3rd International Conference on Innovation in Art Research and Technology – INART 2018

Parma, Italy

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WELCOME REMARKS

The 3rd International Conference on Innovation in Art Research and Technology takes place in Parma, on March 26-29, 2018.
The Conference scope is to create a bridge of communication between interdisciplinary units in the field of archaeometry. It took several years for the scientific and art historical knowledge to be brought together and establish a new era on approaching preservation of cultural heritage. Nowadays, the contribution of natural sciences to characterize and document artistic materials is well known. Generally, these applied sciences, especially physics and chemistry, contribute to a deeper understanding of cultural heritage artefacts and shed light on different aspects related to the origin of the work of art or its chronology.

The topics to be addressed within the conference sessions are (amongst others):
New technological developments
In vitro experimental set-ups and degradation mechanisms
In situ experiments and mobile instrumentation
The need on non-invasive and non-destructive analysis
Imaging techniques
Environmental issues on the preservation of art and archaeological objects
Special Focus on Contemporary Art

Danilo Bersani

Chair, Local Organizing Committee INART 2018

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PROGRAM AT A GLANCE

Monday 26		**Tuesday 27**		**Wednesday 28**		**Thursday 29**	
		9.00	Invited Talk 3: L. Burgio	9.00	Scientific Session 7 Contemporary art	9.00	Scientific Session 8 Museums and databases
9.30	Autorities Speech	9.40	Scientific Session 4 Non -invasive				
10	Invited Talk 1: M. J. Mosquera						
10.40	Scient. Session 1 Pigments	10.40					
11.00	*Coffee Break*	11.00	*Coffee Break*	11.00	*Bus to CSAC*	11.00	*Coffee Break*
11.30	Scientific Session 1 Pigments	11.30	Scientific Session 4 Non-invasive	11.30	*CSAC visit*	11.30	Scientific Session 9 Textile and paper
13.10	*Lunch*	13.10	*Lunch*	12.50	*Lunch*	13.10	Conclusions
14.30	Invited Talk 2: F. Fernandez	14.30	Scientific Session 5 Imaging	14.30	*Social Excursion: Torrechiara Castle + Ariola*	13.30	End
15.10	Scientific Session 2 Inorganic						
16.30	*Coffee Break*	15.50	*Coffee Break*				
17.00	Scientific Session 3 Dating	16.20	Scientific Session 6 Middle and Far East				
17.40	End	17.40	Poster Session				
				18.30	*Come back*		
		18.40	End				
19.00	*Welcome Cocktail*			20.00	*Social Dinner*		

Invited Speakers

I.1 Invited Speaker 1

ABSTRACT I.1.1

INNOVATIVE MATERIALS FOR THE CONSERVATION OF STONE & CONCRETE-BASED CULTURAL HERITAGE

Mosquera M.J.* [1]

[1] *Nanomaterials TEP-243 group. Dto. Química-Física. Facultad de Ciencias. Universidad de Cádiz ~ Cádiz ~ Spain*

In recent decades, the alarming growth of environmental pollution in cities has seriously affected the conservation and maintenance of historic buildings and other exposed works of architecture and art. It is obvious that stone and concrete-based structures, particularly buildings, monuments, sculptures and archaeological remains, are among the most vulnerable to atmospheric pollution since they are continuously exposed in outdoor environments. To date the products commonly employed in the restoration and conservation of these materials have not been specifically developed for preserving such elements of Cultural Heritage. In addition, they are plagued by limited performance and structural drawbacks, such as low adhesion, poor penetration and cracking. Another disadvantage is the requirement for most products to be dissolved in volatile organic compounds (VOCs), which produces environmental and human health risks in their use. In this lecture, I will review the most meaningful achievements of my group in this field. Specifically, we have developed a surfactant-assisted sol-gel synthesis to produce, in-situ on the stonework, crack-free nanomaterials to be used as long-term consolidants. Recently, an inverse-micelle mechanism has been proposed to explain the formation of crack-free, SiO_2 xerogels produced by this route. Additionally, hydrophobic, water-repellent, self-cleaning, and biocidal properties can be incorporated into the product by innovative chemical modifications of the proposed synthesis route.

Finally, I will try to summarize the future challengers of our group in this field. Especially, our investigation related to conservation of historic concrete in the framework of the Horizon 2020 project “InnovaConcrete” will be described. The Portland cement production promoted a complete revolution in construction techniques, giving rise to Modern architecture in the first years of the 20th Century. The new reinforced structures were often left in fair-faced condition and exhibited as a symbolic material. The common use of fair-faced concrete, without coatings or painting, obviously increases its susceptibility to suffer decay, especially when subjected to an aggressive environment. Therefore, the research and development of surface treatments, especially hydrophobic agents to prevent water ingress and consolidants able to fill cracks produced by decay, are identified as a key topic for preserving historic concretes.

I.2 Invited Speaker 2

ABSTRACT I.2.1

NANOMATERIALS CONTRIBUTION TO A MORE SUSTAINABLE CONSERVATION OF CULTURAL HERITAGE

Fernandez F.*[1]

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This contribution aims at presenting the last achievements and the perspectives on the application of nanomaterials to the cultural heritage sector as a driver toward innovation and sustainability. Today several applications of nanotechnologies in the field of conservation of cultural heritage are transforming traditional procedures for intervention, allowing a more reliable and sustainable preservation of artifacts by the use of non-toxic and environmentally friendly treatments.

The contribution presents a general overview of the ongoing researches and of the existing nanostructured products, illustrating the main principles and characteristics of interventions on historical artifacts using nanomaterials. These innovative technologies appear as groundbreaking and promising tools, able to improve the procedures for intervention, overcoming some of the major deficiencies that characterize some of the traditional techniques currently used, also allowing a more reliable and sustainable preservation of artifacts.

The main advantages of using nanostructured products will also be pointed out, compared to the traditional ones, such as the higher compatibility with the historic materials, greater reliability over time, non-toxicity and enhanced respect for the environment.

Furthermore, reliability and durability are two key points for the assessment of the quality of the intervention on cultural heritage. For this purpose, specific tests are used to support research activities, which allow accelerated aging of samples of material treated with the products, monitoring in a controlled environment the behavior and performance of treatments over time. Therefore, some ongoing studies aimed at the validation over time of nanostructured products applied on historical substrates of various materials will be also presented. Thanks to a fruitful interdisciplinary approach, these studies have been carried out both in lab and in situ.

Lastly, this contribution underlines that, even if these nanomaterials are contributing to a more sustainable conservation, we should ensure that the potential risks are identified and controlled, through developing new appropriate standards and codes for their validation and application.

I.3 Invited Speaker 3

ABSTRACT I.3.1

SCIENTIFIC ANALYSIS UNDERPINNING THE MULTIDISCIPLINARY PROJECT “THE LEMAN ALBUM: AN ENHANCED FACSIMILE”

Burgio L.*[1], Manca R.[2], Button V.[1], Rutherston J.[1], Horsfall Turner O.[1], Browne C.[1], Cartechini L.[3], Doherty B.[4], Grazia C.[4], Paolantoni M.[5], Rosi F.[3], Tournié A.[6], Michelin A.[6], Andraud C.[6]

Keywords: Multidisciplinary approach, Scientific analysis, MOLAB, Mellon, Leman Album

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The V&A Leman Album, Europe’s earliest surviving group of dated designs for woven silk, contains 106 designs mostly made by James Leman, a designer and master weaver of Huguenot descent, active in the first half of the 18th century in Spitalfields, London. The Leman album was deemed to be the ideal focus for the V&A Research Institute (VARI), home to a portfolio of collections-based and museum-focused research projects composed of highly interdisciplinary teams: for the past two years the Album has been studied by scientists, conservators, curators, archivists, makers, social historians etc.

The scientific analyses pursued multiple targets, among which finding out the nature of any degradation processes, such as fading or darkening, of the pigments and dyes; identifying the artists’ materials to inform conservation, storage and handling procedures; establishing a comparison between the materials used on the designs and those used in the same period to dye textiles.

For many months the designs were analysed at the V&A using techniques available in house, such as Raman microscopy, optical microscopy and XRF. However, additional support was needed in order to characterize the organic dyes non-destructively and in situ, and to investigate additional aspects of the designs: following a successful IPERION-CH funding bid, three MOLAB teams worked on the Album in 2017, bringing into the V&A a variety of scientific techniques not available in house. These visits generated a wealth of data which is informing the work of the Leman VARI team and has revealed unexpected surprises about the modus operandi of James Leman, and the way his designs could transpose into textiles.

The MOLAB techniques were also used to investigate and improve the legibility of Leman’s own annotations hidden on the reverse of designs which are glued to the backing paper (and are therefore inaccessible), and revealed a number of pentimenti in the underdrawings. The analysis results also provided the V&A conservators with essential information on the lightfastness of the materials and with evidence which will be used to devise the most appropriate conservation procedures and display conditions.

The Leman team also worked on an 18th century silk textile (made following one of the 106 designs in the Album), which was serendipitously offered to and acquired by the V&A in 2016.

The project is still ongoing but it is shaping up in a way that will change the approach the V&A uses in multidisciplinary endeavors; it is fostering a much closer and more organic relationship between specialists

in different fields; it is paving the way for the creation of a virtual research environment where digital access to museum objects and the scholarship accumulated around them will allow additional categories of people to experience and interact with fragile, valuable and irreplaceable items.
For this reason, the Leman VARI team is also working on the creation of a digital enhanced facsimile, fully interactive and available on line, thereby contributing to the wide dissemination of this research among various audiences.

Financial support by the Andrew W. Mellon Foundation and the Access to Research Infrastructures activity in the H2020 Programme of the EU (IPERION CH Grant Agreement n. 654028) are gratefully acknowledged.

[1] B. Sherman, O. Horsfall Turner, V&A Magazine 40, 2016, pp.74-79.
[2] L. Burgio, V&A blogs, http://www.vam.ac.uk/blog/author/lucia-burgio (last accessed 5/10/2017).

O.1 PIGMENTS

O.1 PIGMENTS

ABSTRACT O.1.1

GREEK 16TH CENTURY WALL PAINTING ART: INVESTIGATING THE MATERIALS AND TECHNIQUES OF THE KONTARIS BROTHERS.

Mastrotheodoros G.*[1], Filippaki E.[1], Bassiakos Y.[1], Beltsios K.[2], Papadopoulou V.[3]

Keywords: pigments, gilding, mordant, fresco-secco, post-Byzantine

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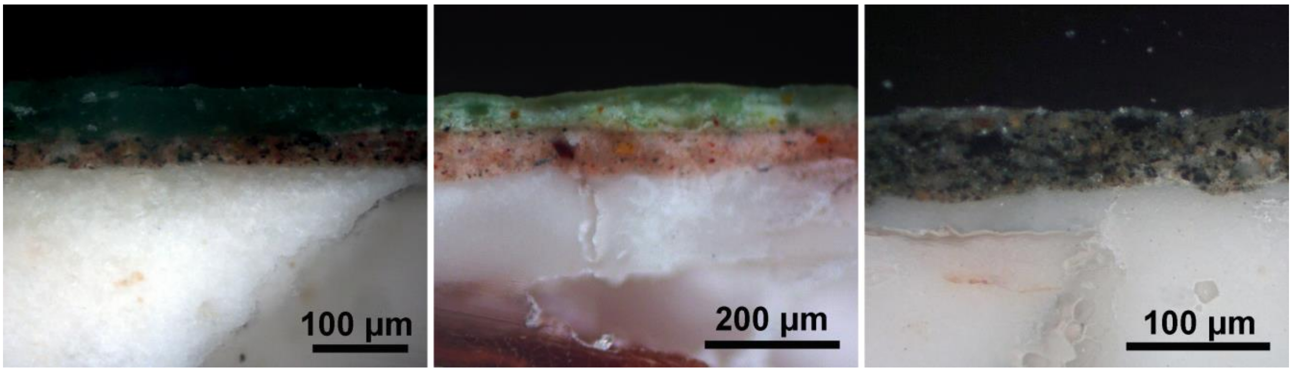
During 16th century the art of monumental painting received a boost in the Epirus region (NW Greece) as several churches were then embellished with wall paintings [1]. Among the various artists of that period, the brothers Georgios and Frangos Kontaris stand out due to their high quality work. Two churches bear inscriptions that testify their collaborative work: St Nikolaos in the Krapsi village (Epirus) which was painted in 1563, and the Varlaam monastery katholikon in Meteora (Thessaly), executed in 1566 [2]. In 1568 Frangos alone was responsible for the wall paintings of the Transfiguration of Our Savior church, a small chapel located at the outskirts of Klimatia village (Epirus); these wall paintings are counted among the highlights of the post-Byzantine monumental painting in NW Greece [3]. Apart from the aforementioned wall paintings, several others are ascribed to the Kontaris brothers on the basis of stylistic criteria [1,2,4].

As part of a major project aiming at the systematic study of the materials and techniques of Epirus 16th century monumental painting, samples from St Nikolaos and Transfiguration churches' wall paintings were examined by means of analytical techniques including optical microscopy, SEM-EDX and XRD. The understanding of the materials/techniques employed by the two brothers in the first monument and the subsequent comparison with those used by Frangos in the Transfiguration church, were expected to produce valuable data that might subsequently contribute to the investigation of various anonymous wall-painted monuments that are stylistically linked to the Kontaris brothers activity.

Analytical data revealed an almost identical –though relatively meagre- palette in both monuments: charcoal black, calcium carbonate white, red Fe-ochre, yellow Fe-ochre, green earth and vermilion; scarce use of blue smalt was traced only in case of St Nikolaos church. The similar compositions and micromorphologies of the identified green earths, yellow and red ochres hint at common geological origins. In addition various hues in the two monuments were achieved upon application of the same techniques, which in some instances differ radically from those employed in other related monuments. The case of greenish backgrounds is indicative: a thin reddish layer –that consists of red and yellow ochre plus charcoal- lies below a green earth layer (Figure 1). It is noteworthy that in case of the closely related Filanthropinon Monastery katholikon the anonymous painters used a mixture of charcoal plus yellow Fe-ochre for rendering the greenish backgrounds [5], while substantially deviating techniques have been traced in other monuments too [6,7].

On the basis of these observations it is inferred that the Kontaris brothers painting exhibits indeed some

idiomorphic characteristics that can serve as fingerprints useful in the case of work attribution controversies.



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[2]Chatzidakis M (1987), Greek Painters after the Fall of Constantinople (1450-1830) (in Greek), Vol. 1, National Hellenic Research Foundation, Athens.
[3]Papadopoulou V et al (2014), Post Byzantine Monuments of Klimatia (in Greek), Ioannina.
[4]Koilakou C (2001), Identification of wall-paintings by the workshop of the Theban painters Georgios and Frangos Kontaris, in the area of their birthplace (in Greek), Deltion of the Christian Archaeological Society 22.
[5]Mastrotheodoros G (2016), Pigments and various materials of post-Byzantine painting, PhD Thesis, University of Ioannina.
[6]Daniilia Sr et al (2008a), A comparative study of wall paintings at the Cypriot monastery of Christ Antiphonitis: one artist or two?, J Archaeol Sci 35, 1695.
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ABSTRACT O.1.2

COMBINATION OF NON-INVASIVE AND MICRO-DESTRUCTIVE METHODS FOR STUDYING DECORATIVE TECHNIQUES AND MATERIALS ON THE BOHEMIAN LATE MEDIEVAL ALTARPIECE

Dánová H.*[1], Šefcu R.[3], Pitthard V.[2], Bilavcíková H.[3]

Keywords: non-invasive methods, Painting, Raman spectroscopy, GC-MS, Pigment

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The aim of this paper is to summarise the results obtained by the investigation of the richly decorated Bohemian medieval altarpiece depicting the legend of St Catherine of Alexandria situated in the St Catherine church in Chrudim, Eastern Bohemia. This altarpiece belongs among the group of the medieval altarpieces uniquely preserved in Chrudim and executed with the highest art quality. The research focused

on a decorative technique of the tin relief (pressbrocade) and use of specific pigments typical for the Bohemian painting in the late Middle Ages. Decorative schemes, prints of used moulds, quality of execution, chemical composition of filler material, production of the tin relief, and its application onto the paint surface were investigated. The material investigation included non-invasive X-ray fluorescence analysis (XRF) and mobile Raman spectroscopy of carefully selected samples prepared as cross-sections. Pigments in particular colour layers were analysed using polarized light microscopy, micro-Raman spectroscopy (MRS) and scanning electron microscopy with X-ray microanalysis (SEM-EDS). Furthermore, gas chromatography - mass spectrometry technique was involved to specify the presence of both lipid and protein binding media in the composition of filler material of the reliefs as well as the use of binding media in paint layers. Thanks to the analytical methods involved in the research, it was possible to determine the presence of pigments in different layers of the cross-sections. A rich palette of white, yellow, red, blue, green, and black pigments was identified. The individual pigments such as lead white, vermilion, red lake, earth pigments, red lead, lead-tin yellow type I, copper-based green, carbon-based blacks and also specific pigment for Bohemian late gothic painting – fluorite – were detected. The research also enabled to specify the admixtures of pigments and binding media in the paint layers and in the filler material of the tin relief technique. The Raman spectroscopy was employed in the mapping mode to show the distribution of the individual pigments in the cross sections in order to reveal the construction of the tin reliefs. The relief imitation of luxury brocade cloth was applied on limited areas of the painting – parts of clothing or textile decorations. The relief applications were completed in colour in order to imitate the greatest possible impression of the real material. This process included also gilding and colour finish of the relief surface. The analysis of the decoration schemes demonstrated use of the combination of vegetable and zoomorphic motifs. The paper offers a systematic view on the outcomes and synoptically consults the analytical results of individual non-invasive and micro-destructive scientific methods. The experimental data obtained during the research serves as the basis for more general conclusions dealing with the workshop practice in the late Middle Ages.

This contribution has been financially supported by the project of the Ministry of Culture of the Czech Republic: Art of the Gothic and Early Renaissance Periods in the Eastern Bohemia Region. Research, interpretation, presentation (DG16P02B003).

ABSTRACT O.1.3

NOVEL APPROACH IN THE STUDY OF EASEL PAINTINGS - NEW CONTRIBUTIONS USING LASER ABLATION-INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY (LA-ICP-MS)

Valadas S.*[1], Barrulas P.[1], Mirão J.[1], Candeias A.[1]

Keywords: Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry, easel paintings, trace elements, material characterization, pigments

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Study of easel paintings may be triggered by the lack of historical references, “lost”, dislocated and “resized” paintings, artist’s technique, organization of work in an workshop and even suspicious attributions [1, 2]. Often the studies are developed under the framework of multidisciplinary teams and based on the combination of historical documental research and material and technical characterization using complementary surface exams, in-situ analysis and micro-analysis and to address the questions.

In this study, we present a new approach using LA-ICP-MS to investigate paintings materials [3-5], namely calcium carbonate raw materials, to address hypothetical groups or unsolved issues and was developed under the framework of a project to (re)define the corpus of the workshop of 16th century Flemish-Portuguese painter Frei Carlos (active between 1517 and 1539-40) who left a large number of works mainly that came from the Espinheiro´s Convent where he made the Profession of Faith (in 1517).

The initial study was carried out by optical microscopy, micro-Fourier-transform infrared-spectroscopy, micro-Raman spectroscopy, scanning electron microscopy coupled with energy dispersive X-ray spectrometry, micro-X-ray diffraction analysis, and high performance liquid chromatography and Pyrolysis gas chromatography mass spectrometry. The complementary surface and analytical research was envisaged for the technical and material characterization of grounds, underdrawings, primings, paint layers and its multi-layered build-up, providing access to the painter´s materials used in the technical execution of the paintings and details of the technique of artistic production. However, the use of LA-ICP-MS to analyze the ground layers of the paintings combining high spatial resolution analysis with low detection limits (that goes up to ppb levels), together with the analysis of the data in the artistic context revealed further similarities and differences in the technical solutions adopted in the paintings allowing to establish groups and reevaluate chronology.

Analysis of grounds in paint cross-sections introduced data at level of minor and trace elements. Also the analysis of Sr/Ca and Mg/Ca ratios allowed to conclude that there were two different sources of raw materials in ground formulations pointing out two different groups that reinforce previous suppositions:

- A predella composed by two panels, Three saints and Mystic Marriage of Saint Catherine, revealing high approximation to Annunciation (dated 1523) regarding support structure, pictorial materials and technical solutions, reinforcing the hypothesis that these panels constitute a same altarpiece.
- Two paintings that had been doubtfully attributed to Frei Carlos workshop and as a result of integrated research it was possible to point out this master as a follower.

Particular attention is given to the ground formulations when two different based-materials were detected, calcium carbonate and calcium sulfates, as it seems to relate it to a possible readjustment into most common materials and techniques of artistic production in Portuguese territory at time [1, 2].

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ABSTRACT O.1.4

NON-DESTRUCTIVE INVESTIGATION OF CULTURAL HERITAGE POLYCHROME STRATIGRAPHIES BY SYNCHROTRON GRAZING INCIDENCE X-RAY DIFFRACTION

Possenti E.*[2], Conti C.[1], Colombo C.[1], Gatta G.D.[2], Merlini M.[2], Realini M.[1]

Keywords: polychrome stratigraphies, pigments, non-destructive investigation, grazing incidence X-ray diffraction, synchrotron radiation

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The polychrome stratigraphies are complex multi-layered systems consisting of the overlapping of several painted layers, each one usually composed by a mixture of different crystalline and amorphous phases. Moreover, historical stratigraphies often display the presence of other newly-formed crystalline phases due to decay processes (e.g., deposits, decay salts and inorganic conservative treatments, etc.). The exhaustive and unambiguous characterization of all the overlapped layers is crucial in order to fully identify the painting technique, the employed materials and their mutual interaction with aging. At the same time, Conservation Science needs to preserve the original materials and one of the major challenge of the last years is to find new approaches able to avoid any sampling from the artworks or to maintain unaltered the collected micro-samples. Unfortunately, the conventional multi-analytical approach is normally destructive or micro-destructive and, in many cases, it involves a specific preparation of the sample [1–4]. In this work, we present a new non-destructive protocol based on grazing incidence X-ray diffraction for the characterization of pigments and crystalline phases used as fillers or aggregates in painted layers of a multi-layered system, avoiding the use of polished cross sections. The X-ray diffraction analyses were performed at the Italian synchrotron radiation facility ELETTRA (TS), beamline MCX, with a grazing angle geometry and the surface of the specimens was X-rayed with different incident grazing angles. The investigations were performed on a set of ad hoc laboratory painted samples and on micro-samples of actual historical artworks. The experimental findings allowed the identification of the crystalline pigments (such as hematite, titanium oxide in the crystalline form of rutile, clinobisvanite, cobalt violet, cinnabar, crocoite, phoenicochroite, lazurite, green earth, etc.) and of paint fillers (such as calcite, dolomite, gypsum, wollastonite, talc and other phyllosilicates, quartz, etc.) in reference stratigraphies as well as in the micro-samples from historical paintings. Thanks to the results obtained from this research, it is now possible to reconstruct the layer succession without any sample damage.

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ABSTRACT O.1.5

THE FADING OF THE YELLOW PAINT IN PICASSO'S FEMME (1907): PHOTOLUMINESCENCE STUDIES

Comelli D.[2], Ghirardello M.*[2], Valentini G.[2], Nevin A.[1], MacLennan D.[3], Phenix A.[3], Patterson C.S.[3], Gross M.[4]

Keywords: Cadmium yellow degradation, Time-resolved Photoluminescence imaging and microscopy, Multi-analytical study, micro-FTIR spectroscopy, Picasso

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Pablo Picasso's Femme (Époque des "Demoiselles d'Avignon", 1907, Fondation Beyeler, Riehen/Basel, collection Beyeler) is an oil study related to Les Demoiselles d'Avignon. A collaborative, multi-analytical technical examination of the painting was carried out to address questions about the artist's materials and technique during an important, but relatively understudied, period of Picasso's career. Of particular technical interest is the nature of two yellow passages, painted using two different cadmium sulphide (CdS) yellow paints [1]: a visibly degraded cool lemon yellow and a seemingly intact warm yellow.

