surface. ATR spectroscopy was applied to water and ethanol extracts of one of the embalmed skin samples. Several embalming substances were tested by matching the IR spectra against a library of diagnostic markers and the excellent superposition of the propolis spectrum supports the hypothesis that one of the embalming substances could have been beeswax (Fig. 1) [2], [3].

Finally, SEM images of some skin fragments showing Natron encrustations will be shown, supplied by XRD analyses.

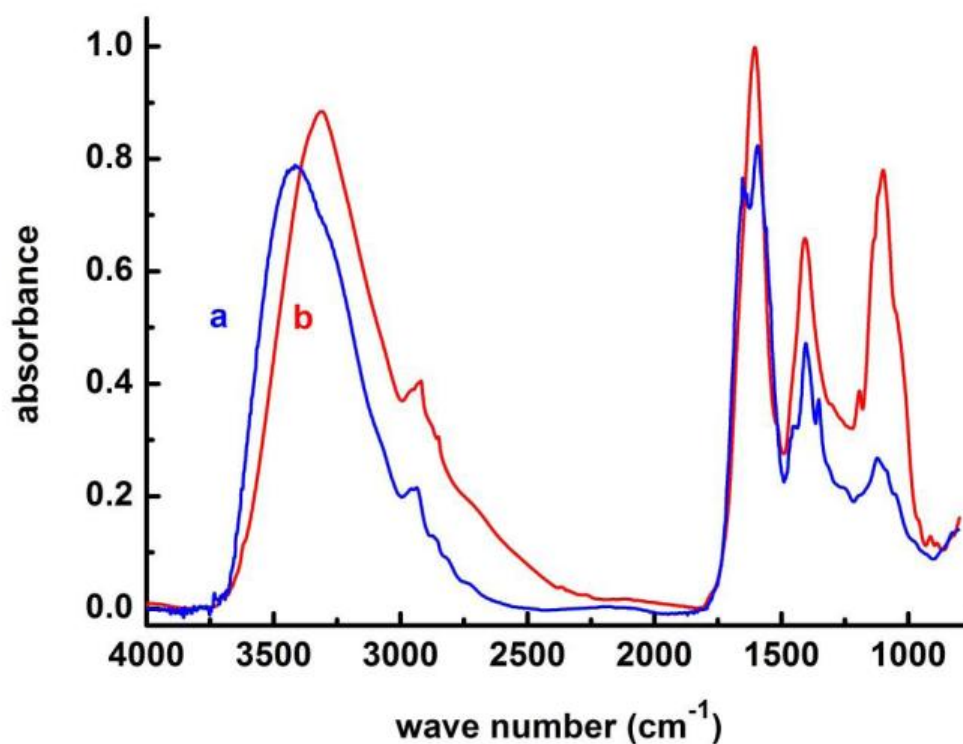


Fig. 1: a) ATR-FTIR spectrum of water extract of embalmed skin (head no 9092); b) propolis (EZ-OMNIC Nicolet).

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Tissue preservation of 16-18th Century mummies of Roccapelago (Modena, Italy): a SEM and FTIR study

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Between 2009 and 2011, during restorative works at the Church of Roccapelago (province of Modena, Italy) a remote mountain village, hundreds of bodies, some of them mummified because of natural processes, were discovered in a forgotten crypt in use from the mid-16th to the 18th centuries. Mummification processes occurred unevenly, with bodies partially skeletonized and bodies only partly articulated, [1]. 12 of these mummies, the most complete and representative, were studied with non-invasive methods and replaced in the crypt, set up as a museum (Fig. 1).

The objects of this study are fragments of a variety of tissues taken from the mummies of the US 23 of the crypt of Roccapelago: skin pieces taken from different parts of the body, muscle, tendon, lung, bone, hair, etc.

The tissues were analyzed by means of FTIR spectroscopy applied in the transmission geometry, on samples obtained by mixing small quantities of the samples with pulverized KBr. In the IR spectrum of the investigated tissues the main absorption bands of the biological components such as proteins, lipids, nucleic acids, and carbohydrates were detected and characterized. The biochemical modifications recorded reveal a partial alteration of the ancient tissues which have been stabilized by the chemical-physical environmental conditions and preserved for hundreds of years. The whole IR spectrum of the tissues reveals traces of these “age-inhibitor” processes: 1) the water OH-stretching band ($\sim 3400\text{ cm}^{-1}$) features are indicative of the twofold role of the dehydration process, as a result of low temperatures and dry air, at the same time responsible for the protein structure modifications and determining the preservation; 2) conformational features of the proteins can be extracted by monitoring Amide I and Amide II bands ($1500\text{-}1700\text{ cm}^{-1}$); 3) in the glucid specific spectral range ($950\text{-}1150\text{ cm}^{-1}$), an increase was measured in the glucid/protein ratio, a spectroscopic marker for the AGE compounds formation as a consequence of the collagen binding to sugars in tissues [2]; 4) the amount of adipocere formation ($2916\text{-}2849\text{ cm}^{-1}$, 1700 cm^{-1}) was correlated with the position of the remains in the pile of the corpses.

The bone diagenesis was monitored by means of the mineralization parameters. SEM measurements were carried out with the purpose of a morphological characterization of the tissues, in comparison with the modern ones. SEM images were acquired with Zeiss Supra40-high resolution apparatus using low beams energies. Mummified collagen fibers and collagen network are shown in the skin and compact bones reveal a lot of well-preserved ultrastructural features such as Haversian canals, [3].

Septate hyphae and spores, characteristic of a fungal colonization were identified, as well as a lot of burrowing insects, such as Dermestidae, commonly referred to as *skin beetles*, which feed on dry animal and their predators, staphilinids [4].

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Fig. 1: The 12 mummies of Roccapelago exposed in the crypt, set up as a museum.

On the rocks – unveiling the richness and specificities of the Guadameci from the Portuguese Templar Charola of the Covent of Christ in Tomar, Portugal

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The Covent of Christ in Tomar is the most emblematic architectural testimony of the Templars in Portugal. In 1983 it was listed in the UNESCO World Heritage, placing it among outstanding universal value sites in the World. The Convent was founded by the Templars during the 12th century. During the late-12th century it was build one of its most emblematic sections: the *Charola*. Built to be the private oratory of the Knights inside the fortress, the *Charola* follows the design of the Church of the Holy Sepulchre of Jerusalem and of the Byzantine churches, combining the influence of the Romanesque architecture and the movement of the Crusades. During the 15th-16th centuries the Convent of Christ suffered several amplifications and artistic interventions. The Guadameci found in the top walls of the *Charola* are attributed to this period. The Guadameci is a decorative gilt leather technique that combines gilding, painting and engraving of leather, [1]. Traditionally, the leather was applied on stone walls with an animal glue, and covered by silver plate that, sometimes, could be covered by a paint decorative layer, [2]. This technique had its flowering period in the Iberia Peninsula during the 16th-18th century. Nevertheless, as the leather support is easily deteriorated over time (when compared with other decorative techniques), there are few examples of Guadameci in its original places, [3]. The Guadameci from the *Charola* of the Covent of Christ is probably the most ancient known Portuguese gilt lather work still preserved in its original place.

This work presents the unexpected specificities of the Guadameci from Tomar. The study of the materials and the production techniques considered a set of 13 micro-samples that were characterized by optical microscopy (OM), elementary (SEM-EDS) and molecular techniques (μ -Raman and FTIR-imaging). The analyses of cross-sections by OM and SEM-EDS did not evidenced the use of the traditional Guadameci technique (silver foil applied over leather), but the presence of false gilt leather (tin foil applied over leather with thickness between 10-65 μ m) upon which was applied a high pure gold foil (*circa* 2% of silver, mass %) with a subjacent layer of bolus or, for some of the cases, a lead tin yellow-based paint, Fig. 1-(a). FTIR-imaging allowed to identify the distribution of the characteristic absorption bands of an animal glue used to apply the tin foil on the stone walls, Figure 1-c. Considering the finishing decorative layers, Raman microscopy identified the use of a mixture of vermilion and read lead for the red paints, Fig. 1-(b). There are references for adulterating vermilion with red lead due to the high price of vermilion dates back to the Roman period and continued until the Renascence period, [4]. Other pigments were identified on the Guadameci decorations, such as the use of azurite for the blues and carbon black of vegetable origin for the darkening of blue shades.