Following the introduction of cadmium yellow pigments in the middle of the 19th century, these bright colors started to be widely employed by modern artists. Despite their popularity, cadmium yellow pigments can undergo severe degradation, evidenced by discoloration, loss of adhesion, and the formation of colourless white globules on the painting surface [2-5]. Studies on degraded CdS paints have reported the presence of several chemical species [2-5] formed by photo-oxidation or as residual starting reagents from an indirect synthesis process [5].

To understand the nature of the degradation encountered in Femme, and to better assess the risk of further alteration, the painting has been inspected through a number of techniques. Initial studies using visible light and UV microscopy together with scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) found that the two cadmium yellow paints have similar overall elemental compositions, but on a micro-scale were seen to consist of very different particle morphologies and distribution, suggesting the use of two different paints. Degradation products – cadmium oxalate, carbonate, and sulfate – were detected at the surface of the altered cool lemon yellow by micro-Fourier transform infrared spectroscopy (FTIR).

Subsequent studies using time-resolved photoluminescence (TRPL) imaging and microscopy were carried out both in situ and on multi-layered microsamples to characterize the emission properties of these two semiconductor-containing yellow paints. The in-situ results revealed that the degraded cool lemon yellow paint is characterized by a defect-related optical emission that is much more intense and with spectral and lifetime properties different than those detected in the non-degraded warm yellow paint. Similarly, TRPL analysis of the microsamples revealed strong differences in both the band-to-band (BB) and trap state (TS) emissions of the two yellow paints, suggesting different degrees of crystallinity and type of crystal defects.Indeed, the features of TS emission detected in the preserved warm yellow are in good agreement with the reference CdS-based paints produced using modern synthesis processes [6]. In contrast, the TS emission from the degraded cool lemon yellow paint suggests it has undergone significant alterations of its crystal defects, which is further supported by the lack of BB emission in the degraded cool lemon yellow.

In general, we demonstrate that the TRPL technique is a highly sensitive analytical method for probing the presence of crystal defects in inorganic and semiconductor pigments. TRPL complements other analytical methods sensitive to molecular species and ions, such as as micro-FTIR, -Xray diffraction, and -Xray

absorption near edge structure spectroscopies, and provides a further step towards a better understanding of how semiconductor pigments change and alter over time.

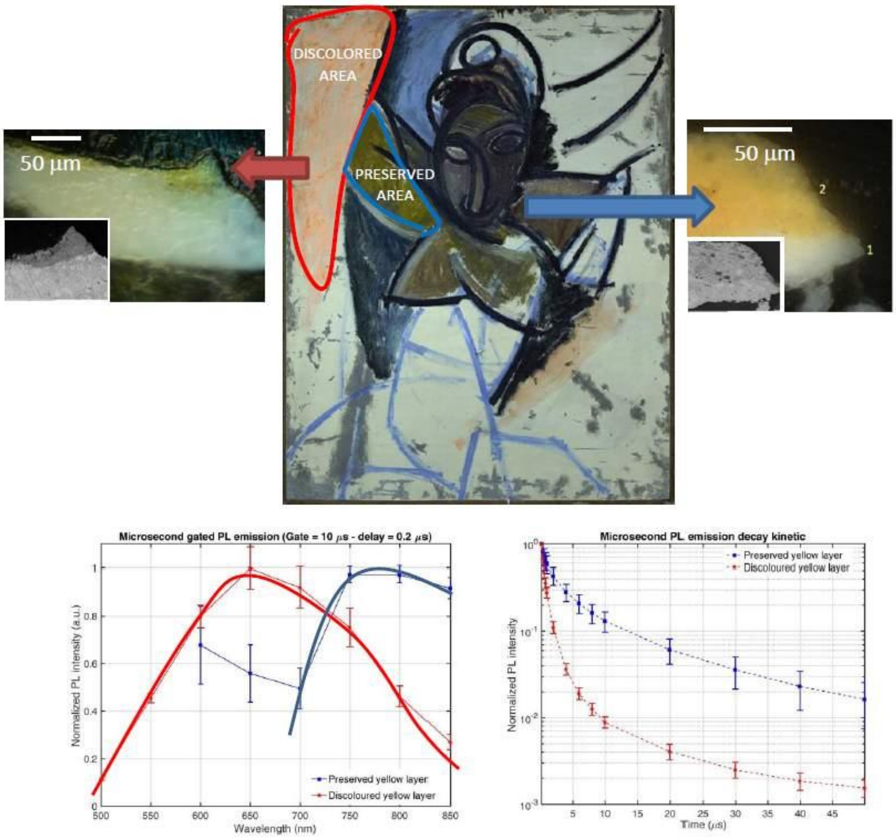

Figure. **Combined image** showing **UV-induced visible fluorescence image of the painting *Femme (Woman)* by Pablo Picasso** with evidence of the preserved (blue contour) and discolored (red contour) areas (top panel); **dark-field microscopy images of the two stratigraphic microsamples** taken from the preserved and discolored areas with SEM-EDX back-scattered electron images shown in the insets (left and righ panel); **trap state photoluminescence spectra and decay kinetic** detected in the preserved and discolored yellow layers (bottom panel)..

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ABSTRACT O.1.6

THE APPLICATION OF FAR-INFRARED MICROSPECTROSCOPY IN THE ANALYSIS OF ARTISTS’ PIGMENTS

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Keywords: FAR-IR, Microscopy, FT-IR, Spectroscopy, Infrared

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In the world of art authentication and preservation, the materials chemical identification represents a key aspect. Indeed, the correct material identification gives important information about the art piece age and suggests precious clues regarding the authenticity of the pieces from the well-made copies.

Furthermore, material characterization guides art conservators in the choice of the proper cleaning and preservations techniques, hence helping them to slow down the natural paintings and sculpture degradation processes.

Infrared spectroscopy is a well-established technique for artists’ materials analyses and identification. Measurements are typically performed in the MID-IR spectral region (4000-400 cm^{-1}). The 400 cm^{-1} low frequency cut-off is due to KBr optics typically employed in Fourier transform infrared (FT-IR) spectrometers. The mercury-cadmium-telluride (MCT) detectors employed in FT-IR microscopes further limit the spectral low frequency cut-off at 600 cm^{-1} range. This situation has limited the potential of FT-IR measurements since many inorganic materials, such as pigments found in artworks, have diagnostic spectral absorption bands in the FAR-IR region below 400 cm^{-1} [1,2].

In this work, we have used a particular FT-IR configuration to analyse selected artwork in the MID and FAR infrared regions. Spectra were acquired using a nitrogen purged Thermo Scientific™ Nicolet™ iS50 FT-IR and Czitek SurveyIR™ microanalysis accessory. Measurements have acquired in attenuated total reflectance (ATR) mode using the SurveyIR diamond ATR and in infrared reflectance.

This analytical setup shows that the combination of FAR-IR and microscopic measurements allows these spectra to be collected with relative ease and speed providing benefits to both authentication and preservation efforts. FAR-IR spectra have given precious information about in-situ inorganic extending the ability in the description of the pigments used in the paintings.

This work open to the far-IR pigment identification in microscopy, providing a wealth of new chemical information for museum scientists, conservators and academics.

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O.2 INORGANIC

O.2 INORGANIC

ABSTRACT O.2.1

APPLICATION OF PHOTOCATALYTIC N-DOPED TiO_2 ON THREE DIFFERENT TYPES OF LIMESTONES

Fornasini L.*[1], Bergamonti L.[2], Bondioli F.[2], Predieri G.[3], Lazzarini L.[4], Paz Y.[5], Lotticci P.P.[1]

Keywords: Titanium dioxide, Nitrogen-doped TiO_2, Photocatalysis, Self-cleaning, Limestones

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Nanostructured titanium dioxide (TiO_2) is one of the most promising photocatalyst in the field of heterogeneous photocatalysis, leading to the transformation of environmental pollutants into harmless species. The development of self-cleaning surfaces with photocatalytic and hydrophilic properties has recently attracted much attention in the preservation of the original appearance of buildings and monuments.

TiO_2-based coatings were synthesized and applied on Israeli limestones in order to test their self-cleaning efficiency: non metal doping was chosen to obtain visible light active photocatalyst [1]. Two different Nitrogen-doped TiO_2 (N-TiO_2) sols were synthesized in neutral and acid medium by sol-gel technique, starting from titanium oxysulfate ($TiOSO_4$) as titanium precursor and ammonium hydroxide and ammonium fluoride as nitrogen sources. The nano-cristallinity was confirmed by X-ray diffraction, transmission electron microscopy and Raman analyses, with particle size of about 3-4 nm, mainly in the anatase phase. Diffuse reflectance spectroscopy has evidenced that both N-TiO_2 nanopowders show a red-shift in the absorption edge with respect to undoped TiO_2.

The self-cleaning efficiency of the two N-TiO_2 coatings was proved on three typical Israeli carbonate stones, Maccabim, Halila and Hebron, mainly composed of calcite and dolomite, in different proportions, and compared to the performance of commercial TiO_2 (Evonik P25). The photoinduced properties of the coatings were tested through the degradation of two synthetic organic dyes (Methyl-orange and Rhodamine-B) by exposing the coated samples to UV-Visible irradiation and by following changes in the hydrophilicity of stone surfaces. The harmlessness of these coatings with respect to the physical properties of the untreated stones was confirmed by means of colorimetric and water capillary absorption measurements.

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ABSTRACT O.2.2

STUDIES ON POTASH-LIME-SILICA GLASS WITH MEDIEVAL COMPOSITION AND THEIR PRESERVATION BY APPLYING SOL-GEL SILICA COATING

Schreiner M.*[1], De Bardi M.[1], Renzo B.[2]

Keywords: Medieval stained glass, Weathering, Sol gel silica coating, ToF-SIMS, SEM/EDX

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Potash-lime-silica glasses typically used in medieval stained glass north of Alps show a low chemical durability due to the low silica content and the high amount of potassium, sodium and other network modifier ions such as Ca or Mg. This glass is sensitive to acidic conditions typical of polluted environments; it is therefore easily damaged due to the ion exchange process, which leads to the formation of a superficial layer with chemical and physical characteristics different from those of the bulk glass. The effect is a hazy appearance, flaking phenomena and the formation of corrosion products such as gypsum ($CaSO_4$ x $2H_2O$) or syngenite (K_2SO_4 x $CaSO_4$ x H_2O) as crystalline and hydrated silica as non-crystalline weathering products. Consequently, the transparency of these glass paintings is reduced and in many cases the entire composition is barely recognizable. Furthermore, the thickness of the glass panel is also reduced. The studies of the mechanisms leading to those effects, particularly dangerous for cultural heritage glass objects, are important to introduce procedures to slow down these reactions and to develop protective methods.

In order to investigate the weathering mechanism of that type of glass and to test preservation treatments, specimen with chemical composition similar to medieval stained glass were coated with sol-gel silica. It consists of an inorganic and transparent layer (~300 nm) applied without any heating treatments. The samples were exposed to controlled atmospheres in climate chambers as well as under natural conditions within an international exposure program. After exposure, the sample surfaces and their cross-sections were investigated in the scanning electron microscope in combination with energy-dispersive microanalysis (SEM/EDX). Additionally, surface analytical investigations were applied using ToF-SIMS (Time of Flight Secondary Ion Mass Spectrometry) and IRRAS (InfraRed Reflection Absorption Spectroscopy) for studying the chemical and structural changes on the glass surfaces during the weathering and to determine the ion migration due to the exchange processes.

The results showed a strong dependence of the weathering process on the glass composition, time, pH, and type of acidic pollutants used. The applicability and the efficacy of a protective sol-gel silica coating could be tested and it could be proved that it enhances the resistance of the glass avoiding cracking and minimizing the formation of weathering products.

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ABSTRACT O.2.3

A PORTABLE FTIR STUDY OF MORTAR MODEL SAMPLES. COMPARISON AMONG INNOVATIVE AND TRADITIONAL TECHNIQUES

Brunello V.*[3], Rampazzi L.[3], Sansonetti A.[1], Tedeschi C.[2], Corti C.[3], Vio C.[3]

Keywords: Mortars, Binders, Non-invasive analysis, Portable-FTIR, Analytical protocols

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Mortars are among the most important building materials, both in case of lime or cement binder. They are classified as composite materials, with several different mineral phases as main components. The recipes used in the past come from local historical traditions; unfortunately their precise composition is not reported in historical sources. Due to the huge variety of recipes, it is always difficult to analyse and identify correctly the mortar composition. The knowledge of past mortar recipes could suggest cultural and technological information and improvements in today’s practice in conservation works.

In recent years non-invasive and portable instruments played an increasing role in conservation science, especially on painting materials; on the contrary there are few published studies on historical building materials. Since the sampling is always a drawback,

In this research a portable non-destructive technique, the external reflection infrared spectroscopy (portable-FTIR), is compared with the traditional analytical techniques, such as powder X Ray diffraction (XRD), optical and petrographic microscopy, scanning electron microscopy (SEM) and traditional bench transmission FTIR. Advantages and drawbacks of this technique are here discussed, taking into account that it was never applied systematically to mortars and cement materials.

The analyses were carried out on model samples, prepared on purpose in order to cover the most widespread mortars mixtures used in the past and in restoration practice found out after a deep bibliographic research. Several inorganic binders were used (Lime both aerial and hydraulic, gypsum and Portland cement), mixed with a quartzose aggregate. The analytical procedure was tested also on mortars sampled from historical buildings and the most meaningful results are shown and discussed.

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Infrared Spectroscopy in the Analysis of Building and Construction Materials - Lucia Fernández-Carrasco, D. Torrens-Martín, L.M. Morales and Sagrario Martínez-Ramírez - DOI: 10.5772/36186.

ABSTRACT O.2.4

ANALYSIS OF THE HISTORIC AND MONUMENTAL BUILDINGS MORTAR IN THE CENTRAL ITALY DAMAGED BY THE RECENT EARTHQUAKE

Alshawa O.[2], Cinaglia P.[3], Di Girolami G.[3], Francola C.[2], Liberatore D.[2], Mirabile Gattia D.[4], Persia F.[4], Petrucci E.[5], Piloni R.[1], Roselli G.[1], Scognamiglio F.*[3], Sorrentino L.[2], Zamponi S.[1]

Keywords: mortars, analysis, historic masonry, vulnerability, earthquake

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Structural behavior of masonry, particularly under seismic actions, is strongly influenced by masonry fabric and mortar quality. Typically, the collapse of existing masonry structures is triggered by: delamination of the outer leaf, out-of-plane mechanisms (overturning or bending), in-plane mechanisms (shear or bending). Usually, the delamination of the outer leaf is the most dangerous mechanism in rubble masonry with two leaves and in the absence of transverse links (headers). In such conditions, the separation between the leaves and the partial or total collapse of the construction occurs. A good quality mortar is essential to delay/prevent the separation of leaves. However, in existing buildings, mortar is often heavily deteriorated and appears as a non-cohesive granular medium. The paper presents an experimental study on mortar samples taken from historical and monumental buildings damaged or collapsed following seismic events in Central Italy (2016). A significant number of samples were taken in the sites damaged by the earthquake, in Umbria, Lazio and Marche regions; the aim is to deepen the acquired data, supplementing them with research on the origin of materials and on the assembly systems. They were analyzed with a set of diagnostic techniques to characterize the mortar and correlate it with the performance of this composite material. The diagnostic techniques used were: X- Ray Diffraction (XRD), calcimetry, FT-IR spectroscopy, solute salt analysis by conductimetry and dosage of anionic species by ion chromatography, particle-size analysis, direct shear test. The diagnostic test have shown, for almost all samples, the use of an underachieving binder mortar. This preliminary work is the first step of a broader study; it will be extended to a wider Apennine area in Central Italy, to provide a vulnerability mapping of historic buildings, linked to their construction systems and in particular to the use of poor quality mortars.

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O.3 DATING

O.3 DATING

ABSTRACT O.3.1

ELECTROCHEMICAL DATING OF LEADED BRONZE COINS: THE CASE OF MAGNA MATER TEMPLE

Di Turo F.*[1], Montoya N.[4], Piquero-Cilla J.[4], De Vito C.[1], Coletti F.[2], Favero G.[1], Domenéch-Carbò M.[3], Domenéch-Carbò A.[4]

Keywords: Dating, Archaeometry, Bronze coins, Electrochemistry, Diagnostic

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Dating ancient metals is an open issue in archaeometry: relevant data for determining metal provenance can be derived from the chemical composition of the alloy, isotope ratios, and the microstructure of the alloy but sampling the metal core of the archaeological objects is in general not allowed. Then, analytical data have to be extracted from metal corrosion patina. Here, it is proposed an electrochemical methodology based on the Voltammetry of Microparticles (VIMP), a technique which provide responses depending on the composition of the base metal (alloy of copper, tin and lead), applied to samples coming from the Roman archaeological site of Magna Mater Temple (Rome, Italy). The coins were found in different strata dated back between the second half and the end of the 4th century A.D. (kingdom of Costanzo II, Valentiniano and Valente) and the 20th century. However, the samples of the Magna Mater cover the entire Imperial Roman period, becoming of great relevance for the history of the site and for the questions related to the reuse of the materials: in fact, the coins resulted older than the deposition's date and the archaeologists explained this chronology for the prolonged use of the Roman emissions. Considering the lack existing on the numismatic documentation of the first period of the high Middle Age, it is possible to suppose that these coins were the only ones available on the monetary circulation during that period [1].

The voltammetric responses of copper and lead corrosion product in contact with aqueous acetate buffer, as well as the catalytic effects produced on the hydrogen evolution reaction, were used for establishing the age of different strata and dating coins belonging to unknown age. The differences in the in depth distribution of different corrosion products, assumed to result from differences in the composition and metallographic structure of the metal core become crucial for the above purpose. Electrochemical techniques clarify also the corrosion processes and then, the conservation conditions of the coins employing. Electrochemical Impedance Spectroscopy (EIS), along with VMP, suggest that the corrosion involved the growth of a secondary patina of porous litharge and cuprite plus tenorite over a primary patina of cuprite and litharge. The compositions of the surface and its corrosion products have been confirmed by Raman spectroscopy and FIB-FESEM-EDX analysis, essential to maintain the multi-analytical approach.

The electrochemical data obtained can be considered consistent with the hypothesis of the reuse of the

coins during the later periods as a result of the economic difficulties associated to the fall of the Roman Empire and the difficulties in find raw materials, as Sn minerals, for bronze coinage. The electrochemical discrimination of the corrosion products, which depends on their usage history, allows the grouping of the studied samples on the basis of their location in the stratigraphic sequence of the archaeological site. Voltammetric data were consistent with calibration graphs for dating leaded bronze, permitted a refined dating of the different strata. Therefore, the methodology can be a useful tool for archaeologist in order to validate and compare the historical data of the samples.

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ABSTRACT O.3.2

INNOVATIONS IN ^{14}C DATING OF MICRO-SAMPLES FROM OILS AND LEAD WHITE PIGMENT IN EASEL PAINTINGS

Hendriks L.*[1], Hajdas I.[1], Ferreira E.S.[2], Scherrer N.C.[4], Zumbühl S.[4], Küffner M.[3], Carlyle L.[5], Welte C.[1], Wacker L.[1], Synal H.[1], Günther D.[1]

Keywords: Radiocarbon, lead white, artwork dating, organic binder, easel paintings

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In the study of works of art there are frequently questions regarding attribution and authenticity. Radiocarbon (^{14}C) dating can be a powerful tool for these investigations. The major drawback of this technique is the necessity of taking a physical sample, which means that it is often used as a last resort when other non-destructive analytical methods have been unable to deliver conclusive evidence. Due to the relatively large sample sizes required in the past, ^{14}C analyses have been restricted to the support material, in the case of easel paintings, wood from a panel or textile fibres from the canvas. However, radiocarbon results based on the support materials alone can be misleading, indeed a support may be older than the actual painting in cases of reused old supports by artists themselves or by forgers. Recent technological advances have significantly reduced the minimum sample size required (Hendriks et al. 2016) which now opens up the possibility of finding other materials within the artwork, datable by ^{14}C.

Artists' oil paints are rich in carbon-based material, ranging from the organic binder to pigments and additives/fillers. In this work the dating of the oil binder was targeted, since it will be representative of the time of creation of the paint. The ^{14}C clock of natural drying oils will initiate with the harvesting of the seeds that were used to extract the oil. The ^{14}C technique, which requires a few hundred µg of sample only, was applied initially to a twentieth century oil painting from Franz Rederer. The painting delivered ideal source material for a case study due to legitimate authorship and consequently a reliably signed date, unvarnished surface and no history of restoration since the time of its creation. Moreover the painting was signed by the artist in 1963 i.e., right at the ^{14}C bomb peak allowing conversion to precise calendar ages. Samples were selected from areas containing inorganic pigments, non-carbonate pigments only. Prior to dating, the oil paint had been fully characterized by combining XRF, FTIR and Raman spectroscopy. The ^{14}C age found for the binder in two paint samples pre-date the execution date of the painting by 4-5 years and correlate with the ^{14}C age of the canvas support. These results illustrate the great potential for ^{14}C dating of the binder, offering a new technique in the study of paintings and their origins (Hendriks et al 2017).

In terms of dating the oil in the presence of a carbonate pigment, mixed results could arise depending on the relative contributions of the two carbon sources in play: the organic binder and the carbon atom in the carbonate anions. Tests were carried out to determine the possibility of focussing on the carbonate source alone. Reference samples of lead carbonate pigments were provided from the MOLART and HART projects. One was produced beginning of the 21th century using the traditional stack process, and two were from 20th century commercial sources and thought to be produced using modern industrial methods where the carbon dioxide source is derived from artificial sources, such as coal combustion. The radiocarbon ages derived for each lead carbonate demonstrate that the pigment produced following the traditional stack process does indeed carry the ^{14}C signature of the atmosphere and hence the radiocarbon data matches the year of production. The modern-industrial pigments on the other hand could not be dated per se but, nevertheless, can be used as markers to identify lead white produced using carbon dioxide streams. This practice was first patented by James Creed in 1749, and was further gradually adapted worldwide replacing the traditional stack process by the 20th century. Thus this work demonstrates that lead white pigment produced following the traditional stack process can successfully be discriminated from other modern commercial-source lead whites by means of ^{14}C dating.

By the successful attempt to date paint materials such as widely used natural oils and lead carbonates with minimal sample sizes we introduce new powerful options to extend the armoury available to solve attribution and authentication questions.