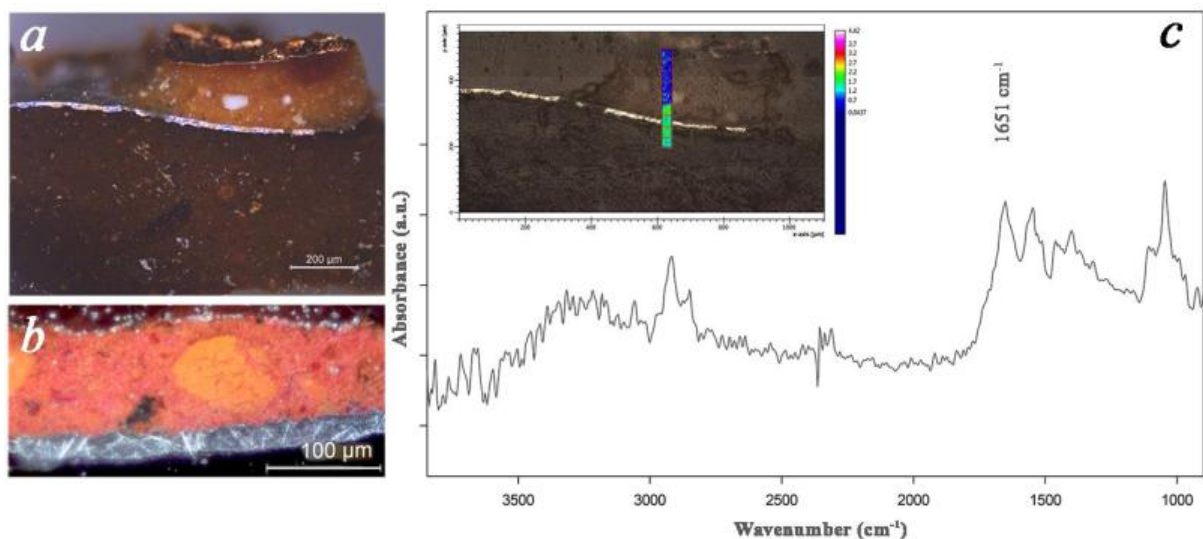


Fig. 4: The study of the materials used to produce the Guadameci from the Covent of Christ: a) and b) optical microscopy images of cross-sections from a gold and a red decorative painting; c) FTIR-imaging spectrum of cross-section a) and distribution of the integration band at 1651 cm^{-1} in the cross-section.

Despite it was not found the characteristic use of silver foil over leather that typifies the Guadameci technique, the quality and purity of the materials used on the production of the Guadameci from Tomar place us the question for the reason of the use of tin foils over the leather (and not silver as it was traditionally used): was it a stylistic choice or budget restriction?

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Technological Survey of Rock Crystal Object

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During the conservation treatment of objects composed of different materials, it is necessary to know properties of all materials and also factors that can influence their degradation. The studied object was mainly created from rock crystal and metal rings decorated with enamel and stones. Therefore it was necessary to perform a relatively wide analytical investigation (Raman spectroscopy, FTIR spectroscopy and SEM/EDS). The conservation work itself was carried out especially to recover the aesthetic value of the object, with regard to the nature of the constituent materials and the reversibility of intervention.

The studied object belongs to a Regional museum in Olomouc. It is indirectly dated to the 19th century - according to a similar object found in Kunsthistorisches Museum Wien [1]. The object is made of 9 crystal pieces and 11 metal pieces. The metal pieces are decorated by enamels, pearls and pink stones. The crystal pieces are glued together and fixed by metal rings. Four pieces fell off due to a bad condition of adhesives.