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O.4 NON-DESTRUCTIVE AND MOBILE TECHNIQUES

O.4 NON-DESTRUCTIVE AND MOBILE TECHNIQUES

ABSTRACT O.4.1

MATERIAL COMPOSITION EVALUATION OF HISTORICAL CU-ALLOY AQUAMANILIA BY IN-SITU X-RAY FLUORESCENCE AND LIBS MEASUREMENTS

Zmuda Trzebiatowska I.[2], Del Hoyo Meléndez J.M.*[1], Bratasz L.[3], Sliwinski G.[2]

Keywords: aquamanilia, Cu-alloys, XRF, LIBS, Quantitative analysis

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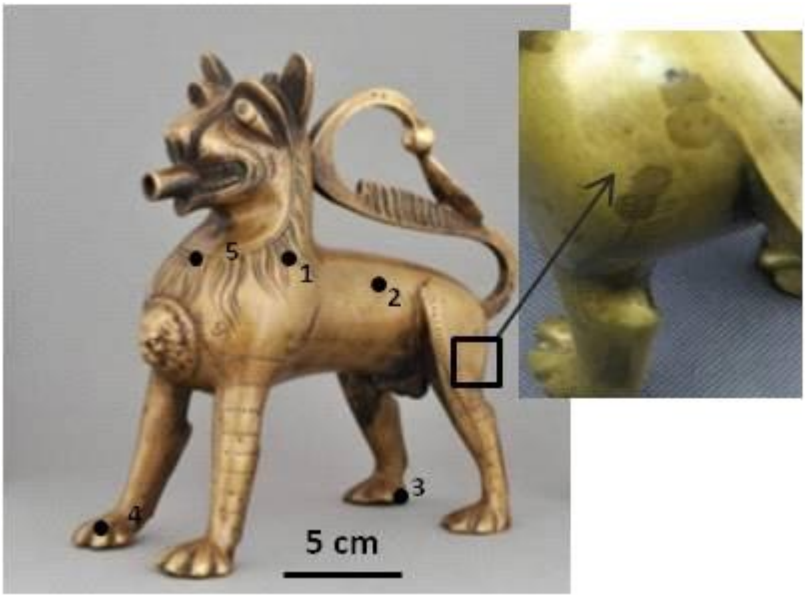
Using in-situ micro-ablation sampling based on laser-induced breakdown (LIB) and X-ray fluorescence spectroscopy (XRF), the surface layers and bulk material compositions of historical aquamanilia (XV–XIX c.) from collections housed in National Museums of Poland in Kraków and Gdańsk were examined in order to provide reliable data for authentication and dating studies. Results obtained in a non-destructive way by means of two portable XRF spectrometers calibrated with the same standards were complemented by results of the LIBS measurements. Consistent data of the alloy compositions were obtained by means of portable/transportable spectroscopic instruments.

Aquamanilia are scarce in museum collections. The uniqueness and design of the finely crafted functional figures - e.g. shown in Fig. 1, both were most probably the reason why aquamanilia often have been copied in various sizes during the XIXth and XXth centuries and which in turn contributes to the authentication problems. In this study seven objects were investigated including one made of bronze and treated as reference [1].

XRF spectrometry revealed that these figures produced during the period from XV c. till early XX c. were cast in the ternary and quaternary Cu-alloys, with the exception of one aquamanile in form of a lion made of Pb-rich alloy (end of XIX c). This was confirmed consistently by the XRF and LIBS spectra revealing in case of Cu-alloys besides the main component the presence of strong bands ascribed to Zn, Sn, Pb and also weaker ones of admixtures and impurities such as Ag, Fe, and Ni [2-4]. For the figure of a lion (XVIII c.) showing a repaired defect area the use of a material (Cu/Zn = 44/40) different from the original (Cu/Zn/Sn = 62/23/4,4) was evidenced and presence of the elements Ba, Ca, and Na, was ascribed to surface contamination. This has been confirmed by the penetration depth dependent band intensities obtained during stratigraphic LIBS measurement. In case of the dragon figure (XIX c.)), a lower Cu content in the superficial surface layer was observed and ascribed to prolonged exposure to seawater [5]. Measurements with instruments calibrated by means of certified reference standards revealed Cu-alloys with a relatively high Zn content in the range of 15,2-23 % with smaller ones of Sn (0,7-4,4 %) and Pb (up to 0,7 %) which is typical for alloy compositions classified as brass. Slight differences observed between quantitative results obtained from LIBS and XRF were ascribed to the effect of surface patina and contamination, surface irregularities and local material inhomogeneity. These have all been identified as sources of error in the analysis [6,7].



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ABSTRACT O.4.2

THE EXPANDED CAPABILITIES OF THE PORTABLE LASER ABLATION SYSTEM FOR ELEMENTAL ANALYSIS

Kradolfer S.*[1], Peter V.[2], Bodo H.[1], Koch J.[1], Van Willigen S.[3], Pernicka E.[4], Günther D.[1]

Keywords: Archeometry, Elemental analysis, Laser Ablation, Portable Device, Minimal invasive

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In the Archaeological community the information about the content of trace elements in artefacts of interest gets more and more attention. This specific and object related information can e.g. be used to discover identify fraud, obtain information about manufacturing processes or constrain the geographical origin of objects. Laser ablation inductively coupled plasma mass spectrometry (LA-ICPMS) is a powerful and particularly versatile micro analytical tool for the analysis of practically any material concerning the elemental and isotopic composition. The quasi-nondestructive sampling and high sensitivity of the methods can achieve limits of detection in the ng/g region (1) compared to e.g. micro-XRF (LOD: ~5 ug/g) when using a spot size of 60 µm (2). This makes it the ideal tool for such analysis.

Nevertheless conventional LA-ICPMS has its disadvantages concerning size and mobility of samples. Specifically the ICPMS analysis requires complex laboratory infrastructure and the measurement is restricted by the dimension of the ablation cell (commonly < 100 mm in size). The portable Laser Ablation system (pLA) developed in our laboratory achieves a decoupling of the sampling procedure from the subsequent analysis with ICPMS and combines the quasi-nondestructive sampling of conventional Laser ablation with the freedom of unrestricted, even field-deployable sampling in the µg-range. The system can provide on-site sampling of a broad range of specimen too precious, too big or simply not removable due to regulatory restrictions. The subsequent analysis can be carried out in the laboratory with various established techniques, such as ICPMS. The direct comparison to certified reference materials and on-site blank measurements enables a quality control and quantitative results at trace element levels in a highly reproducible way.

The pLA consists of a nanosecond laser device (λ = 532 nm), a fiber-based laser beam delivery and an ablation head (3). The ablation-process is performed in ambient atmospheric conditions. The generated material is extracted by a membrane pump and collected on suitable filters for subsequent analyses. These are carried out in the laboratory facilities and can either consist of the re-ablation of the deposits by applying conventional LA-ICPMS or, after digestion of the filters, by conventional sample introduction ICPMS. The pLA can furthermore be used in the laboratory and the generated aerosol can be analysed directly by ICPMS by coupling it to a gas exchange device (4).

In this presentation, we will highlight the recent improvements of the pLA system, especially concerning the technical upgrade of the laser beam delivery. This modification increased the laser-fluence on the sample surface and enables also off-line sampling of transparent materials, which is very important for the analysis of glasses.

In a first case study the analysis of gold was investigated (5). The reference material NA2 was sampled by collecting 2x 5'000 laser pulses on one filter. This approach yielded amounts of 0.2-4 µg of gold collected per filter. The filters were afterwards digested and analysed by conventional ICPMS methods. The analyses provided good agreement not only for the main components as Au and Ag (±10 %) but additionally for most of the certified trace elements with a good performance (± 30%).

In a second case study we demonstrate the successful ablation of Jadeite and Nephrite samples. Here the rare earth elements patterns, which were previously analysed by LA-ICP-MS and reproduced with the pLA-LA-ICP-MS (re-ablation) approach. The results show the possible use of the pLA-system as a sampling tool for such transparent materials.

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ABSTRACT O.4.3

TO THE UNDERSTANDING OF THE COMPLEX MANUFACTURING OF EGYPTIAN YELLOW COFFINS BY NON-INVASIVE TECHNIQUES

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Keywords: non-invasive, XRF-2D, RBS, Pigment, Ancient egyptian polychromy

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The 21st Egyptian Dynasty marks a big change in funeral practices. Decorations are not anymore on walls, but on the coffin itself which acts as an entire grave. Egyptian Yellow Coffins, reserved to priests and priestesses of the Amon temple, are characteristics to this period and are only found in the Theban area. A multispectral and multiscale methodological protocol have been developed at the Centre de Recherche et de Restauration des Musées de France in the way to analyzed the painting materials used for this particular Egyptian production. A dozen of funerary sets, complete or not, of Yellow Coffins from the Egyptian Antiquity Department of the Louvre Museum, have been studied and permit to highlight a global scheme of the painting protocol. The goal of this study, which is taking part of the Vatican Coffin Project, is to get material identification to determine manufacturing process, and to try in fine to identify specific workshops.

First results show that the painting protocol is more complex than we thought and actually can depend on the part of the coffin studied. The classic painting scheme includes a Muna layer on the wood support, a beige preparation layer, a white preparation layer which will receive the polychromy, comprising the yellow background, the red underdrawings and the painting layers; the final part is the varnishing of the object. Generally, variations of this scheme is about thickness of layers and materials used. It have also been noticed that differences of background treatment appear between the inner and the outer part of the case and also the higher and lower part of mummy boards and lids. Those variations can be attributed to workshops, fad or maybe temporal evolutions.

But, one of the more complex part is the understanding of the painting protocol put in place for the inner part of external coffins. The corpus comprise only two, and both revealed a very particular stratigraphy. The first one, which is an entire coffin have been sampled and results showed the presence of yellow background applied around motives (so after the underdrawings and letting white areas in reserve), a local double layer of white preparation and orpiment (yellow arsenic sulphide) in suspension in the varnish layer. Because of the object geometry, it is currently not possible to proceed to non-invasive techniques on the inner part of coffins. However, the study of a decorated fragment from the Louvre collection, attributed to the inner bottom of an external yellow coffin, permits to go beyond this geometry problem by its plane surface. This case of study enabled us to perform XRF-mapping, which is not possible on a complete coffin. This technique allows with computer-generated images the spatial distribution (x,y) of the different elements (As, Cu, Ca etc.), assigned to the corresponding pigments, easily identifiable. Those data are compared to the UV and VIL imaging, which respectively provide spatial distribution (x,y) of the varnish and of the Egyptian Blue. VIL imaging also discriminate the position of blue beside of green, because both are copper pigments. Those analysis give us precious answers at a more representative scale, and confirm the complex protocol used in this particular part of the funerary set, showing that the As distribution (orpiment – As_2S_3) does not match with the yellow background or neither the varnish application. Rutherford Backscattering Spectroscopy (RBS) tests have been done with AGLAE (Accélérateur Grand Louvre d'Analyse Elémentaire) on the panel and will be done on experiment samples which mimic the stratigraphy encountered. The RBS development methodology, never used with this kind of materials and problematic wants to determinate, in also a non-invasive way, the real position (z) of the arsenic in the stratigraphy, and understand this complex implementation. For this purpose, it is necessary to corroborate non-invasive results with sample ones, the multiscale vision is essential.

ABSTRACT O.4.4

IDENTIFICATION OF BLACK INK USED IN OLD ALGERIAN (KABYLIA REGION) MANUSCRIPTS BY NON DESTRUCTIVE TECHNIQUES

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Keywords: black inks, manuscripts, XRF, FORS, Raman

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This paper is about a comparative study of black inks used in different old manuscripts belonging to the Algerian heritage. The 16 analyzed manuscripts belong to Afniq n Ccix Lmuhib , one of the richest and most studied private libraries from Kabylia region – Algeria [1]. They date back from the 14th to the 19th century and treat disciplines ranging from astronomy to poetry [2]. To identify the black inks used by the scribes we used several non destructive techniques such as X-ray fluorescence, fiber optic reflectance and Raman spectroscopy. While the XRF gives the elemental composition of the inks, the FORS and the Raman analysis give the direct identification of the pigment. This cross analysis gives us a strong confidence in our identification (ferro gallic, ivory black) that contradicts what is generally believed about the nature of the

black ink used in the Kabylia region (ink made from burned sheep wool). Our results are confirmed buy a 17th century manuscript that describes how pigments are made. Our work is the first positive identification of inks used in Algerian manuscripts and confirmed by an old manuscript of the 17th century.

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ABSTRACT O.4.5

THE EXEMPLARY CASE OF A REMARKABLY WELL-PRESERVED HISTORICAL MUSICAL INSTRUMENT: THE "TUSCAN" STRADIVARI VIOLIN (1690)

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Keywords: Musical instrument, Material science, SEM-EDX, FTIR, XRF

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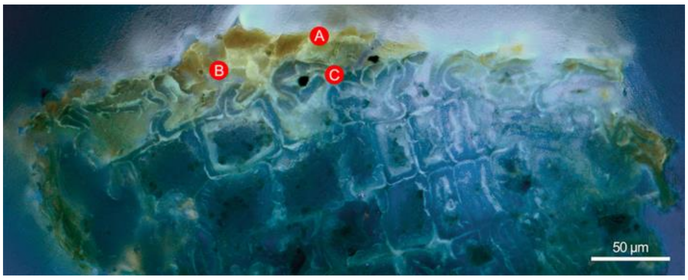
In recent years, scientific diagnostic analysis has increasingly focused on historical musical instruments, especially bowed stringed ones. The materials composing the stratigraphy of these peculiar works of art are characterized by a complex and heterogeneous nature, which is representative of the working techniques employed by the great violin makers of the past. The entire coating system, so called wood finish [1], includes multiple varnish layers on a previously grounded wooden substrate to prevent varnish penetration. Over the time, however, the original stratigraphy of these centuries-old masterpieces could have been affected by the extended handling during performances and practice, the very close contact of the instrument with the musician skin, or, again, accidents and interventions of maintenance and restoration. As a consequence, variations in its coating thickness and composition have most often occurred.

The object of the present study is one of the best-conserved instruments by Antonio Stradivari, namely the "Tuscan" violin (1690) today preserved at the Accademia of Santa Cecilia in Rome (Italy). Commissioned by the Medici family in 1684, as a part of the famous quintet, it is one of the earliest examples of the master's multiple-layer varnishing method [2]. The remarkably well-preserved wood finish of the violin was non-invasively studied by UV-Induced Fluorescence (UVIFL) photography (by B. Brandmair), Fourier-Transform Infrared (FTIR) reflection spectroscopy and X-Ray Fluorescence (XRF) spectroscopy. The hypothesis drawn from the non-invasive approach was supported by a micro-destructive analysis performed on two micro-samples, one taken from the violin's top plate (Fig. 1) and the other from the centre bass rib. The micro-samples were analysed by the Optical Microscope (OM) equipped with visible and ultraviolet lights and by the Scanning Electron Microscope (SEM) coupled with Energy Dispersive X-ray (EDX) spectrometer. The aim of the multi-analytical investigation was the characterization of varnishes, pigments and wood treatments constituting the violin's stratigraphy, trying to understand the methods used by Antonio Stradivari to finish the instrument.

From the results, the varnish is confirmed to be applied in a two-layer system: the uppermost salmon-fluorescent coloured varnish (Fig. 1, level A) is oil-resinous composed, with crystals of calcium oxalates witnessing the age of the varnish as a decomposition product of lipid materials [3]; the lowermost yellow-whitish fluorescent layer (Fig. 1, level B) is also characterized by an aged oil-resinous varnish with an aluminium- and oxygen-rich grain dispersed therein which gives rise to possible attributions, including that of alumina (Al_2O_3) as a substrate for lake pigments [4]. At the interface between the wood and the overlying varnish (Fig. 1, level C), probably related to a wood treatment, a proteinaceous compound can be likely identified as a binder of a few silica and silicates mineral phases. Moreover, rare particles of possible titanium-manganese-iron oxides and/or hydroxides as well as iron-containing aluminosilicates, both suggesting the possible presence of iron-based pigments such as red-ochre or umber earth [5], were found at this level. Under the treatment level, finally, small amounts of chlorine, sulphur, potassium and calcium could be ascribed to a wood pre-treatment method [2].

In conclusion, by combining data from the non-invasive and micro-destructive analytical campaign it was possible to propose a stratigraphic hypothesis of the “Tuscan” violin.



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ABSTRACT O.4.6

IDENTIFICATION OF GEMSTONES USING PORTABLE SEQUENTIALLY-SHIFTED EXCITATION RAMAN SPECTROMETER AND RRUFF ONLINE DATABASE: A PROOF OF CONCEPT STUDY

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Keywords: gemstones, identification, Raman spectroscopy, portable, RRUFF database

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Portable Raman spectrometers have been used recently in several studies that cover the applications related to gemmology. [1-3] These studies illustrate that the portable Raman spectrometers can provide a fast and unambiguous identification of minerals of gemstone quality as well as precious gemstones either as solitary stones or embedded in cultural heritage artefacts. In all these studies, the process that leads to the identification of analyzed gemstones requires a good knowledge of Raman spectroscopy as a method of choice. Improvements of the quality of recorded spectra by baseline correction are typically obtained. In general, positions of obtained Raman bands are compared with previously published reference values in order to unambiguously identify the minerals.

In this current study, we wanted to show that a much more straightforward and easier process that may be followed by a non-spectroscopist could result in an unambiguous identification of unknown cut minerals or gemstones.

A portable Raman spectrometer equipped with a sequentially-shifted excitation (SSE) that allows recording of Raman spectra with supressed fluorescence background was used for acquisition of Raman spectra of a series of 20 unknown cut minerals in gemstone quality. The sophisticated removal of fluorescence is an important improvement; the presence of fluorescence often complicates the acquisition of Raman spectra of good quality. The collection of specimens included in this study are part of a teaching set for training of students of gemmology. Obtained spectra were loaded into the freeware CrystalSleuth program that permits to search in the online database of Raman spectra of minerals RRUFF[4]. In this database, minerals are typically represented by several entries containing Raman spectra collected on samples from different localities, and various excitation wavelengths.

It has been shown here that the CrystalSleuth program complemented with the RRUFF database was able to give high precision matches for the 17 out of 20 samples (iolite, emerald, diopside, chrysoberyl, andalusite, triphylite, grossular, citrine, andradite, topaz, phenakite, baryte, labradorite, orthoclase, datolite, danburite and pollucite) based on the spectra acquired with the SSE-equipped portable Raman spectrometer. Raman spectra for these samples were virtually identical to the greatest match database entries for individual minerals. Two samples (kornerupine, hydroxyherderite) appeared to have a slightly worse match to the database entries, but still good enough for unambiguous identification. One sample, apatite, exhibited intense fluorescence that the SSE mode was unable to mitigate without introducing additional instrument artefact bands, and no automatic match was therefore possible.

Obtained results illustrate that the quality of Raman spectra recorded with the last generation of portable Raman spectrometers is good enough that in conjunction with automated search in free online databases it allows for easy unambiguous identification of gemstones by a non-spectroscopists.

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ABSTRACT O.4.7

IDENTIFICATION OF ARCHAEOLOGICAL OBJECTS MADE OF ANIMAL HARD TISSUES USING PORTABLE AND LABORATORY VIBRATIONAL SPECTROSCOPIC TECHNIQUES

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Keywords: Archaeology, Identification of biomaterials, Animal hard tissues, Raman spectroscopy, FTIR-ATR spectroscopy

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Recognizing biomaterial and animal species of an archaeological object is essential to put a human population in the right context of chronological time, diet, technology and sociology. Unfortunately, the identification of a biomaterial is often not obvious, and nowadays there are no physico-chemical techniques that are fast, non-destructive, easy to implement and with the possibility of carrying out ‘in situ’ analyses.

Raman and Infrared spectroscopic techniques have been successfully applied to distinguish modern samples and artistic objects of different animal hard tissues and animal species [1, 2, 3]. Even if the chemical composition and structure of biomaterials are similar, this distinction is possible because of the slight differences between the organic and inorganic phase organisations, which are influenced by the animal species and the function that the biomaterial studied has in the animal.

For this study, spectroscopic analyses were done in two different kind of archaeological collections:

- Paleolithic objects from Taillis des Coteaux cave, Antigny (Vienne, France), dated 17000 years BP. Such ancient samples exhibit a poor conservation of their organic part;
- Inuit objects (Canada) of the Guy Mary-Rousselière collection of Quai Branly-Jacques Chirac museum in Paris, dated c.a. 800-1800 AD. They exhibit a good preservation state, thanks to a moderate aging in cold climate burial.

The aims of this work were to investigate the performance of the vibrational spectroscopic techniques applied on ancient objects and to recognize biomaterials and animal species of several unknown samples from collections exhibiting various conservation states.

In laboratory analyses were performed using a RFS100/S RamanScope equipped with a laser Nd:YAG (1064nm) and coupled with a RamanScope III FT-Raman microscope (Bruker), and a micro FTIR-ATR Equinox 55 spectrometer combined with an IRscope II microscope and an ATR objective based on a Ge crystal (Bruker).

Given that the Inuit objects of Quai Branly-Jacques Chirac museum could not leave the structure, portable instrumentation are required. A campaign of ‘in situ’ analyses were performed by Raman spectroscopy with a Horiba Jobin Yvon HE785 spectrometer equipped with a near-infrared laser diode (785 nm) and a SuperHead video interface, and by infrared spectroscopy with an Alpha FTIR spectrometer with a diamond ATR interface (Bruker).

The survey method was to make an internal database of the two respective collections using archaeological objects with known biomaterial and animal species.

Several spectra were collected from the reference samples and several relative intensity ratios were investigated in order to find parameters capable of distinguish the biomaterials by using scatterplots and Principal Component Analysis. Successively, data extracted from the unknown samples were compared with the data obtained from the reference samples.

The results show that both laboratory and portable instrumentation are capable of distinguishing some of the different animal hard tissues that constituted the reference objects, even though they have a degraded surface and the state of preservation of the two collections is very different, and this allows us to establish the nature for some of the unknown samples.

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ABSTRACT O.4.8

MACRO X-RAY FLUORESCENCE (MA-XRF) SCANNING AS A NON-INVASIVE TOOL TO STUDY GLAZED CERAMICS: IN SITU CHEMICAL IMAGING ON A MAJOLICA TILE PANEL

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Keywords: MA-XRF scanning, Majolica, SEM-EDX, chemical imaging, Ceramics

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During the last decade, the introduction of mobile MA-XRF scanning instruments in conservation studios and museum galleries has revealed hidden aspects of several iconic easel paintings [1,2]. Often, these new findings did not only have a significant art-historical impact but allowed optimizing the conservation treatment of the paintings under study as well [3]. In this work, the potential of MA-XRF imaging to characterize flat, glazed ceramic objects is assessed through scanning experiments on a high-profile sixteenth century majolica tile panel. This sizeable and colorful tableau, consisting of 98 glazed tiles, depicts an animated biblical scene: The Conversion of Saul. The panel is dated 1547 and is believed to originate from the studio of the famous Antwerp majolica maker Guido Andries (Guido di Savino), one of the Italian craftsmen who brought the majolica technique to the city, after which it developed into an important center for majolica art. While for paintings, the penetrative properties of the impinging X-ray beam combined with the element-specificity of the emitted fluorescence signals permits studying modifications hidden below the paint surface in a highly selective way, the authors investigate to what extent these properties can be used beneficially for studying glazing techniques and revealing the multi-layered build-up of majolica objects. The presented insights are bench-marked by comparative SEM-EDX analysis and elemental mapping of a few extracted cross-sections. Until recently, this type of micro-imaging was the

most prevalent analytical method for obtaining reliable stratigraphic information on majolica objects, but the technique is increasingly contested due to its invasive character, while the representativeness of the few and minute samples is also subject of debate. Whereas mobile Raman Spectroscopy (RS) and/or handheld XRF instruments can be applied in situ as a non-invasive alternative to gather spectral data from selected points of interest, this work demonstrates the added value of MA-XRF imaging by collecting compositional data from the entire surface. Moreover, a careful interpretation of the ensuing elemental images did not only allow identifying the various chromophores, opacifiers and fluxes, it permits deducing the layer sequence as well. Nevertheless, unlike RS, no molecular information is acquired and in contrast with routine SEM-EDX, accurate quantification of components is not feasible. Still, this MA-XRF scanning operation that was conducted ahead of a full scale conservation treatment visualized earlier retouching in high detail and enabled distinguishing original tiles from pieces that were introduced during nineteenth and twentieth century restoration campaigns.

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ABSTRACT O.4.9

THE JACOPO TINTORETTO “WEDDING FEAST AT CANA”: A MULTI-TECHNIQUE NON-INVASIVE STUDY OF PAINTING MATERIALS

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Keywords: Tintoretto, Raman spectroscopy, Wedding Feast at Cana, FORS, Reflectography

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The “Wedding Feast at Cana” by Jacopo Robusti, known as Tintoretto, is a stately painting realized for the Crociferi oratory in 1561. After the abolition of the religious order in 1656 by the will of Pope Alexander VII, in 1657 the painting was moved to the S. Maria della Salute sacristy.

In 1984 SaveVenice Inc. foundation financed the first restoration campaign, mainly aimed to the removal of the yellowed vanish strongly affecting original painting colors. The same organization supported a new intervention in 2016-2017 with the same goal since also the product applied during the previous works underwent strong alteration processes that greatly compromised the scene readability.

In the frame of a wide project involving professionals from different fields, a series of non invasive studies have been carried out in order to obtain a detailed characterization of painting materials used by Tintoretto to realize the “Wedding feast at Cana”.

Images in R-NIR, UVF and UVR have been preliminarily acquired and interesting results about changes operated by the artist were obtained together with the recovering of figures no more visible because of the strong varnish browning.

Spectroscopic data, collected by means of Raman (i-Raman 785S by BWTEK with a 785 nm laser, and a RaPort by Enspectr operating at 532 nm) and Reflectance Spectroscopy (FORS) on a total of 205 points, allowed identifying the pigments used by the author and in a few points also retouches probably due to restoration works of 1984. The artist palette resulted in a quite classical one in the Venetian area in the XVI century, especially for the presence of verdrigris or copper resinate, typical of the Tintoretto materials, as well as for lakes, here detected in red and purple areas. Some of other pigments, more or less altered, were identified by Raman spectroscopy, such as lead white, cinnabar, lapis lazuli, realgar (together with its polymorph pararealgar, due to the original pigment alteration), and orpiment, while others could be detected only by Reflectance Spectroscopy. This is the case of abovementioned lakes and green pigments, used together with green earths; also red, yellow and brown ochres were identified by FORS, likewise smalt.

The application of two spectroscopic techniques on the same point analysis allowed discovering mixtures or superimpositions of pigments that often could not be revealed by only one of them, thus resulting as a very effective yet non invasive method to obtain a detailed characterization of the artist palette in a totally non invasive way.

In addition, an interactive map of all analyzed points, including all data based on the Raman and FORS mapping realized during the campaign, is currently in progress for valorization purposes.

Archivio di Stato di Venezia, Senato, Deliberazioni, Terra, Reg. 158

Wells Conner Horn S., Discoloration of a Green Pigment in Tintoretto's Allegorical Figure of Spring and Analysis of the Chemical Properties and Stability of Copper Resinate (2016), Chemistry and Biochemistry Thesis & Dissertations, Old Dominion University, Norfolk, Virginia, USA.

O.5 HYPERSPECTRAL, MULTISPECTRAL AND IMAGING TECHNIQUES

O.5 HYPERSPECTRAL, MULTISPECTRAL AND IMAGING TECHNIQUES

ABSTRACT O.5.1

HYPERSPECTRAL IMAGING COMBINED WITH THE CHEMOMETRIC APPROACH IN THE INVESTIGATION OF CULTURAL HERITAGE OBJECTS

Lydzba-Kopczynska B.*[1], Mendys A.[2], Majda A.[3]

Keywords: Hyperspectral imaging, chemometric methods, molecular spectroscopy, plastic, cultural heritage

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It is the most common situation that during forensic and cultural heritage object investigation is not allowed to take samples, that could destroy fragile analysed objects. . Therefore the development of nondestructive and noninvasive analytical procedures, suitable for identification of various materials is of utmost importance. Due to the fact that only the analysis based on noninvasive, complementary techniques could deliver comprehensive information about investigated objects, the application of multifunctional research instrumentation would be very practical and time-saving.

In recent years, the hyperspectral imaging (HSI) technique has gained a great attention in the fields of forensics and cultural heritage analysis. HSI is technique based on reflectance spectroscopy, that enables the acquisition of an image of the object with full spectral information within every pixel of the image, creating a three-dimensional data cube, or a so-called ‘hypercube’. The spectral characteristics included in every pixel can be extracted from an image and analysed externally using statistical methods. The statistical approach, applied directly to the full hypercube, enables classification of different regions and analysis of the spatial distribution of characteristic features.

The hyperspectral imaging (HSI) technique was successfully applied in some forensic investigations of documents written in inks and gel-pen inks which have been subsequently flooded, charred, or treated with biological substances [1]. Studies were performed using a VIS-NIR camera with 1312×1082 pixels resolution, within a spectral range of 400–1000 nm. The performed analysis enabled the enhancement of text on damaged documents as well as the establishment of distinctions between different traces.

Recently the application of HSI technique has been tested in investigation of cultural heritage objects made of synthetics polymers (plastics) and copal resins (amber) from the collection of the National Museum in Krakow. The applicability of a portable HIS system was evaluated in the in situ non-invasive characterization of plastics used in modern and contemporary art. The results obtained during analysis of works by Tadeusz Kantor [2] delivered information about the main polymer used by the artist in the manufacturing process. . The preliminary results of the provenance investigations of objects made of amber, for example the amber altar from XVII century (Fig.1), were satisfying. The provenance identification of various types of amber with the application of Raman and FT-ATR spectroscopy is a well established method [3,4]. The application of HSI system allowed us to scan the whole objects, on the contrary to the mentioned above techniques usually based on point analysis. The identification of the geological origin of amber is possible due to the comparative analysis with the gathered reference data. The developed spectral database based on the fully documented copal resin samples originated from the collection of the Polish Academy of Sciences Museum of the Earth in Warsaw.

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ABSTRACT O.5.2

X-RAY IMAGING FOR CONTEMPORARY ART: "PAOLO E FRANCESCA" BY G. PREVIATI (FERRARA, 1909)

Impallaria A.*[1], Gollini G.[2], Tisato F.[1], Petrucci F.[1], Evangelisti F.[3], Squerzanti S.[3]

Keywords: Radiography, Contemporary Art, scannner, X-rays, image processing

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X-ray radiography provides information about the conservation state, the artistic technique and the presence of pentimenti or paintings underlying the visible one [1]. In recent times, the introduction of organic pigments and artistic materials with low Z elements has limited the use of radiography: the possibility to see something related to the pictorial layer is lower, due to the less radiopacity of the materials employed [2].

However, in some cases, X-ray radiography can be helpful also for modern and contemporary art, not only for restoration purposes. It's the case of "Paolo e Francesca", depicted in 1909 by Gaetano Previati, the most important Italian divisionist artist. The canvas of big dimensions (2.60 x 2.30 m^2) represents the two protagonists embraced in the whirl of the hell, described by Dante in the Canto V of the Divine Comedy. The request for the whole radiography has come for restoration purposes, in order to prepare the work of art for the exhibition in Ferrara in March 2018 [3].

The digital radiography of the painting has been performed directly in situ, by means of the portable radiographic scanner developed at the University of Ferrara [4]. The scanner is composed of two units, one dedicated to the digital detector and one to the X-ray source. It is easy transportable, thanks to its dimensions (1.40 x 1.53 x 0.74 m) and weight (55 kg each unit), and scans an area of 1 m^2. However, it is possible to get the whole size radiography of paintings of any dimension, because there are no mechanical bound between the two units. Furthermore, the radiographic scanner is very adaptable: for "Paolo e Francesca" only the detector stage has been used, placing it in front of a new X-ray tube not yet included in the other stage. The detector moved in order to scan an area (74 x 94 cm^2 or 74 x 63 cm^2) of the canvas, while the X-ray tube was stationary, illuminating the same area.

To collect all the radiographic images needed to reconstruct the whole painting (1137), the acquisition has been divided in 12 squares (108 or 72 images per square): 3 rows and 4 columns. For the acquisition of the images of the central row, the detector unit and the X-ray tube have been lifted.

The digital detector (a CMOS matrix of photodiodes coupled with a scintillator screen, 1024 x 1000 pixel, 96 µm side) allows the immediate control of the images setting the best parameters of exposure. Then, the depth of digitization at 12 bit/pixel involves a huge range of grey levels, which means more information achieved than films or fluorescent screens. Finally, the digital correction of images gives more uniformity in the final radiographic images, eliminating the contribution of the uneven irradiation in different areas of the paintings. Furthermore, no segmentation is visible thanks to the digital stitching between the images.

But the biggest advantage of the digital images is that they can be processed in order to eliminate the contributions of stretchers on canvas paintings, which can make the radiography not easy to read [2] [5]. Having digital images with such a huge range of grey levels allows to choose the best contrast for the wooden areas, similar to the canvas ones, with no loss of information and with no counterfeit. The whole radiography of the Previati's painting has been corrected in this way and the read ability of the radiographic pictorial layer is improved.

The final radiography of "Paolo e Francesca" revealed a lot of pentimenti, through all the scene. Looking at the radiography, it's possible to see the former edition depicted by Previati of "Paolo e Francesca", so reconstructing the evolution of the artist's creativity.

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ABSTRACT O.5.3

IMAGING OF VISIBLE FLUORESCENCE INDUCED BY MULTISPECTRAL UV EXCITATION FOR ORGANIC MATERIALS IDENTIFICATION IN WORKS OF ART

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Keywords: UV fluorescence, UV multispectral imaging, organic artistic materials, binders and varnishes, cultural heritage

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Imaging of visible fluorescence induced by UV lamps (365 nm peak-emission spectrum) is one of the most traditional techniques in the field of conservation and Heritage Science. By irradiating the artwork with an UV lamp, it is possible to acquire the visible fluorescence with a camera and to obtain information about the artwork top layer and state of preservation. Unlike punctual analyses, imaging techniques provide information about the overall artwork surface, representing a guideline for the conservative intervention. UV fluorescence allows to map the varnish, to detect previous restoration interventions and to recognize specific pictorial materials such as red lakes and shellac. Being of easy application, conservators extensively use it before, during and after the intervention.

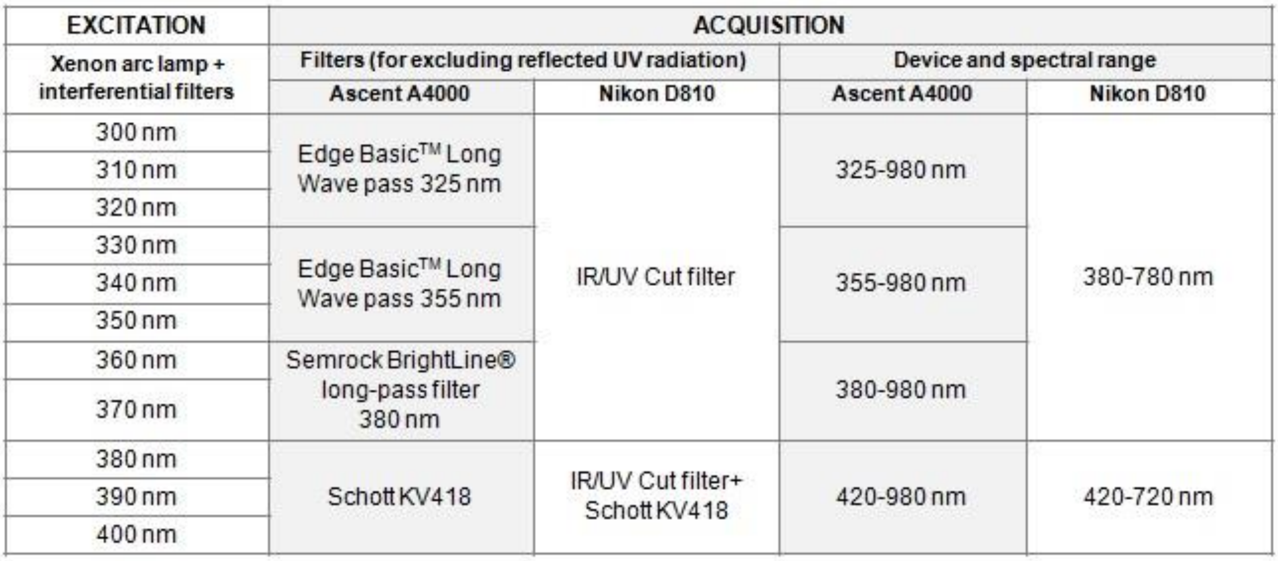
Here we present a new imaging method for discriminating organic materials such as dyes, binders and varnishes commonly used in works of art. The method is based on the acquisition of the fluorescence induced by 11 excitation bands comprised in the 300-400 nm range. The aim is to improve the efficacy of the UV technique in mapping and identifying organic materials maintaining the advantages of the imaging noninvasive techniques. The new method has been tested on beeswax, rabbit glue, gall of ox, turpentine, acrylic resin, boiled linseed oil, discolored linseed oil, cold-pressed linseed oil, walnut oil, poppy oil, egg tempera, dammar, amber resin, Arabic gum, colophony.

The multispectral excitation has been obtained by filtering a xenon lamp with 11 interferential band-pass filters mounted on a wheel in front of the lamp. Bands of excitation have a 10 nm FWHM and transmittance peaks centered at every 10 nm from 300 to 400 nm (Tab. 1).

The acquisition has been carried out with two instruments, comparing advantages and limits of each one: a DSLR Nikon D810 (full frame, modified for extending the CCD sensitivity) with a 50 mm AF Nikkor lens, and a monochromatic Ascent A4000 camera (monochromatic array) with quartz lens. Specific long pass filters have been used for excluding the reflected UV contribution (Tab. 1). Thus, two series of 11 images of fluorescence have been acquired for each mock-up together with a dark and a white reference.

Using ImageJ software, images have been post-processed by subtracting the dark and normalizing to the white and to the specific transmittance of each filter. Comparing the materials fluorescence behaviours to the fluorescence spectra reported in literature, the method has proved to be reliable: fluorescence differences in terms of colour and/or intensity obtained for the different UV excitation bands have shown to be characteristic of each material, indicating the high potentiality of this diagnostic technique and its comparability with spectrofluorometric techniques.

For future applications to real artworks, the method non-invasiveness has been verified by measuring the quantity of UV radiation able to reach the mock-up surface (UNI 10829/1999, artworks preservation).



EXCITATION	ACQUISITION			
Xenon arc lamp + interferential filters	Filters (for excluding reflected UV radiation)		Device and spectral range	
	Ascent A4000	Nikon D810	Ascent A4000	Nikon D810
300 nm	Edge Basic™ Long Wave pass 325 nm	IR/UV Cut filter	325-980 nm	380-780 nm
310 nm				
320 nm				
330 nm	Edge Basic™ Long Wave pass 355 nm		355-980 nm	
340 nm				
350 nm				
360 nm	Semrock BrightLine® long-pass filter 380 nm		380-980 nm	
370 nm				
380 nm	Schott KV418	IR/UV Cut filter+ Schott KV418	420-980 nm	420-720 nm
390 nm				
400 nm				

Table 1. Scheme of the acquisition set-up and filters.

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ABSTRACT O.5.4

MULTISPECTRAL IMAGING FOR CULTURAL HERITAGE: DIAGNOSTIC ANALYSIS ON THE "CRUCIFIXION" PANEL PAINTING IN VITERBO (ITALY)

Pelosi C.[1], Agresti G.[1], Calabrò G.[2], Colantonio C.*[2], Serone G.[3], Rocca A.[4], Gnignera E.[4], Melis M.[5], Cotte P.[6], Apicella S.A.[7], Matteucci C.[7]

Keywords: multispectral imaging, diagnostics, cultural heritage, painting, digital image processing

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This paper describes the results coming from innovative multispectral imaging analysis on the panel painting of "Crucifixion" in the Museo del Colle del Duomo of Viterbo. This 16th century painting owes its relevance to a still discussed attribution to Michelangelo Buonarroti, whose presence in Viterbo area and relationship with Vittoria Colonna and Spirituals (also known as ecclesia viterbensis) are documented in that period.

The clear interest raised by “Crucifixion” panel has led to an extensive diagnostic campaign in which non-invasive investigation such as infrared reflectography (IRR), false colour infrared (IRFC) and ultraviolet fluorescence (UVF) photography, and X-ray fluorescence (XRF) spectroscopy were applied [1].

XRF spectra outlined the presence of lead, calcium and iron in different counts per second (cps), suggesting a probable use of ochres for a coloured ground in the areas with a high number of counts (over 200 cps); for the red pigment the presence of mercury indicates the use of cinnabar/vermilion and the lack of any element associable to blue pigments, such as copper or cobalt, suggests the use ultramarine for the blues. XRF results confirmed IRC photography data indicating that all the pigments detected are compatible with a palette of the first half of 16th century

Recently, multispectral imaging analysis on the Crucifixion was performed with two different technologies: Hypercolorimetric Multispectral Imaging (HMI) by Italian SME “Profilocolore” [2] and Lumiere-Technology, the latter in the framework of cultural agreement with the Conservation Science Laboratory for Cultural Heritage, University of Bologna [3].

HMI is based on a modified camera with specific optical filters for the acquisition of 7 monochromatic high-definition digital images between 300 and 1000 nm, while Lumiere-Technology is a multispectral scanning system with 13 interference accurate filters providing 3.2 billions of data. Both multispectral techniques confirmed results from classic physical diagnostic methods (IRR and UVF) and gave further contribution for the panel readability, which is currently compromised by some pictorial retouching and especially by a hefty layer of a darkened varnish after a previous restoration.

Relevant information about the state of conservation, technique and constitutive materials of the painting was collected and quite interesting details concerning graphic and pictorial evolution’s stages were unveiled. Some anomalies in the painting such as Christ’s face, (which is particularly darkened if not abraded) and the female figure at the foot of the cross, whose clothing seems referable to around 1560’s, suggest a possible remaking of the original composition or maybe later additions.

Other singularities such as the pinky nuance of the Christ’s loincloth (an unusual choice in respect to traditional iconography, suggesting a connection between the liturgical meaning of pink colour as joy in penance and Spirituals’ religious thought emphasizing the centrality of the sacrifice of Christ seen as the prefiguration of Christians’ salvation and therefore of their eternal joy) deserve further investigations in the near future (i.e. Raman spectroscopy and radiographic investigation) after a desirable restoration to remove the altered varnish.

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O.6 MIDDLE AND FAR EAST

O.6 MIDDLE AND FAR EAST

ABSTRACT O.6.1

NEW PERSPECTIVES FOR MOLECULAR SPECTROSCOPY

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Molecular spectroscopy is an important analytical area with wide impact and extent. In this field, Raman and Infrared spectroscopies are powerful and complementary techniques, with an extensive use spanning from biomedical, pharmaceutical and material sciences, to name a few.

In last decades applications related to Art samples have become more and more demanding about several topics, like the possibility to perform in situ analysis of organics and inorganics in an easy way and with a non invasive and non destructive approach and the possibility to get precise information on micro-scale of layered materials when it is possible to have a sample to be analysed into the laboratory.

Moreover, the request to perform imaging in conjunction to the unambiguous molecular identification on micro and macro scale is continuously increasing.

Today all the latest technologies have been applied by Bruker to IR and Raman Spectrometers, both for portable and in lab instrumentations. So, latest innovations will be presented in terms of commercial products, with the state of the art compromise between sensitivity and effective usability. Lot of examples of real applications related to Art samples and to Cultural Heritage will be shown.

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Investigation on a low environmental impact solvent mixture applied to a wooden painted slab, International Journal of Conservation Science, Volume 7, Special Issue 2, 2016: 789-796

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Noninvasive Analysis of Paintings by Mid-infrared Hyperspectral Imaging, Angewandte Chemie, Int. Ed. 2013, 52, 1–5

ABSTRACT O.6.2

NON-INVASIVE NIR-MIR SPECTROSCOPY FOR THE DISCRIMINATION OF ORGANIC DYES AND PIGMENTS IN UKIYO-E PRINTS

Biron C.*[2], **Le Bourdon G.**[1], **Servant L.**[1], **Perez Arantegui J.**[3], **Chapoulie R.**[2], **Floréal D.**[2]

Keywords: non-invasive methods, organic colourants, infrared spectroscopy, ukiyo-e prints, multivariate analyses

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The identification of colourants, especially organic dyes, needs analytical techniques able to discriminate both organic and inorganic compounds used alone or in mixture as found in Japanese ukiyo-e. As these woodblock prints or paintings (produced from the 17th to the late 19th century) are fragile, non-invasive and contactless analyses are needed. Moreover, they are thin and complex artworks. Various compounds are used to prepare them such as inorganic and/or organic pigments, rice starch (binder) and Japanese papers (substrate). Currently, inorganic pigments are mainly identified by well-established techniques, such as Raman or X-ray fluorescence spectroscopies. On the opposite organic matters are more difficult to differentiate. Hyperspectral imaging in the visible range (HSI) and colorimetry are also employed, as the reflectance spectra in the visible region characterise the colour on the print. However, these spectra depend on different parameters: mode of extraction from the plant, pH, fillers to which they are fixed (alum, carbonates), mordants for the indirect colouring agents…

Infrared (IR) spectrometry has proven to be useful to identify inorganic pigments [1,2] as well as organic compounds such as binders [3]. Acquisitions in reflection mode and the use of Fibre Optics Reflectance Spectroscopy in the near infrared range (FORS NIR), used in the cultural heritage field for two decades, allow non-invasive analyses with a fast response time in any geometrical configuration. In addition, infrared spectra provide characteristic molecular signatures and fingerprints that are well suited to discriminate inorganic and organic compounds (pigments, dyes, binders) as well as their mixtures.

The present work focuses on the infrared results obtained on reference printouts prepared with some selected organic colourants that could be found in Japanese prints (safflower, cochineal, dragon's blood, indigo, turmeric or gamboge). A series of 40 samples were made of a single or two colourants (mixed with rice starch) printed on a reference (pure cellulose) were prepared and studied by FORS NIR and mid-infrared spectroscopy (MIR) in reflection mode.

However, some difficulties have been encountered like, for instance, the identification of the specific bands of the pigments in the both infrared ranges due to the overlapping of the paper or the binder signals. To overcome this difficulty, a specific methodology has been developed in order to extract characteristic information related to the pigment. Different post-treatments and a multivariate statistical approach were applied to the raw data acquired on the reference printouts such as derivative transformation of raw spectra, spectral subtraction and Principal Component Analysis (PCA). Spectral subtractions demonstrated to be relevant to extract and to highlight the specific marker bands for some organic pigments such as indigo or gamboge. The application of PCA was effective to cluster the different groups of pigments based on their main absorption bands. The proposed method was applied to a ukiyo-e print belonging to the Federico Torralba collection (Museum of Zaragoza, Spain).

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ABSTRACT O.6.3

COMPARATIVE ANALYSIS OF THE STRATIGRAPHY OF V&A ASIAN LACQUER OBJECTS

Risdonne V.*[1], Burgio L.[1]

Keywords: Lacquer, Cross-section, V&A, Asian art, Optical microscopy

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The Victoria and Albert Museum holds one of the largest and most comprehensive collections of Asian lacquer ware in the world, including objects from Japan, China, Korea, Burma, Vietnam and Thailand, dating from the second century AD to the present day. The museum features a formidable range of types of lacquer that were made for the domestic market and for export across Asia and to Europe, and displays a variety of manufacturing techniques and decorative styles. Individual lacquer items have been displayed in all the V&A Asian galleries as products of a specific culture, but have never been interpreted in the wider context of Asian lacquer manufacture, circulation and consumption, to provide a comparative perspective. The V&A developed a research plan over five or more years, to create a pan-Asian perspective which will examine the production of lacquer ware, in addition to making crucial comparisons between cultures and manufacturing methods across Asia and in a global context, whilst also taking full advantage of the vast and rich collection of lacquer ware at the V&A. This project is known as the "Lustrous Surface" and is informing a temporary display throughout the Museum (which opened in October 2017). The methodology used combines art historical investigations with science-based analysis in order to explore the full spectrum of cultural and technological exchanges taking place in the Asian continent and beyond over the past few centuries. Objects from the Asian collection of the Museum were sampled to be analysed in the V&A Science Section. Visible and ultra-violet optical microscopy, X-ray fluorescence spectroscopy and Raman spectroscopy were carried out in the V&A Science laboratory. Additional samples were taken from most objects and sent to the Getty Conservation Institute in order to be analysed by pyrolysis-Gas Chromatography Mass Spectroscopy. Thirty-two objects were studied in total and more than one hundred and fifty samples were taken in order to study the layer composition of the lacquer coating and decoration. The objects analysed are from China, Korea, Japan and South and South-East Asia. Most were made between the seventeenth and the twentieth centuries and one dated from the thirteenth century. This study aims to initiate the analysis of lacquer objects from different countries in order to collect new evidence and eventually put together a database of lacquer knowledge. It is clear that the 32 objects studied here cannot represent a statistically significant sample. More objects need to be studied and additional analyses need to be undertaken on the objects already studied. This research is the first step in this ambitious project, which will eventually support new exhibitions, publications and in general a better understanding of Asian lacquer.