Samples taken from the adhesives were analysed using FTIR microscope Nicolet iN10 in ATR mode (germanium crystal), number of scans 128, resolution 4 cm⁻¹, cooled detector MCT-A. There were three different types of adhesives found (may be because of previous conservation treatment). The nitrocellulose was found between the crystal body and the metal stem. The chloroprene-based adhesive was found between smaller crystal parts and the body of the object. Protein-based adhesive mixed with polysaccharide was detected between spout and body. In the last case, microchemical tests were also performed. Tests for occurrence of proteins (reaction with ninhydrin) and polysaccharides (reagent containing aniline, diphenylamine and phosphoric acid) were positive. On the other hand, the test for presence of starch (reaction with iodine solution) was negative.

All crystal pieces were analysed by means of Raman microspectrometry (Nicolet DXR). There are bands characteristic of rock crystal at 466, 356, 206 and 129 cm⁻¹, [2]. Therefore glass was disqualified as a major material. Also pink stones were analysed by Raman spectroscopy. Bands at 749, 644, 417 and 379 cm⁻¹ are characteristic of corundum, [3]. The origin of pearls was verified by presence of bands at 1084, 704 and 205 cm⁻¹ [4], [5].

For the analysis of metal pieces, stones and enamels, SEM/EDS was used. Metal rings were made of partially gilded silver alloy. Blue enamels were created from low-melting glass. The comprehensive analytical study performed was crucial for dating the object, for guiding the conservation treatment and also for preventive conservation actions.



Fig. 1: Object before conservation



Fig.2: Object after conservation (M. Knezu Knizova)

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Spectroscopic non-destructive characterization of gamma irradiated paintings

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Many cultural heritage items are bio-degradable by nature. Gamma irradiation treatment is an efficient mean of mass disinfection of cultural heritage items, deteriorated by biological attacks. In this work we present our investigation on changes after gamma irradiation, which may appear in the color and the molecular structure of painting materials from paintings using advanced analytical techniques: Fourier transform vibration spectroscopy and colorimetry [1].

Molecular structure characterization was performed by FTIR/Raman spectroscopy using a Bruker Vertex 70 class equipped with a Raman RAM II module (LN2 Ge detector) with a RAMPROBE fiber. Color was measured with a portable reflectance spectrophotometer (Miniscan XE Plus, HunterLab) in diffuse/8° geometry with a beam diameter of 4 mm and specular component included.

The results obtained by vibrational spectroscopy and colorimetry showed no significant changes. Analysis of covariance was used in order to get a clearer picture of correlations between the measured and interpreted data.

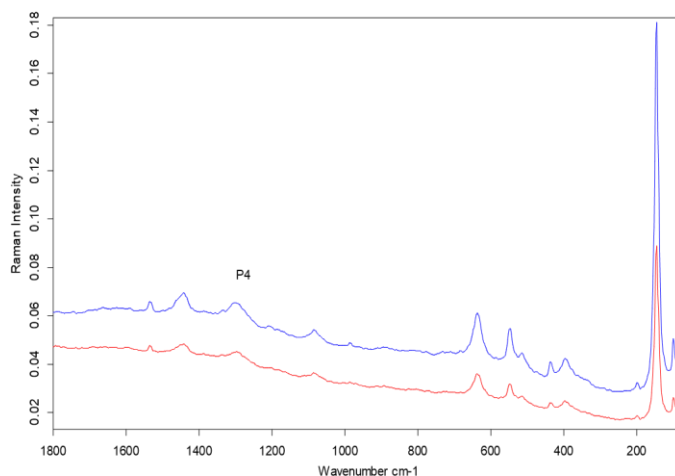


Fig. 1: Raman spectra before and after irradiation for the pigment in painting: *Seascape*, Benone Suvaila – 2013 (blue-unirradiated, red-irradiated)

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Acknowledgement:

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“PigmentX” application for pigment identification

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The investigations performed over time on paintings had to be archived not only in order to have a record of analysis and constitutive materials identified, but also for observing the painting modification in time. Building of an archive containing data on the known historical pigments (standard) is an absolute necessity, the unknown pigments from paintings under study being identified by comparing the parameters found for the unknown samples with those from the database for the known samples.