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ABSTRACT O.6.4

THE MORPHOLOGY AND CRYSTAL STRUCTURES IN PURPLE-GOLD GLAZE OF QING DYNASTY EXCAVATED FROM THE FORBIDDEN CITY

Wei X.*[1], Wang L.[1], Lei Y.[2], Liu Z.[1]

Keywords: Purple-gold glaze, e-Fe_2O_3, Crystallization, Microstructure, The Forbidden City

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Crystallization is an important structural feature in the ancient high temperature glaze. The morphology and crystal structures in the purple-gold glaze of Qianlong years, excavated from the Forbidden City in 2014, were studied by SEM-BES, SEM-EDS, HR-TEM, TEM-SAED, synchrotron radiation 2D-GIXRD and micro-XRF elemental mapping. The metastable ε-Fe_2O_3 crystals with high purity were found and their size is in micron order. The distribution of the crystal over the surface is much uniform and most of their size is about 1-3μm. In some fields with large anorthite crystals, the size of ε-Fe_2O_3 crystals is about 30μm. In the depth direction, the ε-Fe_2O_3 crystals distribute in manner of multilayer and their size in the upper layer is about 100nm from the side view. ε-Fe_2O_3 crystals grow in twin structure and have certain growth orientations. The interesting thing is that, as for the metastable phase, it is very difficult for modern material scientist to synthesize high purity and large size ε-Fe_2O_3 crystals, but it seems somewhat easy for the ancient scientists. It is of great significance to study the crystallization mechanism of ε-Fe_2O_3 not only for understanding the ancient ceramic techniques, but also for drawing lessons from the ancient scientists.

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O.7 CONTEMPORARY ART

O.7 CONTEMPORARY ART

ABSTRACT O.7.1

INVESTIGATING SYNTHETIC POLYMERS IN HERITAGE OBJECTS: THE ROLE OF INNOVATIVE METHODS BASED ON ANALYTICAL PYROLYSIS

Modugno F.*[1], La Nasa J.[1], Biale G.[1], Colombini M.P.[1]

Keywords: Analytical pyrolysis, Modern art, Synthetic polymers, evolved gas analysis - mass spectrometry, Contemporary paint

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Gas chromatography coupled with mass spectrometry (GC/MS) analysis is recognised as one of the more successful analytical techniques to investigate organic materials in artworks and archaeological objects at a molecular level [1].

The chemical knowledge of organic materials often requires the determination of the molecular profile of complex mixtures of organic molecules, that is why the best analytical approaches are based on chromatographic separation and mass spectrometric identification. In some cases the organic materials can be identified on the basis of qualitative analysis, while more often quantitative and semi quantitative information is useful to highlight degradation processes or to distinguish among very similar materials.

Synthetic polymers present as binders, coatings, consolidants or constituents in heritage objects can't be analysed by classical GC/MS methods due to low solubility and non-volatility. In this cases, the coupling of GC/MS with analytical pyrolysis (Py-GC/MS), which allows direct analysis of high molecular weight molecules or macromolecules in a solid micro sample without any pretreatment, has emerged as a fundamental tool. This technique, often considered to be a screening technique is now showing new potentialities in conservation, thanks to the new instrumental developments represented by double shot and multi-shot pyrolysis [2,3].

Although analytical pyrolysis can’t be considered a quantitative technique in the strict sense, it has been optimized in recent years and has been increasingly used to obtain semiquantitative data on a variety of materials.

Recent applications will be shown including the characterisation of different outdoor mural painting By Keith Haring [4] and of the paintings by David Alfaro Siqueiros on the walls of Polyforum in Mexico city, where PY-GC/MS analysis has permitted the identification of mixtures of acryl, alkyd and polyvinyl acetate based paints.

The direct coupling of pyrolysis with mass spectrometry in the analytical asset of evolved gas analysis -MS (EGA-MS) permits to have information on alteration processes of polymers linked to depolymersation or cross-linking phenomena, evaluating the relative amounts of evolved materials during thermal degradation at increasing temperature. The analysis of samples of polyurethane foams constituting 1960s sculptures, including the Tappeto Natura “Disgelo” by Piero Gilardi [5], has permitted to characterize the materials and the degradation phenomena.

As a last example, the use of double shot Py-GC/MS to investigate consolidant material in archeological wood from a Roman shipwreck will be presented, showing the potentiality of the multi-shot pyrolitic technique in investigating complex mixtures of different natural and synthetic polymers.

Figure1. Details from Tappeto Natura “Disgelo” (1968) by Piero Gilardi.

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ABSTRACT O.7.2

UV-VIS-NIR REFLECTANCE SPECTROSCOPY: A REVIEW OF ITS APPLICATION TO THE STUDY OF CONTEMPORARY ART MATERIALS

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Keywords: Contemporary art, FORS, Colored plastic objects, Non-invasive analysis, UV-Vis-NIR spectroscopy

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In the analysis of artworks, reflectance spectroscopy has already been accepted as a common technique by the conservation community due to its non-destructive nature and in situ application. When used as a preliminary investigation tool and complementary method to other micro-invasive/non-destructive techniques, reflectance spectroscopy can support the comprehensive understanding of chemical composition and physical properties of artists' materials. To this end, the use of ultraviolet–visible–near infrared (UV-Vis-NIR) spectrometers coupled with optical fibers for working in the reflectance mode (technique known as Fiber optic reflectance spectroscopy, FORS) is widely reported in the conservation science literature.

Based on the interaction between UV-Vis-NIR radiation and the matter/materials, FORS makes it possible to obtain compositional information on the analyzed materials. Whereas UV-Vis-NIR FORS is a well-established technique in the study of traditional artworks on parchment, paper, textiles, stained glass/windows, wall, canvas and panel paintings, its application to the study of contemporary artists' materials resulted to be more difficult due to the inherent complexity of the contemporary artworks themselves as well as to the availability of a great amount of new synthetic paint products.

The plethora of constituents obtainable by mixing traditional artists' materials with new synthetic and unconventional materials lead to the creation of innovative works of art that are particularly challenging to be studied. The heterogeneity and, in some cases, the incompatibility of the materials used underline the importance of applying analytical techniques on those contemporary artworks with the aim of characterizing their composition. Several works have been already published regarding the use of in situ FORS technique for both studying contemporary art objects and defining their state of conservation. Thus, FORS has already revealed how this technique can support the characterization of the materials used by the artists in order to define the most suitable treatments and conservation strategies. The increasing interests in the application of FORS in this context is testified by some EU, such as POPART [1], or national research projects, such as the Italian COPAC [2]. The number of FORS applications has also increased resulting into the assessment of early degradation stages [3] and efficacy of conservation treatments (e.g. cleaning and consolidation) by also monitoring the color changes [4].

However, a new interesting field of application of FORS is related with the study of colored plastic objects. The identification of the colorants, dyes and pigments, in the UV-Vis visible range has been also extended to plastic-based objects which have become part of our cultural heritage in the form of artworks, design, historical and everyday objects. Although the concentration of the colorants in the polymer matrix is small (0.5%–5%), the use of FORS combined with elemental analysis can provide preliminary information about the organic and/or inorganic nature of the colorants used.

In this work a critical review of some case-studies in contemporary art conservation are presented highlighting the potentialities and limits of FORS in the non-invasive diagnostics of 20th – 21st centuries artworks. In detail, FORS as a preliminary step in a multianalytical protocol for the identification and degradation assessment of contemporary artists' materials is underlined and investigated together with its efficacy.

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ABSTRACT O.7.3

NON-INVASIVE ANALYSES FOR THE IDENTIFICATION OF FLUORESCENT, PHOSPHORESCENT AND CONVENTIONAL PIGMENTS IN “BLACK LIGHT ART” PAINTINGS

Boscacci M.[1], Cavaliere I.[1], Francone S.[2], Guglielmi V.[1], Sali D.[3], Bruni S.*[1]

Keywords: non-invasive analyses, Contemporary art, Black light art, Fluorescent pigments, Phosphorescent pigments

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UV- and daylight-fluorescent pigments, as well as phosphorescent ones, belong to the wide group of the so-called “special effect” colorants and pigments [1]. Fluorescent pigments are complex colouring materials, containing one or more organic fluorescent dyes dissolved in transparent solid carriers such as synthetic resins (e.g. formaldehyde-based ones) [2]. After being used during the Second World War for visual signalling, such pigments began to be employed sporadically by artists around 1944. In Italy the first painter known to exploit the properties of fluorescent pigments was Lucio Fontana in his black light installation Ambiente spaziale a luce nera, exhibited in Milan in 1949. American painters such as Frank Stella in the 1960s and 1970s as well as Peter Halley and Ryan McGinness in more recent years also produced works containing fluorescent colours, to be displayed depending on the circumstances in the daylight or in the dark under UV light. Differently from fluorescent pigments, phosphorescent pigments were developed in the last three decades of the 20th and beginning of the 21st century and are typically inorganic compounds. A real artistic current has recently developed under the name “Black Light Art”, receiving a great contribution from Italian artists like Mario Agrifoglio. In their paintings the so-called “metameric defect” is exploited, giving rise to different colours under visible light and UV light, and fluorescent and phosphorescent pigments are used together with conventional ones. Given the complex choice of materials, the direct identification of pigments in “Black Light Art” paintings requires the combined use of different non-invasive techniques. In the present study, fluorescent, phosphorescent and conventional pigments could be recognized “in situ” in a series of works by Italian painters belonging to the artistic current, by means of a portable Raman spectrophotometer based on the patented SSE technology and of visible-excited spectrofluorimetry and visible reflection spectroscopy. To the best of the authors’ knowledge, this is the first report about the “in situ” identification of such “special effect” pigments in works of art. The complementary spectroscopic techniques allowed to recognize synthetic organic pigments such as phthalocyanine blue (PB15) and indanthrone blue (PB60), phthalocyanine green (PG7), perinone orange (PO43) and benzimidazolone orange (PO6), pyrrole red (PR254), as well as the inorganic yellow pigment bismuth vanadate $BiVO_4$. At the same time, rhodamine-based red fluorescent pigments were identified together with a yellow one based on the coumarin dye solvent yellow 160 : 1 and a benzoxazole optical brightener for white. Inorganic blue and green phosphorescent pigments were identified as, respectively, strontium magnesium pyrosilicate $Sr_2MgSi_2O_7$ and zinc sulphide ZnS.

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ABSTRACT O.7.4

ALUMINUM-COATED SERS SUBSTRATES FOR THE DETECTION OF DETERIORATION PRODUCTS IN PLASTIC ARTWORKS

Lazzari M.*[1], Gomez M.[1], Reggio D.[1]

Keywords: SERS, Contemporary artworks, Plastics, Polymer ageing, oxidation

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Plastic preservation is a challenge for scientists and conservators. In fact, numerous contemporary art collections and design objects comprise extensive amounts of synthetic and natural polymeric materials, which are intrinsically perishable. Almost any collections containing polymeric artefacts, either as objects in their own or as a part of a more complex assembly, have to face serious problems of deterioration and restoration [1,2].

Material-based solutions for the rapid and reliable identification of degradation products are being investigated within the European Commission Horizon 2020 project “Nanomaterials for the restoration of works of art”. Within this presentation, we focus on the introductory results of our investigations on the fabrication of surface enhanced Raman spectroscopy (SERS)-active substrates for the detection of low molecular weight degradation products of plastics, herewith considered as early markers of deterioration of artworks. Macroscopically, the deterioration of plastic objects as an effect of ageing may consist in a series of variations such as colour and gloss changes, loss of transparency and mechanical properties, which are related to molecular and structural changes often due to oxidation processes. Ageing products have functional groups that were not present in the pristine material, and eventually have molecular weights far different from the initial ones, up to the point that may have molecular weight in the range 200-1000 (i.e. the so-called low molecular weight degradation products) or even be volatile (often called volatile organic compounds, VOCs).

SERS is a very powerful technique in which the Raman scattering of molecules is enhanced by several orders of magnitude due to their adsorption to plasmonic metal surfaces or nanostructures, which allows obtaining Raman spectra with very low amount of substances [3]. In particular, we used especially fabricated Al-coated nanostructured substrates prepared by UV cured nanoimprint lithography made of a tetrafunctional urethane methacrylate perfluoropolyether [4] or commercial hybrid materials, followed by Al deposition by thermal evaporation [5]. The substrates have an enhancement factor of around 1x107, as determined for rhodamine 6G [6], and were validated against natural media and reference polymers submitted to artificial accelerated photo-ageing.

We show the results concerning a two-steps sampling strategy and the identification of low molecular weight degradation products from, e.g., artificially aged reference poliisoprene, acrylonitrile-butadiene-styrene copolymer and poly(vinyl acetate), and naturally aged polymers from contemporary artworks. In general, the presence of molecules containing different oxygen containing groups is observed, together with the presence of different ratios of the groups present in the pristine polymer. Their exact chemical nature is also revealed by complementary analytical techniques such as FTIR spectroscopy, size exclusion chromatography and gas chromatography coupled with mass spectrometry.

Acknowledgements. This work was supported by the European Union (CORDIS) Project NANORESTART (H2020-NMP-21-2014/646063).

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O.8 MUSEUMS AND DATABASES

O.8 MUSEUMS AND DATABASES

ABSTRACT O.8.1

THE INTERNATIONAL MULTIDISCIPLINARY CONSERVATION PROJECT OF THE METROPOLITAN CHURCH OF AMFISSA (GREECE): THE MURAL PAINTINGS OF SPYROS PAPALOUKAS

Tavlaridis G.*[8], Borrelli E.[1], Bortot A.[2], Casoli A.[3], Farmakalidou E.V.[6], Giuffrè E.[4], Isca C.[3], Karatasios I.[6], Kilikoglou V.[5], Photos – Jones E.[9], Pizzolo F.[4], Sartorato N.[7]

Keywords: Mural Painting, Conservation Project, GC/MS analysis, A “secco” Painting, Pigments

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The Holy Mary Annunciation Metropolitan Church of the city of Amfissa (Greece) was built in the period between 1859–1869 over the remains of the floor of an Paleochristian Basilica. The interior of the building was entirely decorated (1.500 m^2 surface) by the Greek artist Spyros Papaloukas between 1926 and 1931. It’s a work with the pictorial and aesthetic characteristics very innovative compared to the Byzantine and post-Byzantine painting[1]. Nowadays the conservation state of the painted surface presents very precarious conditions. Between 2011 – 2012 an international multidisciplinary conservation project of the Church was carried out. This project is divided in two parts: the conservation study of the mural paintings and the architectural, structural and electromechanical project of the building. Regarding the study of the mural paintings, initially a preliminary investigations was done to evaluate the conservation state and to study the pictorial technique of the painting. Particularly, the 3D geometrical survey by laser scanning of the mural painting was performed including the graphical representation of the deterioration2. For the detection of the detachments electromagnetic and thermographic investigations were carried out, as well as the study of indoor microclimate behavior of the building. The organic mural painting binding media, the pigments, the plaster and the deterioration materials of the Metropolitan Church were characterized. From the on-site observations and the GC/MS analytical data, it was noted that the particularity of these artifact is that the entire surface of the mural painting was painted by a “secco” technique, using only organic binding media. This is one of the few worldwide examples so that a wide surface was painted “a secco”. The conservation study of the mural paintings is based on the results of the preliminary investigation. In the laboratory and on site tests were carried out regarding the consolidation and the cleaning of the painting. Moreover, special mortars have studied and tested that will used during restoration.

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ABSTRACT O.8.2

TOWARDS A TUSCANY ANCIENT CERAMIC DATABASE: THE “OPEN FABRICS” PROJECT

Fatighenti B.[1], Raneri S.*[2], Gabriele M.[3], Lezzerini M.[2], Cantini F.[1]

Keywords: Tuscany, archaeology, archaeometry, ceramics, open database

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The identification of the provenance of ancient potteries as well the raw materials employed in different workshops is one of the main aim of the archeoceramic studies, involving both archaeology and archaeometry disciplines. In these framework, the correct evaluation of these aspects, cannot disregards the availability of reference groups having certain provenance and clays database; the experimental archaeology can also provide fundamental insights, producing laboratory samples by using known raw materials to verify feature of ceramics made with reference clayey sediments.

The archaeological and archaeometric studies of ancient ceramics and laboratory samples provide, usually, a large number of dataset, including typological and stylistically analysis, as well the results of petrographic, mineralogical and chemical studies. However, all these dataare mostly published in single scientific contributes, sometime providing only some examples and/or partial results, so that the comparison between a new set of archaeological findings and already studied materials is quite difficult.

In the last ten years, archaeologists and archaeometrists had proposed some tentative of centralization of the results, for a easy and quickly comparisons of ceramic materials on regional or national scale, by using geomatic tools [1-5]. In this streamline is framed the “Open Fabrics” Project [6], finalized to collect, for the first time, in a unique free and open database, a wide unpublished dataset about ancient ceramics from numerous archaeological sites in Tuscany with dating ranging from Late Antiquity to Middle Age; the database take also advantage from data about laboratory samples produced by experimental archaeology routines by using clays samples from the most suitable local geological sources to manufacture ceramic materials.

The database, currently under construction, is managed by using Microsoft Access database and it is characterized by a great flexibility, being expandable for its implementation with multidisciplinary studies. Following the principle of GIS tools, the access to the database will allow to the usera easily comparison of studied ceramics by queries regarding both archaeological and archaeometric features. Each target (i.e. archaeological artifact) included in the database is geo-referenced, allowing a global overview on the distribution of a certain archaeological/fabric type over the regional context; it is also provided by both typological description and results of archaeometric analysis (fabric classification, mineralogical and chemical composition by X-ray fluorescence analysis). Apart from ceramic objects, the database includes as target also clays sources, each of them providing geological and geochemical characterization and geolocalized in respect to a geological map level.

In this contribute, we propose the architecture of the database and its working principle, along with some data already loaded in.

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ABSTRACT O.8.3

CREATING THE FORGOTTEN AND BIGGEST PICASSO'S ARTISTIC PROJECT IN A NEW VIRTUAL WORLD

Oles K.*[1]

Keywords: Picasso, modern art and architecture, concrete monumental sculpture, digital art history, virtual reality

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Since the beginning of this year I have uncovered plans for a lost Picasso masterpiece in the archives of the University of South Florida (USF) Library*. "The Bust of a Woman" is one of Picasso's biggest and last artistic project, yet never completed, which was to be erected at USF campus in Tampa. The sculpture originally created in small scale as Pablo Picasso's abstract cutout masterpiece was planned to become the 100-foot most towering sculpture in Maestro's oeuvre and the world's tallest modern art piece. The abandoned colossal idea left behind only a small-scale bozzetto, visualization project, correspondence, newspaper clippings, and two photomontages** to which I have responded by means of 3D modeling and virtual reality.

The aim of my paper is to present that although, the project was never completed, as a researcher, using new technologies, I am going to refer and continue the Picasso USF initiative, after 50 years. The aim of my paper is to present the digital workflow of creating the virtual world in which the sculpture was to be constructed and to identify the visual interactions, which the art piece was expected to create. This would allow for preserving Picasso's heritage in Maestro's most demanded way – as visual drama – the intertwinement of art piece and surrounding landscape.

At USF surroundings for the sculpture were planned as an Art and Visitor Center representing a spectacular and extraordinary modern architecture with very progressive construction solutions at that time. The art complex was strictly connected and dedicated to the dominant sculpture, creating the phenomenal visual frame for the gargantuan monument. Several techniques were employed to create the initial version of the virtual world for the sculpture. Firstly, historic records were collected and interpreted. Secondly, image-based modelling of the bozzetto allowed for the creation of a 3D model of the projected art piece.

Although, the construction documentation is lost, thanks to the new modeling and designing technologies as well as elaborated analyses of historic records, the Art and Visitor Center were virtually re-created. Next,

airborne laser scanning data were used to generate high quality Digital Surface Models of contemporary campus. Additionally, several sets of historic aerial photography were investigated and analyze. These datasets were acquired in different flight campaigns using photogrametry and Terresial Laser Scanning, and thus, it was possible to track the landscape changes caused by the USF development. Structure-from-Motion and Multi-View Stereo algorithms were used to reproduce temporarily diverse landscapes, including the one before the agreement between Picasso and the university, modelled versions of the historic campus with the implemented sculpture, as well as a present-day USF area.

Even though, the project was never fully materialized, the proposed digital workflow, which will be presented during my presentation, allowed for a peculiar realization of the artist's idea. Therefore, his expectations to create a monumental art piece and thus to develop a meaningful architectural landscape were somehow met. The meeting space is a virtual reality. However, unlike most traditional approaches, I do not uproot the sculptures from their precisely designed space. In this sense, the fundamental relation – between the monuments and the urban and rural landscapes in which the masterpieces situates in – will be emphasized through the digital lens. Despite the virtual character of the obtained results, the confrontation of different datasets and modeling techniques evokes the intangible cultural heritage of modern history. Manifested in his art, Picasso's worldview represented some of the essential concepts of his time, and the presented digital approach will share his ideas in a new, virtual world.

* USF Special Collections Library

** USF Archive

ABSTRACT O.8.4

A DECISION SUPPORT SYSTEM FOR PREVENTIVE CONSERVATION: FROM MEASUREMENTS TOWARDS DECISION MAKING

Schalm O.*[1], Anaf W.[2], Leyva Pernia D.[3], Callier J.[4]

Keywords: preventive conservation, monitoring, indoor air quality, visualization, mitigation actions

[1]University of Antwerp, Conservation Studies ~ Antwerp ~ Belgium, [2]War Heritage Institute ~ Brussels ~ Belgium, [3]University of Antwerp, Department of Mathematics, Computer Science ~ Antwerp ~ Belgium, [4]Royal Museums of Fine Arts of Belgium ~ Brussels ~ Belgium

An important goal of heritage caretakers is to maximize the life span of their collections and this goal must be realized with a restricted budget. With the given budgets and considering that some collections consist of more than a million objects, it is very hard to take care of each object individually. An alternative solution is preventive conservation where the preservation conditions are systematically improved in order to lower the average degradation rate of the collection. To improve the preservation conditions, mitigation actions should be implemented. However, for heritage caretakers it is difficult to select the appropriate mitigation actions that will extend the lifespan of the collection (without introducing unexpected risks) at the lowest possible cost. Decisions are often supported by temperature and relative humidity measurements. However, such measurements are limited and many events and hazards remain unidentified.

We present an innovative and user-friendly monitoring device that simultaneously and continuously measures (1) environmental parameters and (2) material behaviour. An extended combination of off-the-shelf sensors for temperature, relative humidity, air pressure, air speed, CO_2, NO_2, O_3 and particulate matter are connected to a multipurpose datalogger [1,2]. In-house developed sensors for the shrinkage and expansion behaviour of wood, as well as sensors for metal corrosion rates are connected to the same datalogger. In addition, a motion sensor is connected because human activity can be a factor of influence on several (environmental) parameters. The monitoring of more parameters shows the identification of a wider range of events and hazards.

Besides the innovative monitoring device, we also present a new method that converts the multiple measurements into environmental appropriateness judgements [3]. The method estimates how well the environment is performing by considering a specific material, specific parameters and corresponding material dependent target values. All these parameters are combined by using a weighted Euclidean distance into a single indoor air quality (IAQ) index. The evolution of the IAQ-index is visualized using colour codes. The advantage of this visualization is that decision makers with limited environmental expertise are also able to identify harmful moments and estimate the overall situation.

Finally, it is now possible to evaluate the efficiency of mitigation actions, by comparing the IAQ-index before and after a mitigation action has been performed. It allows heritage caretakers to evaluate the mitigation action in an objective way and to further optimize it if needed.

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ABSTRACT O.8.5

OPTIMIZATION OF THE OFF-GASSING ANALYSIS OF COMPLEX MUSEUM OBJECTS. CASE STUDY: THE RUBY SLIPPERS FROM THE WIZARD OF OZ

Álvarez Martín A.*[1], Kavich G.[1]

Keywords: Headspace-solid phase microextraction, Gas chromatography, Volatile organic compounds, Heritage preservation, Museum objects

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Thanks to a very successful Kickstarter campaign, the Smithsonian Institution’s National Museum of American History was able to pursue conservation efforts to preserve the Ruby Slippers from the movie The Wizard of Oz (1939) [1]. This will result with the design of a display case achieving optimal environmental conditions that will ensure millions of people can enjoy them for years to come.

In a preliminary study carried out by the Museum Conservation Institute, more than fifteen different materials constituting the slippers were identified. The wide range of materials complicates the conservation strategy, e.g. special care must be taken since cellulose nitrate, highly sensitive to degradation, is the main component of the red lacquer applied on the sequins.

Solid Phase Microextraction (SPME) is a fast, reliable and non-destructive sampling technique used to evaluate the formation of volatile organic compounds (VOCs) in museum collections. In the last decade, numerous studies have investigated the off-gassing of different types of single matrices (plastics, paper, wax, etc.), inside display cases and storage facilities, by means of SPME/GC-MS [2]. The goal of this project is to formulate a protocol for the analysis of a complex object composed of a large number of different materials.

In order to find an adequate sampling method that yields a broad range of the substances emitted by the Ruby Slippers, two types of SPME fibers with different coating materials were tested, and the sampling conditions were optimized.

Each slipper was placed in a 5 L Tedlar® bag, and SPME fibers were exposed for 2, 24 and 96 h. Measurements were taken in triplicate over a period of six weeks (i) to assess the reliability of the sealed bags, (ii) to study the variability between the measurements and (iii) to optimize the sampling time versus the detected emissions from the object. The identification of some VOCs detected during the analyses were confirmed by comparison of their retention time with a certified standard solution.

A large number of acids, alcohols, aldehydes, ketones, and other compounds were detected such as acetic acid, furfural, styrene, 2-ethyl-1-hexanol, camphor and naphthalene. Acetic acid, which can affect the preservation of historical objects [3] was identified in both slippers. Naphthalene, heavily present, may be associated with its intensive use in the museum collections as pesticide during the 20th century [4].

The detection of several compounds depends on the sampling time; at short exposure times these compounds showed more variability. This could be due to the fact that the adsorption equilibrium between the headspace and the SPME fiber has not been reached yet. On the other hand, longer exposures and thus possible saturation of the fiber renders the identification of some volatiles an arduous task. Optimum conditions were found at 24 and 96 h of exposure. The analysis of the VOCs emitted by The Ruby Slippers leads to the identification of analytes released by specific materials, previous conservation treatments and past storage conditions. Not all the identified compounds necessarily endanger integrity of the object. However, since acetic acid can accelerate the degradation of cellulose nitrate, the final display case will need to adequately remove this VOC.

Acknowledgements

The present research has received funding from the Kickstarter campaign 'Keep them Ruby' and the MCI (Smithsonian Institution). The authors express their gratitude to R. Barden, Supervisory Conservator at NMAH Preservation Services, and D. Wallace, NMAH Object Conservator for giving access to the object, and M. Ormsby for invaluable advices.

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ABSTRACT O.8.6

THE INTERDISCIPLINARY IDEAL: THE NETHERLANDS INSTITUTE FOR CONSERVATION+ART+SCIENCE+

Rous B.*[1], Van Langh R.[1]

Keywords: interdisciplinary research, conservation, technical art history, diagnostics, material dynamics

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This paper showcases a functioning research centre bringing together various research disciplines involved in cultural heritage research. The Netherlands Institute for Conservation+Art+Science+ (NICAS) brings together the humanities (especially the disciplines of art history, history, and conservation), the natural sciences (chemistry and physics) and data science (computer science and mathematics). NICAS seeks to integrate these disciplines in a lasting framework that is geared towards solving cultural heritage research problems, resulting in a research community that operates across and beyond disciplinary boundaries.

Research within NICAS focuses on three interlinked focus areas: technical art history (how was the object made and what did it look like?), material dynamics (how did the object change and how will it change?), conservation (what can and should we do about change?). Advanced diagnostics and data science support these focus areas: how can we detect and visualise and model what is taking place in objects? Ideally, research projects bring together as many disciplines as possible, looking at objects and processes from complementary angles. The aim of NICAS is to fully understand cultural heritage objects, with an emphasis on the making process, original appearance, the biography of the object and the processes of ageing and/or degradation.

Research projects will produce fundamental knowledge on hitherto little understood processes of change. However, NICAS also seeks to find practical applications of this knowledge in the heritage field in the form of guidelines and best practices. An important goal is to find the safest ways of presenting the objects to the public and heighten public appreciation for the object as a dynamic material entity, and to optimally preserve cultural heritage objects for future generations by slowing down degradation processes and, when possible and desirable, reversing harmful effects of change over time.

NICAS actively disseminates knowledge among professionals working within the cultural heritage field as well as the general public, and in close cooperation with universities educate and train the new generation of cultural heritage care professionals.

O.9 TEXTILE AND PAPER

O.9 TEXTILE AND PAPER

ABSTRACT O.9.1

RESEARCH ON THE TRADITIONAL TECHNOLOGY OF PATTERNED WALLPAPER OF LODGE OF BAMBOO FRAGRANCE(ZHUXIANG GUAN) IN PALACE MUSEUM

Ma Y.*[1], Zhao C.[1], Leiyong L.[1]

Keywords: wallpaper, pigment, Qing dynasty, architecture, Forbidden City

[1]Palace Museum ~ Beijing ~ China

Located in the fourth yard of the garden of Ningshou Palace (Qianlong Garden), Lodge of Bamboo Fragrance (Zhuxiang guan) was built in the 37th year (1772) of the Qianlong Period of the Qing dynasty, in imatation of Bilin guan in Jianfu Palace. Patterned wallpaper was found on the ceiling of south room of the second floor.

"Bao Hu" is one of the eight famous traditional crafts in late Qing dynasty. The practice is related to the weather and the architechtural features of Beijing. The main functions of mounting paper on walls are to keep the room warm, to prevent dust and to make the room brighter. A large amount of wallpaper was used in the inner decoration of buildings in the forbidden city, including painted and printed wallpaper. The printed wallpaper was usually colorful with a continuous pattern.

The wallpaper found in Zhuxiang guan has six layers. Chinese traditional patterns were printed on from the first layer (the innermost layer) to the fifth layer. The pattern of the outmost layer is rose, which is rare in the Forbidden city.

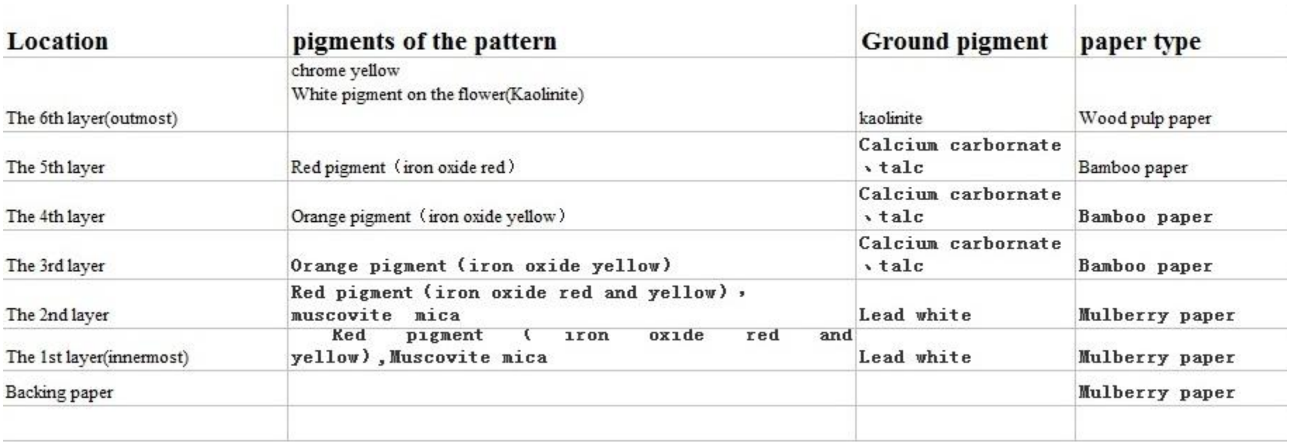
Wang Zhongjie, specilized in architecture, gave a research on the traditional craft-"Biao hu"[1]. The conservation project team of Juanqin Zhai in the Palace Museum conducted an investigation and conservation treatment on the printed wallpapers. The fiber and the inorganic elements of the pigments on three layers of wallpapers were analysed. Some wallpapers were partially removed and remounted[2].Yang Hong has conducted a systematic study on the development of traditional Chinese wallpapers[3]. Jiang Boguang gave an introduction on the materials used in the wallpaper [4]. Ma Yue gave a systematic research on the techniques and material composition of the wallpaper in Yu cuixuan[5].

In order to investigate the techniques and composition of the materials used, samples were collected from on the ceiling of south room of the second floor in Zhuxian guan. Analysis were then carried out, including cross section studied with a polarized light microscope (PLM) using visible and ultraviolet light, and staining. Elements mapping of each layer were done by Micro X-ray Fluorescence. The binding media materials were analyzed by Fourier transform infrared microscopy (micro-FTIR) and pyrolysis-gas chromatography-mass spectrometer (PY-GC-MS). The morphology of the plant fiber of the backing paper was examined with PLM in order to deduce the paper type and its processing technique.

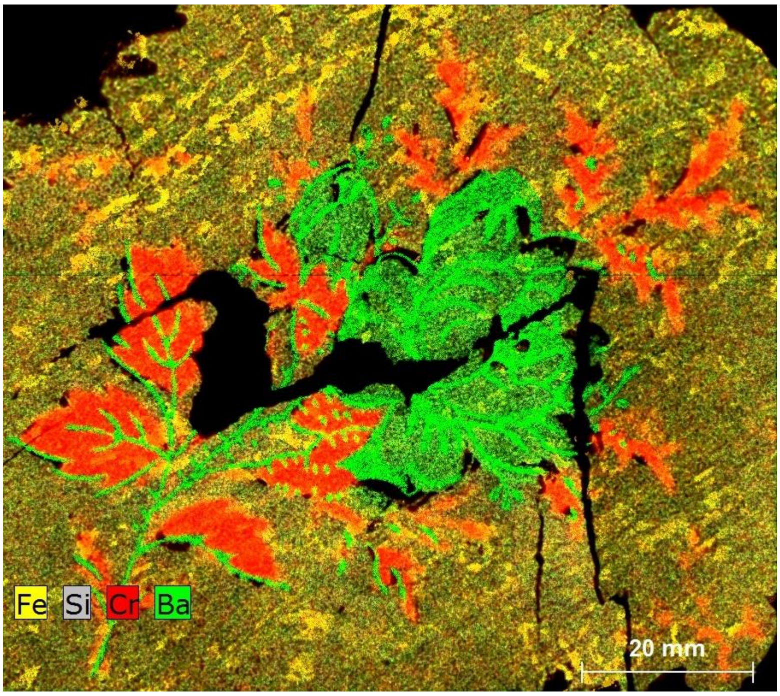
The results shows that different materials and technique were used on each layers(Table 1).Comparing with other layers,the outmost layer is unique (fig.1). Wood pulp paper and chrome yellow were not common used in Qing dynasty, on the other hand,the rose pattern was also not traditional in ancient China. There may exist communication between China and the West. On other five layers, the pigments and paper were

often used in Qing dynasty.

This article provides analytical evidence for the manufacturing techniques of wallpaper in different periods of the Qing dynasty,comparing with literature on manufacturing techniques, and to provide scientific support for the conservation of wallpapers.



Location	pigments of the pattern	Ground pigment	paper type
The 6th layer(outmost)	chrome yellow White pigment on the flower(Kaolinite)	kaolinite	Wood pulp paper
The 5th layer	Red pigment（iron oxide red）	Calcium carbornate 、talc	Bamboo paper
The 4th layer	Orange pigment（iron oxide yellow）	Calcium carbornate 、talc	Bamboo paper
The 3rd layer	Orange pigment（iron oxide yellow）	Calcium carbornate 、talc	Bamboo paper
The 2nd layer	Red pigment（iron oxide red and yellow），muscovite mica	Lead white	Mulberry paper
The 1st layer(innermost)	Red pigment （ iron oxide red and yellow）,Muscovite mica	Lead white	Mulberry paper
Backing paper			Mulberry paper



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ABSTRACT O.9.2

ANALYTICAL EVALUATION OF THE USEFULNESS OF NATURAL STARCHES AS ADHESIVES IN PAPER RESTORATION: KUDZU AS ALTERNATIVE

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Keywords: Kudzu, Adhesive, Starch, Paper, Restoration

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In recent years the use of natural starches as paper adhesives has been increased especially considering the environment and restorers' health. Wheat, rice and corn starches are the most popular ones; however, their most important disadvantage is the amount of starch obtained from them (between 30-80%). In this regard, the Kudzu starch, which comes from the Pueraria lobata plant, after being extracted and processed by natural way can be almost 100% pure but it is unknown in the restoration and conservation field. Thus, this starch seems to be a viable alternative to traditional starches.

Taking all of these into account, the aim of this work was to demonstrate the usefulness of the Kudzu starch as alternative adhesive in the paper restoration. For this purpose, the analytical characterization of handcrafted Kudzu starch was carried out by different techniques, as well as, the comparison between it and the already used starches in restoration (wheat, corn and rice from Lineco) and purified starches (wheat, corn and rice starches from Sigma-Aldrich).

First, the characterization of the selected starches was carried out by spectroscopic techniques to compare their compositions and therefore, their qualities and purities. In this sense, an innoRam spectrometer (785 nm laser excitation) from B&WTEKINC and a M4 Tornado (Bruker Nano GmbH) energy dispersive X-ray fluorescence (EDXRF) spectrometer were used. The EDXRF analyses showed some traces of iron in the Kudzu starch. Anyway, compared with theoretically pure starches these traces were always below in Kudzu starch, showing that it is more pure than the industrially purified starches.

Once confirmed the quality of the Kudzu starch, an accelerated aging test was carried out by a camera SOLARBOX HR 1500e according to ISO 9142:2003. The evaluation of the color variation was carried out using a GretaMacbeth ColorEye XTH spectrophotometer. Regarding the tendency to yellowing, the ageing test revealed that kudzu is a viable alternative having the same or even better long-term stability than the other starches. Specifically, the Kudzu starch showed the same tendency as wheat starch and fewer tendencies than the other ones to yellowing.

Moreover, it was carried out an adhesive strength test (T-peel) according to ASTM D1876 to evaluate the adhesive capacity of Kudzu. The test demonstrated that the adhesiveness of the Kudzu starch was similar to the studied starches, maintaining its flexibility.

Finally, the evaluation of the reversibility was also carried out by the use of vapor and water to remove the starches. A scanning electron microscope EVO®40 from Carl Zeiss NTS GmbH coupled to an X-Max X-ray energy dispersion spectrometer from Oxford Instruments (SEM-EDX) was used to determinate the possible traces of the paste in the surface of the samples after their removal. The SEM images revealed that the reversibility of the Kudzu was satisfactory and the observed residues in the sample were even less than in other starches.

Therefore, this work points out that Kudzu is a very good alternative for natural starches being more

efficient than other starches in its characteristics and quality.

This project has been funded by the MADyLIN project (ref BIA2017-87063-P) funded by the Spanish Ministry of Economy and Competitiveness (MINECO) and the European Regional Development Fund (FEDER).

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ABSTRACT O.9.3

NOVEL CANVAS WEAVE ANALYSIS OF REMBRANDT'S SAUL AND DAVID AT THE MAURITSHUIS

Pottasch C.*[1], Smelt S.[2], Erdmann R.[2]

Keywords: Rembrandt, restoration history, automated canvas analysis, primary and secondary cusping, original format

[1]Mauritshuis ~ Den Haag ~ Netherlands, [2]Rijksmuseum ~ Amsterdam ~ Netherlands

Recent research showed that Rembrandts' painting Saul and David had a turbulent restoration history before entering the collection of the Mauritshuis in The Hague (The Netherlands). At a unknown moment the painting was cut into two separate pieces: one with the figure of Saul, and the other with David playing the harp. These parts were later put together again, and a fragment of another 17th century painting of c. 50 x 55 cm, was inserted in the top right corner. New automated canvas analysis techniques using prints from the original x-ray negatives scanned at high resolution made a plausible reconstruction of the original size of the canvas possible.

Historical background

The restoration history of Saul and David had immense implications for the appearance and format of the painting: the original top right corner is missing, very damaged paint layers, and an unusual canvas join. Manual thread counting performed by Petria Noble (then Maurtishuis) and Michiel Franken (Netherlandish Institute for Art History) in 2007, indicated that the linen of the two rejoined pieces of canvas match. Their research in collaboration with Don and Rick Johnson of the Thread Count Automation Project at Cornell University showed an added strip of canvas under David originated from the original painting, but was relocated during a previous treatment and strips along the top and bottom were cut from the non-original insert in the top right corner. From the weave angle maps they concluded that: "the picture has been reduced, possibly as much as 18 cm along the vertical join between the two figures, and by a similar amount at the bottom edge as well, suggesting a possible original format of c. 145 x 180 cm^2, as compared to the present format of c. 130 x 164 cm^2."

New research possibilities

In September 2014, Carol Pottasch and Susan Smelt took over the restoration of the painting and continued the research of the Saul and David. The removal of over paint made it clear that only about 2 cm is missing between the two pieces of canvas. Newly scanned x-rays at 1200 dpi allowed Robert Erdmann to precisely stitch the x-rays for the first time.

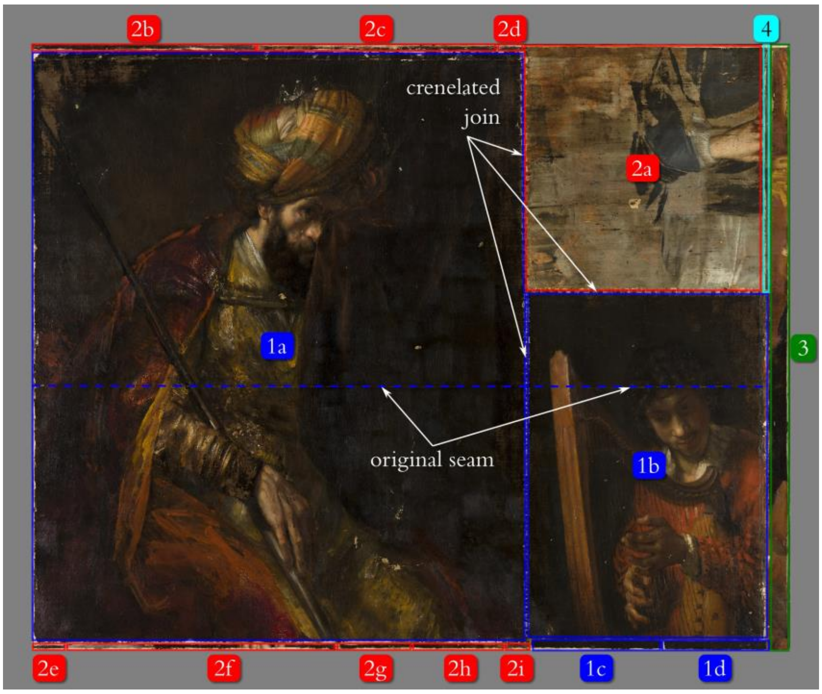
Recent work under his supervision on automated canvas analysis conveys two benefits over the past techniques: (1) they can be used to process canvases with very little regularity in the placement of threads

(2) they are able to resolve minute and subtle details where the other techniques cannot. Whole-painting maps of these spacing's show distinctive patterns arising from manufacturing defects, so that spacing pattern matches between canvases can reveal that they were cut from the same bolt of cloth, providing valuable art-historical information. Maps of the angles of the threads relative to the horizontal or vertical reveal primary and secondary cusping and so-called "weft snakes", suggesting the possibility to gain further insight about studio practice, format modifications, past conservation treatments, and the current stress state present in the canvas.

In the case of Saul and David we could determine that the top and bottom are connected at the selvedge, as the warp runs vertical and that the pieces have an opposite direction to each other. Also, we were able to identify not only the cusping of the original stretching of the canvas, but also cusping related to much later stretching is visible.

Conclusion

After removal of overpaint, it was found that the painting consisted of no less than fifteen separate pieces of canvas. Two small strips belong to the original painting by Rembrandt. Eight small strips and a bigger piece belong to the fragment of the copy after Anthony van Dyck. Of two other strips the origin is unknown. This research, in combination with the treatment of Rembrandt's Saul and David painting, also shows the direction in which it had been woven and only 2 cm are missing between the figures of Saul and David. We can reconstruct the width and propose that the original format of the painting was already adapted quite early in the paintings existence.



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ABSTRACT O.9.4

DUST DEPOSITION AND EVOLUTION ON TEXTILE IN INDOOR CULTURAL HERITAGE

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Keywords: dust deposition, textile, indoor air quality, particulate matter, artificial ageing

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Dust deposition is a preservation concern in museums and historic monuments (1, 2), especially for textiles whose cleaning is delicate. In the study of this phenomenon, assessing the chemical composition of both the deposited particulate matter and the aerosols is imperative. However, once on the fibers, the deposit is not inert and its evolution in indoor environment has to be studied.

To address these challenges, three contrasted sites were selected: the Cluny Museum (Paris, urban), the Château de Fontainebleau (semi-rural) and the Villa Kérylos (Beaulieu-sur-Mer, marine). Each monument was equipped with various sensors and collectors to monitor the environmental conditions and evaluate the dust deposition rate and degree of textile alteration.

Thus, a comprehensive characterization of each environment was conducted. Microclimatic conditions (indoor temperature and relative humidity) and main gaseous pollutants (CH_2O_2, NO_2, O_3) were monitored. The Particulate Matter (PM) size-distribution was measured with a Mini-WRAS®, both when the museums were crowded and empty. The chemical composition of PM and Deposited PM (DPM) was determined through SEM-EDS and ion chromatography, thus allowing determination of the main PM sources. The particle deposition rate was evaluated after 2, 6, and 9 months on inert glass coupons exposed near the artifacts.

These in-situ experiments allowed describing each environment precisely and provided guidelines for the selection of alteration parameters to be retained in textile artificial-aging experiments. These experiments were performed in CIME (3), an environmental chamber specifically designed to reproduce dry deposition on cultural heritage materials and study their interactions with gaseous pollutants.

The deposition of marine (halite), anthropogenic (soot and mascagnite), terrigenous (calcite and clay) and mixed (all of the above) particles matching the composition of the DPM found at each site was thus reproduced on a variety (cotton, wool, silk) of textiles samples. In addition, textile samples were also displayed at each site to collect a layer of real dust. Then, the samples soiled in-situ or in the chamber were exposed to O_3, SO_2 and CO_2 in CIME to age them artificially. All these experiments were performed at controlled temperature (20°C) and relative humidity (75%).

SEM-EDS observations before and after ageing showed that reactions already occurred during deposition in the artificial dust, leading to the formation of spike-like thenardite efflorescences. After ageing, glauberite and gypsum had formed, sometimes between the textile fibers. These needle-like growths could be a problem when removed with vacuum cleaning. However, no structural damage was noticeable on the fibers at this alteration stage.