The multitude of available analytical investigation techniques, in our case: digital microscopy (with visible, infrared and ultraviolet light), Fourier transform infrared spectroscopy (FTIR) and X-ray fluorescence spectrometry (XRF), allow complex characterization of reference pigments, which helps in pigments identification. In order to determine the nature of unknown pigments we have built an application, named “PigmentX” (Fig. 1).

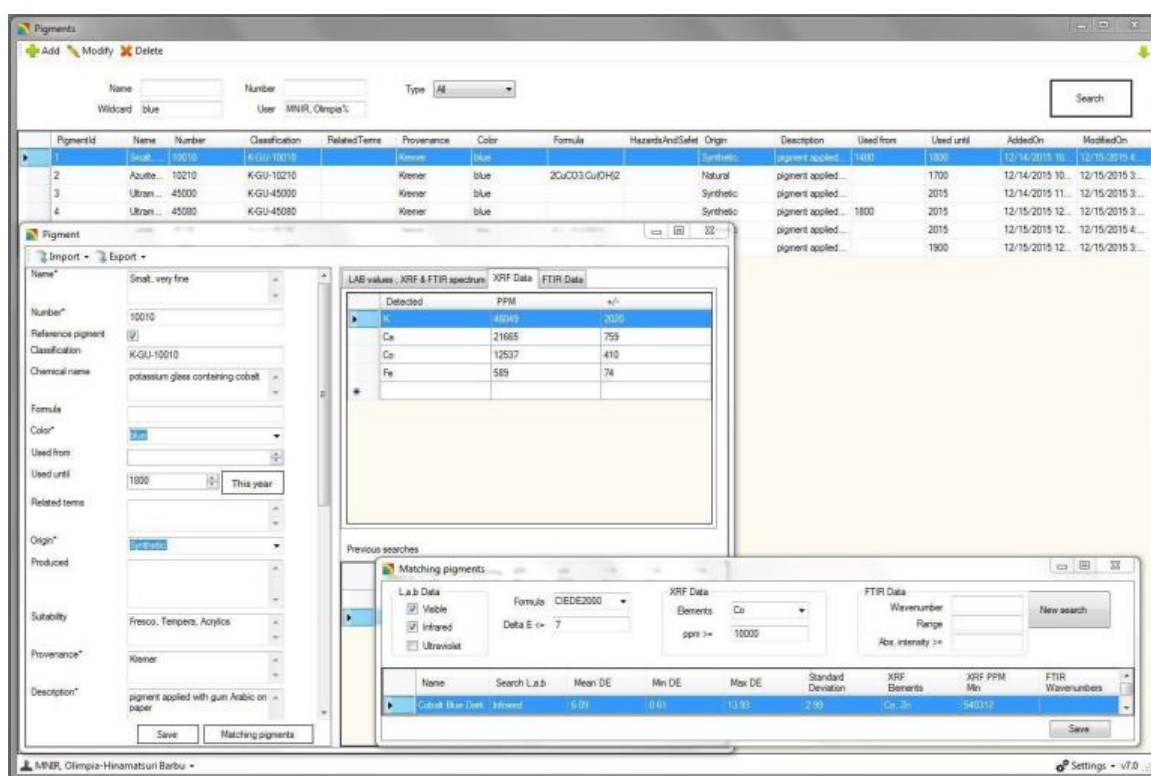


Fig. 1: Screen capture showing Pigments / Pigment / Matching pigments windows of the “PigmentX” application

Firstly, the data comparing proceeds considering the L*, a* and b* parameters, extracted from RGB photography taken with a microscope under visible light, [1] (optionally, also those taken under infrared and ultraviolet light illumination), based on color difference ΔE , in this case calculated using

CIE1994 or CIE2000 formulas. The second selection criteria of pigments from the database is the elemental composition, based on XRF analysis, followed by a new filtering depending on the presence/absence of characteristic absorption bands in FTIR spectra. The results of matching between the unknown pigments and the known ones from the database can be saved in “PigmentX” application, multiple searches being possible depending on the chosen selected criteria: limit value for ΔE , existing chemical elements identified by XRF and absorption bands in FTIR spectra.