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ABSTRACT O.9.5
METHODOLOGY DEVELOPMENT FOR IDENTIFICATION OF NATURAL TEXTILE DYES

Peets P.*[1], Vahur S.[1], Kruve-Viil A.[1], Haljasorg T.[1], Herodes K.[1], Leito I.[1]

Keywords: textile dyes, FT-ICR-MS, MALDI, ESI, HPLC

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Identification of textile dyes is important in archaeology and history research. By identifying the dye composition, it is possible to learn more about the origin, age and usage of the textile findings. Besides that, information about the composition of dyes can help the conservators to use right materials and methods.

Natural textile dyes are based on a wide range of organic molecules that give intense colour already in small quantities. Diversity, complex composition – many natural dyes are based mixtures of dye molecules, rather than a single molecule – and small concentration of dyes in samples makes the identification very difficult and due to that very sensitive and information-rich methods are needed. [1]

In this work methodology development for red textile dyes was done using different chromatographic and mass-spectrometric methods. Comprehensive research was done from collecting different dye sources (plants, insects, mushrooms) to interpretation of mass spectra and chromatograms. With all the collected dye sources, wool colouring was carried out and solutions from different dyeing steps were collected and analysed. Firstly for the analysis of chemical composition HPLC-QQQ-MS was used and characteristic retention times and mass spectra were recorded for different dye components [2]. For obtaining high-resolution and high mass accuracy spectra of dye molecules at low concentration, FT-ICR-MS with MALDI and ESI ion sources were used [3]. FT-ICR-MS allows recording mass spectra with mass accuracy below 1 ppm, enabling reliable identification of low-level analytes in complex samples. MALDI source enables to ionize and analyse samples without completely dissolving them, and it is possible to analyse samples that are (partly) polymeric, nonvolatile and that cannot be easily separated by chromatographic methods. For all the analytical methods suitable solvents, internal calibrants and parameters were found. [2,3]

Altogether nine red dye sources (dyer’s madder, redwood, logwood, sandalwood, safflower, alkanet, bloodred webcap, kermes, cochineal) were analysed and more than 20 dye molecules identified and characterised. Thanks to high resolution and sensitivity, FT-ICR-MS enabled to identify low concentration components that were not detected with HPLC-MS like santal and maackiain in sandalwood extract.

The developed methodology was applied to a real-life sample from Estonian National Museum. Analysed red fibre piece was from a carpet that was brought to museum in 1934/1935. With both chromatographic and direct-mass-spectrometric method, carminic acid and flavokermesic acid were detected which indicates the usage of cochineal dye.

The methodology can further be transferred (with minor modifications) to all other natural dyes. Collection of mass spectra and chromatograms of dyes is right now in working process and can be further used to identify dye components from historical and archaeological findings.

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P.01 Poster

P.01 poster

ABSTRACT P.01.1

“L’AVVENTUROSO (1936) PROJECT”: FIRST STUDIES FOR THE CHARACTERIZATION OF PRINTING MATERIALS IN COMICS

Anchisi A.[1], Rovetta T.[2], Fiocco G.[2], Malagodi M.[2], Lazzari M.[1], Merlo C.*[1]

Keywords: XRF, XRF mapping, FTIR, Comics, Pigment

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The history of modern european comics began in the first half of the 19th century, as a representation of ideas by images, often combined with text or other visual information [1]. Like any art form, comics has its own medium-specific properties that allow to express ideas that can’t be expressed in any other way. For these reasons, original hand-drawn pages and historic printed comics should be considered in some cases object of artistic and cultural relevance, needing appropriate conservation methods. The object of this research is represented by an issue pressed in 1936 of the Nerbini series “L’avventuroso”. This was the first Italian “ballooned” story dedicated to the superheroes adventures, a genre that was already very popular in the United States, but subjected in Italy to the fascist censorship. The editor Nerbini (Florence) was probably in the first half of the 20th century one of the most famous printer of mass papers, party publications i.e. L’avanti! Della Domenica and the Italian publisher of Mickey Mouse.

“L’avventuroso Project” deals for the first time the characterization by non-invasive diagnostic techniques of the materials used in the printing process in comics, in particular during the Italian fascism. Before the restoration process, a multi-analytical approach was applied starting with imaging investigation (i.e. UV-induced fluorescence photography, IR reflectography and IR false-color), followed by spectroscopic measurements through FTIR (ATR and diffuse reflectance mode) and XRF (single point and Mapping). XRF maps were post-processed by PyMCA software to find out correlation between elements (Figure 1) [2].

From the results, many information about the characteristics of the paper support and the color printing materials were collected: the used paper is slightly pre-treated (carbonate and sulphate) [3] and contains wood pulp, cyano/blue and black colors were made by prussian blue (band at 2089 cm^{-1} and high Fe signals) probably mixed with zinc oxide and carbon black respectively; yellow was chrome yellow (Cr and Pb XRF signals); red was made with chrome yellow and lead oxide, probably mixed with lithopone (S, Ba, Zn); the green was a mixture of prussian blue and chrome yellow [4]. Furthermore, the pH test on the sheets showed the tendency to acidity (pH 6.0-6.5), probably due to the presence of lignin. The restoration intervention was developed in subsequent steps: initial dry cleaning, washing in deionized water, restoration of gaps with leaf casting machine with paper pulp, Japanese tissue and methylcellulose and, finally, resizing with methylcellulose of the whole sheet.

Further analysis will be performed on other later issues of this comics series (1937 and 1938) in order to compare the pigments and verify the state of conservation of the materials. In conclusion, this research presents the first non-invasive analysis of historical comics materials with the primary aim of favouring recovery and valorization of such historical artworks.

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ABSTRACT P.01.2

20TH CENTURY PAINTINGS: A MULTI-ANALYTICAL APPROACH FOR TESTING AUTHENTICITY

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Keywords: Contemporary art, paintings, non-destructive techniques, spectroscopic analyses, SEM-EDS

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Scientific techniques provide information (or evidence) on the complex structure characterising a painting, helping to face the challenges presented in the authentication of artworks. Usually one single negative evidence is able to invalidate the authenticity, for example by detecting anachronistic pigments. Instead, finding positive evidence, and hence compatibility with the attributed period or artist, does not make authentication decisive. Moreover, during the 20th century, paintings are often composed of a wide variety of materials and products, still used in art.

This work presents a multi-analytical approach applied to some case studies of canvas paintings of contemporary art, among which artworks of private collections attributed to Edvard Munch (Bathing Women, date unknown) and Pablo Picasso (mon Amour, 1913-14).

After an initial set of non-invasive techniques, such as VIS photography, UV fluorescence, infrared reflectography (IRR), energy dispersive spectroscopy - X-ray fluorescence (EDS-XRF), with the purpose of ruling out chronological inconsistencies of the materials with the time proposed by the attribution, an in-depth research was conducted. A sampling protocol was applied, following the non-invasive methodologies results. The samples embedded in cross section were preliminarily documented through optical microscopy (OM) in VIS and UV light, and then a series of non-destructive analyses (scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS), Fourier transform infrared (FTIR) and Raman microscopy) were performed [1-3].

The results demonstrated the strength of the integrated set of techniques on the identification of almost all painting materials, even in the presence of complex mixtures of both organic and inorganic compounds.

All the pigments, binders and extenders found were compatible with the art history of 20th century [4-6]. Molecular techniques as Raman and FTIR microscopy seem more suitable for the investigation of modern materials (like Prussian blue and synthetic organic compounds as phthalocyanine), while additional information can be acquired through SEM-EDS analyses.

The data obtained from the combined techniques were then correlated with those reported in literature, showing correspondence with compounds and pictorial techniques of the artists and thus corroborating the attribution. Although, the little information available about materials and art techniques of contemporary artists opens an almost unexplored field of study. Therefore, this work is a part of a wider research aiming at creating and sharing a technical catalogue raisonné on contemporary art materials and techniques.

Finally, the complexity of mixtures and the continuous pictorial technical evolution of 20th century artists do not make it easy to establish the authenticity of a painting. Hence the necessity for further investigations on other artworks of the same artist and in the same period, in order to complement them with art historical and provenance studies and judgment of a connoisseur, deepening the research of materials, working methods and creation process, limiting the subjectivity in an interdisciplinary approach and, eventually, identifying fakes and forgeries.

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ABSTRACT P.01.3

A LADY IS REVEALED

Ganetsos T.*[1], Papathoma E.[2]

Keywords: in-situ, Raman, mobile, pigments, raman

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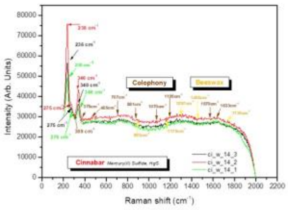
The research topic of this study is the application of Non-destructive Spectroscopic Techniques for the identification of the materials used for the painted decoration and the protection of the surface of the 5th c. B.C wooden female figurine that has been discovered at the sanctuary of Artemis in Brauron, under waterlogged condition. The female figurine preserves traces of red colour on her sakkos. The rarity of this archaeological find and its state of preservation made indispensable the application of non-destructive techniques and the use of portable measurement devices. Therefore, Fluorescence Spectroscopy (XRF) and Raman Spectroscopy have been applied for the detection of pigments, while for the detection of the organic compounds of the binder and the coating material has been applied a combination of Raman Spectroscopy and IR Spectroscopy. The evaluation and the synthesis of the results from the applied methods have been proven very interesting. More specifically, cinnabar pigment has been identified in the red colour, while the use of beeswax as binder and colophony as varnish or as coating material has been verified on the object. Finally, it should be noted that the results of this research study also verify the correctness of the planning process and the usefulness of the combined application of the methods XRF, Raman and IR.



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ABSTRACT P.01.4

ANALYSIS OF PIGMENTS AND INKS IN MOROCCAN ILLUMINATED PAPER MANUSCRIPTS OF 11TH AND 12TH CENTURIES BY ENERGY DISPERSIVE X-RAY FLUORESCENCE (EDXRF)

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Keywords: manuscripts, XRF, environmental alterations, paper, ink

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Hand-written paper documents present an important part of Moroccan cultural heritage. A major problem of these documents is their preservation especially some dating from 11th and 12th centuries. Alteration is caused by the effect of aggressive atmospheres, humidity and temperature, paper constituents, and by added materials such as ink or coloring pigments or dyes [1-2]. Identification of pigments and inks is of great importance for the dating and systematic characterization of illuminated manuscripts. Currently, Moroccan manuscripts investigations are limited to codicological studies in which reports on illuminations and colored vocalizations are limited to visual descriptions. Hence scientific investigations are required for an objective characterization of this universal heritage [3].

The aim of this study is to determine the composition of the inks and pigments used for the calligraphy of nine Islamic illuminated manuscripts belonging to the Royal Moroccan Library of Rabat, some dating from the 11th to 12th centuries, and five manuscripts originating to a private library in Meknes, belonging to different scribal schools of the western Arabic Mediterranean region. Energy Dispersive X-ray Fluorescence (EDXRF) was used for determining the elemental composition of the inks and pigments in the investigated manuscripts.

The obtained results showed the inorganic structure of the inks and pigments used by the illuminators/calligraphers. Iron-gall ink (Fe (Ca, Cu, K)) were used for the text. The main pigments used in the illumination and titles are found to be vermillion (HgS), hematite (iron oxide Fe_2O_3) in red samples, malachite $CuCO_3.Cu(OH)_2$ in the pale green, lazurite $Na_6Ca_2[SO_4|(AlSiO_4)_6]$and azurite $2CuCO_3Cu(OH)_2$ in blue color, and gold pigment.

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ABSTRACT P.01.5

ANALYSIS OF STRING INSTRUMENT PROTECTIVE LAYERS – NONINVASIVE AND MICRO-INVASIVE METHODS

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Keywords: string instruments, varnish, microscopy, spectroscopy, micro invasive

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In 2016, we got a request from the National museum of Slovenia to analyse protective layers of selected string instruments. Due to their preservation state or private ownership, the sampling was supposed to be reduced to minimum, however as much information as possible was supposed to be achieved, not only of surface layers, but also of deeper layers. String instruments are mostly varnished. The lacquer finish of the instruments is an important part of the violin making process. Varnish should protect the wood from environmental impact, but it also influences the objects' appearance (Darnton, 2009) and sound (Schleske). Varnish layer is composed of several layers with different functions. The bottom layer, called the ground layer or primer “seals” the surface of the wood so that the varnish overlay cannot be absorbed in the wood (Kolneder, 1998). Egg white or glue was used traditionally, often filled with mineral particles (Darnton, 2009; Tai, 2009). Sometimes clear organic solvents based varnish were used as primer (Darnton, 2009). Varnishes used on musical instruments used to consist mainly of resins. There is a distinction between spirit varnishes based on organic solvents and oil varnishes, where resin is dissolved in a type of drying oil, mostly linseed oil or walnut oil (Darnton, 2009; Tai, 2009). We investigated surface coatings of 7 instruments and 2 violin bows, made between late 17th and mid-20th century. Mainly our work based on microsampling, but also non-invasive reflectance FTIR spectroscopy (Alpha, Bruker) was used to analyse surface layers. All microsamples were embedded in polyester resin to observe their layers' structure under optical (Olympus BX60) and scanning electron microscope (5500 LV, JEOL). Organic binders were analysed using micro-FTIR transmission spectroscopy (Spectrum Spotlight 200 attached to Spectrum 100, PerkinElmer) on raw samples, compressed in diamond anvil cell. For analysis of some pigments, Raman micro-spectroscopy (HR800, Horiba Scientific) was also used. Only in the newest two violins a ground layer was observed, made with tempera binder. Older violins were made only with resin (diterpenoid or triterpenoid) varnishes. Usually only a few layers (mainly 1 or 2) of varnish were applied to older instruments, whereas both instruments made in 20th centuries were varnished with several relatively thick layers, made from two different resin types, most probably shellac and copal. Some of the varnish layers were pigmented or filled, mainly with earth pigments and calcite. A lute was interesting with its ornamental decoration, made in tempera and traditional pigments. As seen from our results, the period was not the only influence on structure of the instrument varnish layers. They differed between different regions or workshops, all in search for "the perfect sound".

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ABSTRACT P.01.6

ANALYSIS OF THE MIDDLE NEOLITHIC TRICHROME POTTERY: CHARACTERIZATION OF THE DECORATION USING XRF AND RAMAN

Angeli L.[1], Brunetti A.[2], Legnaioli S.*[3], Fabbri C.[1], Campanella B.[3], Lorenzetti G.[3], Radi G.[1]

Keywords: Neolithic ceramic pigments, X-Ray Fluorescence, RAMAN, Serra d'alto colture, Manganese

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Trichrome painted wares spread out during the Middle Neolithic (between 5000-4500 cal. BC) along the Adriatic side of the Italian Peninsula. The pottery production was characterized by a very fine-granulated paste defined figuline and by a decoration painted with red and black colours. This research reports the results of X-Ray Fluorescence (XRF) and micro-Raman spectroscopy analysis focused on the decoration of the ceramics from two distinct geographical areas, corresponding to Ripoli culture in Abruzzo [1-2] and Serra d'Alto culture in Basilicata [3-4]. The production of Ripoli figuline pottery includes cups with vertical handles and plastic applications on the top, bowls and jars with narrow neck and four small handles under the rim. Red bands (referring to the previous tradition of Catignano culture), delimited by black lines and black spots or by black geometric lines, characterize the painted decoration. The production of Serra d'Alto figuline pottery includes jars, hemispherical and with long neck cups with handles and zoomorphic plastic applications on the top. The thickness of the vessels is particularly thin while the decoration shows geometric patterns painted in black. A representative set of samples belonging to the two cultures has been studied. XRF and micro-Raman analyses reveal that black decoration was obtained using a black pigment based on manganese-iron oxide, whereas the red one includes iron oxides. The results, together with the data achieved on samples of Serra d'Alto figuline from Matera's sites, allow to confirm the figuline production hypotheses [5-6]. In particular, a technological evolution is proven by the selection and control of raw materials to the technologically advanced firing system. Moreover, the choice of a manganese pigments is a further technological connotation of figuline potteries.

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ABSTRACT P.01.7

ANALYTICAL METHODOLOGY TO EVALUATE THE NON-VISIBLE SOLUBLE SALTS IMPACT IN THE POMPEII HOUSES

Prieto-Taboada N.*[1], Veneranda M.[1], Fdez-Ortiz De Vallejuelo S.[1], Marcaida I.[1], Morillas H.[1], Maguregui M.[2], Martelone A.[3], De Nigris B.[3], Osanna M.[3], Madariaga J.M.[1]

Keywords: Soluble salts, LIBS, EDXRF, POMPEII, Conservation

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Pompeii is considered to be one of the most important archaeological site in the world. However, despite of the efforts done so far to ensure its conservation, several environmental factors are constantly threatening the preservation of the wall paintings conserved therein. Among them, rainfalls, thermal fluctuations, biological colonization and atmospheric acid gases are responsible of triggering critical degradation processes, such as the development of efflorescence salts. Considering that soluble salts can crystallize on the surface (efflorescences) and the painting subtrate (sub-efflorescences), their formation must be controlled in order to avoid the related physical and chemical damages.

Sometimes damaged walls show a clear level of salts (front of salt) which is supposed to be the indicator of the level reached by them. In these cases, the work of restorers is mainly focused on cleaning and consolidates the affected areas without solving the problems that lead to the accumulation of soluble salts in the walls. This is the case of the perystile of the house of Gilded Cupids of Pompeii, which shows clear conservation problems despite the conservation works carried out in 2013. Even though a recent work demonstrated that the observed salt crystallization is triggered by the lack of protection in the wall painting backside, an important question still needs to be answered: all salts are crystallized or a part of them is still inactive (solubilized) below the painting surface? To answer this question, the analysis of two walls of the perystile of the house of Gilded Cupids were carried out by in-situ energy-dispersive x-ray fluorescence (EDXRF), laser induced breakdown spectroscopy (LIBS), infrared thermometry and hygrometry. The selected walls were the following two: (1) one of the most affected wall by soluble salts (A2) with a front of salts at 90-105 cm and (2) a non-affected wall (A6) restored recently with a lack of wall painting at 80-110 cm. The measurements in the A2 wall were carried out each 15 cm up to 255 cm in a vertical line (between 80-105 and 135-165 cm the measurements were carried out each 5 cm). In the case of the A6 wall, measurements were carried out each 15 cm up to 225 cm. Data collected from the A2 wall revealed the presence of a front of sulphur between 45 and 120 cm. This range includes the front of salt but it is much larger that the observed salts damage. In the case of chlorine and potassium, the maximum values were detected at 105 and 90 cm respectively, which perfectly fit within the front of salts. Regarding temperature not relevant changes were observed but in the case of relative humidity, a clear maximum was detected at 95 cm. This results clarly highlight that the area affected by the presence of soluble salts is much broader than the front of salts visually observable.

Similarly, high concentrations of sulphur were also detected along the A6 wall (the minimum values were observed in the restored area). Chlorine and potassium presented a maximum at 105 cm and 75-105 cm respectively, which is the area of the mortar restored in 2013. This fact suggests that these anions were probably present in the materials used by conservators. At this height the highest relative humidity values were also observed. Considering that salts efflorescence are not visible in this area, it can be assumed that

soluble ions are accumulating in the wall but still inactive. To sum up, the presence of inactive soluble salts has been analytically proved and this fact could have important repercussion for the planning of future conservations works. Indeed, hidden salts could lead the formation of new damages if are not effectively removed. Thus, it is clear the need of carrying out analysis prior the conservation works.

This project has been funded by the MADyLIN project (ref BIA2017-87063-P) funded by the Spanish Ministry of Economy and Competitiveness (MINECO) and the European Regional Development Fund (FEDER).

ABSTRACT P.01.8

APPROACHES FOR THE PROTEIN BINDERS' DETERMINATION ON EASEL PAINTINGS

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Keywords: fluorescent labelling method, protein binders, electrophoretic profiling, easel paintings, immunoenzymatic assay

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Proteins have been commonly used as paintings medium, adhesives and coating layers in easel paintings. Hence, the proteins recognition is one important factor for the construction of an easel painting's conservation strategy. This work explores different approaches for proteinaceous binders' identification namely; conventional electrophoretic profile, fluorescent labelling method and immunological assay. The fluorescent labelling method was firstly tested on proteins extracted from an easel painting paint model. The paint models were made by mixing proteins such as ovalbumin, casein and rabbit glue with different pigments (lead white, chrome yellow and black bone). From the conventional electrophoresis, protein bands extracted were hardly observed on the electrophoresis gel. However, fluorescent band between 25 kDa to 35 kDa were clearly observed on the electrophoresis gel with fluorescent labelling. Results revealed that with fluorescent labelling, proteins extracted from the paint models, in a concentration of 6.0 µg/ml could be detected. Subsequently, proteins were extracted from samples of easel paintings by Giorgio Marini (1836–1905), from the museum of Évora and private collections. The extracted proteins were then submitted to the fluorescent labelling method and immunoenzymatic assay. The fluorescent labelling was done using Coumarin 392 TFP ester (C392) (4-sulfotetrafluorophenyl coumarin ester) as fluorophore, which was mixed with the proteins extract for a period of 24 hours. Simultaneously, immunoenzymatic assay (ELISA) was carried out on each sample, according to a previously optimized procedure by Salvador et al., 2016. These extracted proteins could be clearly observed in the electrophoretic profiles after fluorescent labelling, which was not possible in the conventional electrophoresis performed. Proteins such as ovalbumin, collagen and casein also proved to be present in the paintings, through the immunological assay. The results indicate that fluorescent labelling, followed by electrophoretic detection is a simple and fast method with high sensitivity; this method is like the immunoenzymatic assay which can act with high specificity in the identification of proteinaceous binders used in easel paintings.

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ABSTRACT P.01.9

ARTIFICIAL IMPREGNATION FOR MODELLING WATERLOGGED WOOD CONTAMINATED WITH IRON SULFIDES

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Keywords: waterlogged wood, extraction method, iron sulfides, biotechnology, green chemistry

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Archaeological waterlogged wood degraded rapidly after exposure to oxygen. Indeed, during the burial time in anaerobic environment, sulfate reducing bacteria produce hydrogen sulfide that reacts with the present iron(II) ions to form iron sulfides. Mackinawite and pyrite are the main species formed and are very stable under these conditions. However after excavation, iron sulfides are converted into iron sulfates and/or iron oxyhydroxides salts and sulfuric acid is produced[1]. The acidification and salt precipitation led to irreversible chemical and physical damages on the wooden structure. Among the different conservation methods developed for the preservation of waterlogged wood the most used is the impregnation in a polyethylene glycol (PEG) solution that replaces water inside the wood vessels and consolidates the structure. However, the iron that can be still present in the wood causes the degradation of PEG.

We propose an innovative and green extraction method for Fe and S species, that can be applied while excavated objects are still wet before consolidation. The goal is to develop a pioneering extraction method using microorganisms harmless for the object itself, but also for the users and the environment. A preliminary phase implies to test selected bacteria on model samples. To prepare these model samples, two impregnation protocols were evaluated on fresh wood to form iron sulfides. Balsa wood was selected due to its high porosity and similarity with archaeological wood. In the first protocol, a set of wood samples was immerged in an equimolar solution of $FeCl_2·4H_2O$ and $Na_2S.·9H_2O$ under vacuum. In the second protocol a similar set of samples was impregnated under inert atmosphere by a neutral solution of $FeCl_2·4H_2O$ and $Na_2S·9H_2O$[2,3]. Non-invasive and non-destructive analyses of impregnated wood samples were then carried out to characterize wood degradation and Fe/S contamination, that occurred during the impregnation protocols.

The variation of colour was measured and a change to a darker hue was observed. Microscope observations showed the formation of crystals at the surface and inside the pores of the wood. The degradation of the carbohydrates content (cellulose and hollocellulose) was also evaluated by Fourier Transformed Infrared (FTIR) spectroscopy using an Attenuated Total Reflectance (ATR) accessory. The intensity of the peaks at 1506, 1374 and 1158 cm^{-1} (respectively assigned to lignin, cellulose and hollocellulose) were measured and two ratios calculated: R1=I(1506)/I(1374) and R2=I(1506)/I(1158)4. Comparing with raw balsa wood, the ratios showed a decrease in the carbohydrates content. In particular, measurements showed a highest degradation at the edge of the samples. Finally, Raman spectroscopy allowed to determine the Fe and S compounds formed. Partially oxidized mackinawite was identified with the presence of characteristics peaks at 312 and 326 cm^{-1} and greigite in formation was also detected as indicated by the peak present at 138 cm^{-1}.