Technically, the application “PigmentX” is written in C#, using NET 4.0, in order to assure the compatibility with Windows XP operational system. The application uses ColorMine open source library, [2], to calculate Delta E values and store the data in SQLite, a very robust base, adopted on large scale in various applications range.

The advantage offered by the application “PigmentX” is that it allows not only digital archiving of identifying data for pigments, but also the search and matching of pigments according to some selection parameters - i.e., color, XRF and FTIR data. We intend to add also other experimental results (X-ray diffraction and Raman spectroscopy). Further information will be available at <http://www.mnir.ro/>.

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Complex methods of fine-art objects research

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Modern examinations of works for attribution and restoration are impossible without prior research. In this abstract I consider carrying out a research of some works of art, evidence from physical and chemical laboratory of Grabar Art Conservation Center.

On the one hand, the improvement of products quality and the progress of science makes it easier to conduct research: there is modern equipment for qualitative and quantitative analyses. These analyses are very accurate. On the other hand, restoration technologies allowing the use of modern polymers are well-developed, [1]. However, after the use of such polymers it is sometimes difficult to identify the original composition. Unfortunately, those who forge paintings resort to it too.

So the process of any physical and chemical examination at the Grabar Art Conservation Center involves “complex” methods: Infrared FTIR and Raman Spectroscopy (allows to identify the molecular composition of the sample), X-ray fluorescence analysis (provides the elements composition), microscopical analysis in polarized light, micro-chemistry tests of the samples. For paintings, it is mandatory their examination in IR and UV radiation to identify the drawing under the paint and the entirety of the varnish layer.

It is worth mentioning that any research is unique, there are no identical works of art. Every object is examined on an individual basis. But some items, for instance, works of artists belonging to one and the same school of painting may have their distinctive features (Italian schools of 15-18 centuries [2], schools of Rokotov and Borovikovskiy and other famous schools).

If research of easel painting and icons are well developed due to their great popularity and world-wide interest to the genres (experts, collectors, galleries, etc), when it comes to decorative and applied arts research, the items have their peculiarities connected to the materials they are made of.

For example, Grabar Art Conservation Center examined Byzantine removable (procession) crosses. The difficulty was not in mere identity of the composition of the crosses, (patina and decorations) but also in finding out if they belonged to the cross. This task has turned out to be quite difficult.

The results of the complex research have revealed the composition of the metal parts of the cross. Patina examination on the surface of one cross using the FTIR method has given: zinc oxide, atacamite, copper acetate. Thus, the examination of such decorative and applied arts items is hard in terms of science and expertise. Only complex research gives more accurate information about physical and chemical properties, recommendations for attribution and conservation of the object.

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Analysis of Lucerne auction paintings by mobile Raman and complementary analytical and imaging techniques

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In 1939 the controversial auction of paintings and sculptures of modern masters owned by German museums is held in the gallery Theodore Fischer in Lucerne (Switzerland). This bashful title covers in reality a selling intended to get rid of an art considered as degenerate, in other words non-compliant with the Third Reich ideology. The city of Liège bought 9 paintings from Chagall, Picasso, Ensor, Kokoschka, Laurencin, Liebermann, Marc, Gauguin and Pascin. We have analyzed them by mobile Raman spectroscopy and complementary analytical and imaging techniques as X-ray fluorescence, infra-red reflectography and high resolution UV and visible photography to characterise the different pigments and the conservation state. Elemental mappings have been acquired as well by XRF. We will present the results of these analyses concerning the paintings by Picasso, Gauguin and Chagall. For example, we have been able to distinguish the different versions of the background in the Picasso's painting "La Famille Soler".