These results showed the efficiency of using impregnation protocols to prepare model samples from fresh wood and hence to simulate waterlogged wood contaminated with iron sulfides. Next steps will include the validation of the protocols on aged wood before testing selected bacteria using these model samples.

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ABSTRACT P.01.10
CALCIUM CARBONATE PASTE: HOW IONS CONTROL MECHANICAL PROPERTIES

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Calcite is one of the basic constituents of ancient and modern construction materials such as limestone, marble and concrete. In the recent construction practice, calcite as limestone flour is used to produce high performance concrete with enhanced rheological properties. Moreover, calcite slurry is one of the components of injection grouts for the restoration and consolidation of historical buildings and vernacular architecture[1]. In this work, we show that adding simple ions to calcite allows to explore a wide range of mechanical properties, interesting for application. In particular, we use rheological measurements on calcite paste to probe the influence of several ionic species on the interaction forces between calcium carbonate particles. Calcite paste exhibits a typical colloidal gel behavior, with an elastic regime and a clear yield strain above which a plastic regime occurs. In a previous study, we characterised the elastic domain of pure calcite suspensions for a wide range of volume concentrations and investigated the relation between microstructure and macroscopic behavior [2]. A wide range of ionic strength, pH and ionic species are analysed, adding calcium hydroxide ($Ca(OH)_2$), calcium chloride ($CaCl_2$), hydrochloric acid (HCl) and sodium hydroxide (NaOH) to reach the best conditions in terms of elasticity and yielding of the paste with respect to pure calcite suspension [2]. For this purpose we characterise the rheological properties as a function of the solid concentration to determine the fractal structure of the colloidal gel and we performed ζ potential measurements on the paste to correlate surface modifications with the rheological response of the calcite suspensions [3]. Thanks to this rheological study we are able to control and improve the final properties of the calcite suspension, which may be crucial for specific application.

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ABSTRACT P.01.11

CHIARAVALLE CROSS: HISTORICAL AND SCIENTIFIC INSIGHTS DURING THE RESTORATION

Di Martino D.*[1], Benati G.[2], Alberti R.[3], Baroni S.[4], Bertelli C.[5], Blumer F.[6], Caselli L.[7], Cattaneo R.[1], Cucini C.[8], D'Amico F.[13], Frizzi T.[3], Gagetti E.[9], Gorini G.[1], Lazzarini L.[7], Musa M.[12], Perelli Cippo E.[10], Riccardi M.P.[11]

Keywords: multidisciplinary study, in situ measurements, non destructive measurements, neutron analyses, SEM

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Chiaravalle Cross, a jewelry masterpiece dating to the XIII century, is a processional cross made of silver and gold laminas, combined to filigrees, crystals, gems, cameos and red jasper. This piece from the Museo del Duomo's collection, on loan to the Veneranda Fabbrica from the Oblates of San Celso, was restored as part of the project “Restituzioni 2016” [1].

The original provenance and commission of this treasure is still unknown (no documentation is available), and several hypotheses were proposed by art historians.

The University of Milan-Bicocca, in collaboration with the Veneranda Fabbrica del Duomo, coordinated a number of scientific investigations during the restoration, including in situ and laboratory measurements [2], both on small fragments made available for further studies and small parts unmounted for consolidation and cleaning procedures. Several techniques were used, all non-destructive and tailored to this case study, like gemological examinations, Raman and XRF spectroscopic measurements, SEM analyses and neutron based experiments. This wide multidisciplinary research combined characterization of all gems adorning the Cross, the cameos, the gold, silver, jasper and glass parts, to derive indications on the gold composition as well as goldsmith’s techniques, materials provenance, various alterations and the questions of authenticity after the different restorations that occurred over time. All analyses were shared with the restorer and art hystorians in a real mutual exchange of different expertise.

The presentation will focus on main results which were collected in the proceedings of a dedicated workshop entitled “Chiaravalle Cross: historical and scientific research during the restauration” [3], in order to reveal new secrets or confirm hypotheses.

We outline that the preference for a multidisciplinary collaboration, when possible, is a great benefit for cultural heritage objects. In fact, the study of a complex masterpiece like the Chiaravalle Cross has taken really advantage from the exchange of knowledge and skills in the field of gemology, restoration, art history, physics and chemistry, just to cite a few.

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[2] see for example: http://www.iperionch.eu/project/sofia/
[3] “La Croce di Chiaravalle. Approfondimenti storico-scientifici in occasione del restauro” by Giulia Benati and Daniela Di Martino, Booktime Edition, Milan (2017) ISBN code: 978-88-6218-293-5

ABSTRACT P.01.12

CLEANING OF TEXTILE MATERIALS USED FOR SEAL ATTACHMENT

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Keywords: textile conservation, cleaning agents, wet cleaning, microemulsions, dry cleaning

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Textiles used for pendant seal attachments form a part of archival units that consist of a deed (usually made of parchment), textile or parchment pendant attachment and a seal (e.g. lead, wax), see Fig. 1. Cleaning constitutes a significant part of preserving archives of this type. Textile pendant attachments can be contaminated by dust particles or by particles that were created during manufacturing seals or as a consequence of the prior conservation (so called secondary impurities). Particular parts usually need to be cleaned separately. The study examined different options of local cleaning of textile pendant attachments on model samples. It also investigated the impact of selected cleaning agents on textile degradation. The tests were done on silk – the most frequent material used for pendant seal attachments.

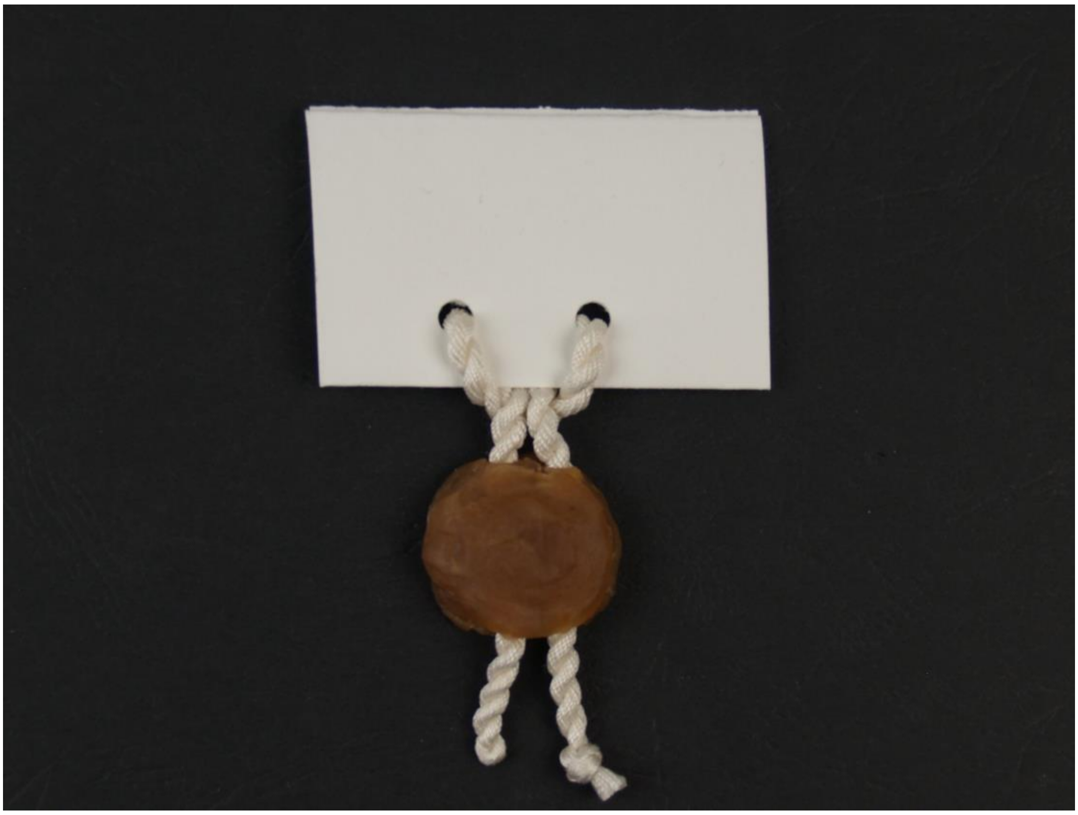
The options for removal of common impurities by local cleaning were tested on model samples of twisted silk cords (19 cm long, 0.5 cm in diameter). The samples were contaminated with repository dust and artificially aged in the next step (with UV light of a wavelength 302 nm and intensity 24 W/m^2, 240 h). The samples were then cleaned with a vacuum cleaner (with adjustable suction), a surgical suction pump, a sponge CePurus (PVC, supplied by Ceiba s.r.o.) and pearl cellulose compresses Perloza MT100 (regenerated cellulose, supplied by Ceiba s.r.o.). Other tested cleaning methods included cleaning with organic solvents (perchlorethylene) and wet cleaning (with distilled water and water with the detergent Syntapon L- sodium lauryl sulfate, manufactured by Enaspol a.s.).[1,2]

The method assessed as the most suitable one based on the results was cleaning with a sponge CePurus – it removes dirt effectively without damaging the surface of the cords. Wet cleaning and cleaning with perchlorethylene have also been assessed as very efficient methods, yet they require separation of the textile from the rest of the archival unit.

The study also examined the impact of selected cleaning agents on silk properties. The agents were selected with regard to the type of contaminant to be cleaned off the textile and the possibility of using wet or dry cleaning systems. Perchlorethylene and anionic surfactant Syntapon L were selected from the agents tested to clean off dust and greasy impurities. By contrast, xylene and microemulsions (87.1% H_2O, 3.9% sodium dodecylsulfate, 6.5% 1-pentanol, 2.5% xylene)[3] are suitable for cleaning off secondary impurities. The cleaning agents were tested on model samples of artificially preaged textiles. The impact of the cleaning agents on silk degradation was examined by means of colorimetry, limiting viscosity number and thread tensile strength. These parameters were measured before and after the artificial ageing.

The results show that perchlorethylene, xylene and Syntapon L (in case it is thoroughly rinsed off) do not markedly impact the physical and chemical properties of silk after both wet and dry ageing. When using perchlorethylene and xylene, occupational safety and health standards need to be respected due to their toxicity. Microemulsion caused considerable changes in colour of the textiles; therefore, a cleaning system with a different surfactant will be tested in further research.

This work was supported by project of Ministry of Culture NAKI II "Development of conservation methods for seals and textile materials used for their attachment" (DG16P02R040).



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ABSTRACT P.01.13

CLIMATIC INDUCED DEFORMATION OF PANEL PAINTINGS: EXPERIMENTAL OBSERVATIONS ON INTERACTION BETWEEN PAINT LAYERS AND THIN WOODEN SUPPORTS

Allegretti O.[1], **Dionisi-Vici P.***[2]

Keywords: Panel paintings, Hygroscopic asymmetry, Panel thinning, wood - paint layer interface, vapor barrier system

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This work describes the experimental deformative response induced on a XVI century oak panel painting by climate uncontrolled fluctuations and on structural replicas under controlled laboratory conditions.

The objects under measurement have a very thin wooden support (6 mm), caused in the original artifact by a thinning made during a restoration at the beginning of the XX century.

This kind of artifacts is very susceptible to severe warping and to mechanical damage.

This is due to their high ratio between painted layer and wooden support thickness, causing hygroscopic and mechanical asymmetries.

The data show a characteristic behavior similar to bimetallic warp and the iteration between hygroscopic asymmetry and mechanical asymmetry induces a peculiar stress dynamic in the interface wood-paint layer during climate fluctuations.

In collaboration with the conservators involved in the restoration process of the panel, the effect of innovative vapor barrier systems on the warping has been studied. The possibility of applying them in a reversible way allows to reduce significantly the warping and the related damage.

Allegretti O., Dionisi-Vici P., Bontadi J., Raffaelli F., The case study of The daughters of the Emperor Ferdinand I by Jakob Seisenegger, in Trento (Italy): analytical hygro-mechanical results as a support in risk assessment for technical interventions, Appl. Phys. A (2017) 123: 38, DOI: 10.1007/s00339-016-0609-3

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ABSTRACT P.01.14

COLOUR CHANGES OF RETOUCHING PAINTS: MAIMERI RESTAURO VARNISH COLOURS

Kavcic M.[1], Legan L.*[1], Retko K.[1], Penko A.[1], Kranjc D.[1], Ropret P.[1]

Keywords: Maimeri Restauro Varnish Colours, retouching paints, colour changes, colorimetry, spectroscopy

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In general conservation practice, aesthetical reintegrations of fine art objects are frequently done with commercially available retouching paints. One of the registered trademarks routinely utilised are Restauro Varnish Colours, manufactured by Industria Maimeri S.p.A, containing mastic resin, selected pigments and organic solvents.[1] Some alteration occurrences of retouched areas with the aforementioned paints have been detected in the past and the paints analytically investigated to some extent.[2,3] In this work, research on Restauro paints was set using different methods such as colorimetry, non-invasive IR reflection spectroscopy, transmission IR spectroscopy, and Raman spectroscopy to better understand possible grounds for certain modifications. Preliminary research included exploration of potential differences between old (c. 15 years) and brand-new paint tubes. Conservators often employ several years old paints, mostly due to economic reasons. To our knowledge, the aspect of the possible unsuitability of old natural resin paints has previously never been investigated. Furthermore, potential influences of chosen organic solvents for workable paint preparation were also investigated. In the principal research, the entire palette (33 colour tubes) of the Restauro paints was included (half chosen among older and half amid newer paint tubes). Besides the retouching paints, different formulations of mastic resin binder/varnish were also selected for the study. Altogether 43 specimens were prepared in several batches. One was subjected to accelerated aging in Xenotest Alpha chamber, simulating solar radiation behind a window glass to determine the photochemical stability of the samples, following the ASTM D 4303-3 standard. The exposed samples were evaluated by means of colorimetry and the results compared with the colorimetric values obtained prior the artificial aging. Computations were performed in the CIE L*a*b* and CIE L*C*h° colour space and colour differences calculated according to ΔE*Lab (ΔE*76) formula[4]. The least pronounced colour differences (ΔE* < 1) were obtained for samples of Maimeri Restauro paints labelled 242 (Indian Red), 228 (Cadmium Red Medium), 336 (Chrome Oxide Green) and 167 (Alizarin Carmine). The most pronounced colour differences (ΔE* > 5) were observed for 131 (Yellow Ochre), 133 (Yellow Ochre Pale), 390 (Ultramarine), 372 (Cobalt blue) and 104 (Naples Yellow); these paint samples also showed notable chroma difference (ΔC*), while only paints labelled 390 and 372 exhibit considerable metric hue (ΔH*) and lightness (ΔL*) difference. Additionally, aged samples were also spectroscopically evaluated utilising infrared and Raman spectroscopy.

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ABSTRACT P.01.15

COMBINED GC-MS AND NMR COMPARISON APPROACH TO THE BINDING MEDIA STUDY

Czarnecka M.*[1], Brzozowska L.[2], Lydzba-Kopczynska B.[1]

Keywords: binding media, GC-MS, NMR, Antwerp altars, organic media identification

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The identification of natural substances used in works of art is often necessary to understand undergoing morphological and chemical changing and aging process. Such tests are usually performed during restoration and conservation works. Then one of the main question ask is which organic compounds like drying oils waxes, resins, gums, proteinaceous glues and other binders were used? The answer may be obtained by various procedures. Besides there are many factors, which make identification of the chemical nature of the binding media difficult. Firstly the amount of sample taken for analysis is usually very small. Secondly it's complex and low purity, because the sample consist of small amount of organic media apart from the pigments, overpaints conservation's media and other substances.

Variety of analytical methods are used to identify organic compounds, such as a Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, nuclear magnetic resonance spectroscopy (NMR) and very sensitive techniques such as gas chromatography coupled with mass spectrometry (GC-MS). Infrared spectroscopy is one of the most widely used techniques in the field of art and conservation: it gives ability for providing structural information's of inorganic and organic materials. But still the answer we are looking for is not so specific. Current trend in FTIR microspectroscopy is imaging in the reflection mode. Identification of organic materials by Raman Spectroscopy is very difficult because of the variety and complex sample what causes high fluorescence.

GC-MS is one of the most widely applied chromatographic technique for identifying organic media and varnishes present in artworks. Each one of the used techniques has advantages and limitations. I want to present comparison data given by GC-MS analysis and NMR of present organic media at samples. The NMR spectroscopy is used for recognizing the organic remains found in archaeological artefacts, and it is extended in the last two decades to the identification of binding media from artworks. This techniques mainly based on capabilities for the molecular characterization of the organic materials and their degradation products. However its use for the analysis of complex mixtures commonly found in paint samples is limited. The main advantage of NMR spectroscopy in the comparison to GC-MS analyzes is the preparation of the samples before measurements. In the NMR to study solvent extracts of paint, is its non-destructive character. The derivatization procedures is multistage process. On the other hand due by derivatization and GC-MS analyzed of the organic compounds, it is possible to detect almost all of the various chemical substances (amino acids of protein, sugars of the vegetal gums, fatty acids of the oil and terpenoids of the resins). However this identification could become complex while pollutants, mixed materials or degraded compounds are analyzed simultaneously[1].

The goal of the presented study is to characterize the binding media used at several of the Antwerp altars: Altar St. Rajnold, Passion Reredos from altar of Pruszcz Gdański, Passion Reredos from altar from Żuków and the altar of St. Adrian at St. Mary's Church in Gdańsk (Figure 1).This particular study is a part of the wider interdisciplinary project focused on deeply understanding of the late Medieval and early Renaissance Antwerp's contractors and carvers workshops[2]. Study shows advantages and disadvantages of both applied methods.

Acknowledgment
The presented study is financed by The Polish Research Infrastructure for Heritage Science (ERIHS PL - The European Research Infrastructure for Heritage Science PL). The 1st call of application MOLAB/FIXALAB 2017.

Figure 1. Altar of St. Adrian at St. Mary's Church in Gdańsk dated to 1510-1520.

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ABSTRACT P.01.16

COMBINED SPECTROSCOPIC ANALYSIS ON THE CORK MASTERPIECE OF THE PANTHEON OF ROME MADE BY ANTONIO CHICHI

Rousaki A.[1], Lycke S.[2], Monsieur P.[3], Martens M.[4], Moens L.[1], Vandenabeele P.*[2]

Keywords: Antonio Chichi, cork model, Raman Spectroscopy, X-ray fluorescence (XRF), Pantheon

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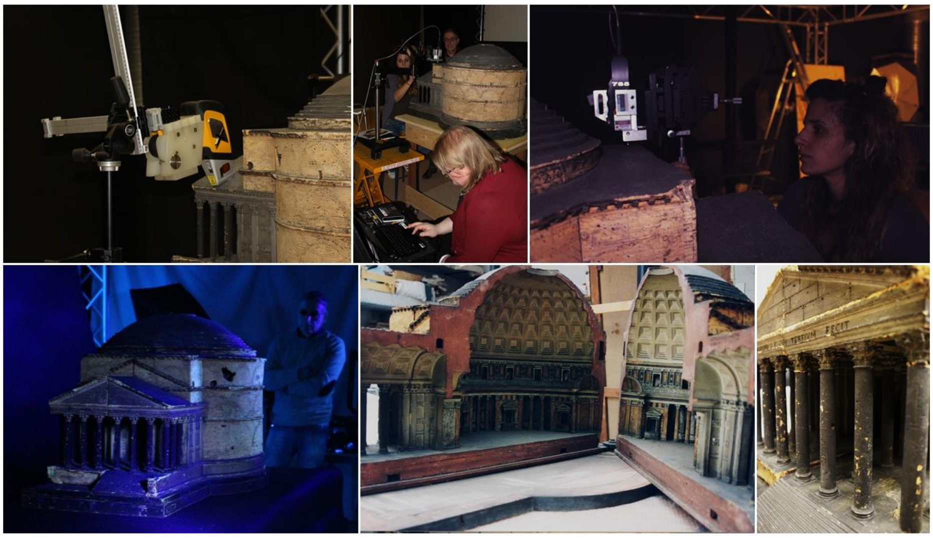
The archaeological collection of Ghent University Museum hosts a very peculiar cork model of the Pantheon in Rome. It was made by Antonio Chichi (1743-1816), the most famous and talented cork modeller of his time. Only 4 Pantheon models by Chichi survived through time and are now kept in Kassel, Darmstadt, St. Petersburg and Ghent. The cork model was obtained shortly after the foundation of Ghent University in 1817, its acquisition being most probably financed by King William I of the Netherlands. Ghent University started a restoration campaign dedicated to this masterpiece of great artistic value.

The cork model of the Pantheon opens in two halves where the interior with its detailed multi-coloured marble decoration and impressive dome can be observed. On the exterior the granite and marble columns of the portico and the brick walls of the rotunda are finely worked out. The neoclassical façade of the Aula Academia and the logo of Ghent University were inspired by the front entrance of the Roman Pantheon.

Next to a detailed photographical campaign, portable Raman spectroscopy and handheld XRF instrumentation were deployed for the physicochemical analysis of this work of art. The molecular and elemental analysis revealed the palette of Antonio Chichi and the materials used for constructing the different components of the model.

After the contribution of archaeology, art history and applied sciences on the detailed documentation of the cork model, conservators will restore the model which will be exhibited in the newly created Ghent University Museum.

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



ABSTRACT P.01.17

COMPARISON OF DERIVATIZATION METHODS FOR GC-MS ANALYSIS OF BINDING MATERIALS IN OIL PAINTS

Tammekivi E.*[1], Vahur S.[1], Leito I.[1]

Keywords: GC-MS, GC-FID, derivatization, oil binder, oil paint

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Paints are complex multicomponent mixtures, that consist of organic binders (oils, waxes, proteins or their combinations, in modern times also numerous synthetic binders), pigments (inorganic or organic) and various additives. Due to their chemical nature paints age with time and the organic constituents undergo complex reactions (mainly degradation), to produce foreign compounds and therefore further adding complexity to the chemical analysis. Knowledge about the organic binder in paints and coating materials would give valuable information to art historians and conservators about the preparation and degradation processes of the materials. However, for obtaining the maximum possible amount of information from such complex paint samples, accurate methodologies for the analysis of small sample amounts and very low analyte contents, are needed.

Gas chromatography (GC), combined with MS or FID detector, is a widely used method for the analysis of organic compounds in coating materials. Generally GC analysis requires small sample sizes (1 µg – 1 mg), is selective and sensitive. The organic components of oil paints (polymerized triacylglycerides) are macromolecules and are not volatile enough for GC analysis. It is necessary to disintegrate the polymer and derivatize its components. The most common outcome of this are the corresponding methyl or ethyl esters of the fatty acid residues of the triacylglycerides. Various derivatization reagents have been used for this purpose. However, there have been almost no studies where these derivatization methods are compared to each other in order to enable potential user to make informed decision as to which of them to use.

The practical part of this work involved the development of derivatization procedures for Agilent Technologies 7890A gas chromatography system used by our work group. Three methods were chosen for comparison – the novel TMTFTH (product name Meth-Prep II) derivatization, widely used NaOEt combined with BSTFA derivatization and acid-catalyzed methylation [1–4]. The derivatized samples were analyzed with GC-MS or GC-FID system.

The developed procedures were applied for the GC-MS analysis of linseed oil, where the components and degradation products were identified. Also, an experimental ageing study of linseed oil was conducted to determine how the content of these compounds changes over time. Based on the results of this study we demonstrate the advantages and disadvantages of the mentioned derivatization methods. The most efficient TMTFTH and acid-catalyzed methylation were applied for the analysis of samples taken from the 20th century painting made by an unknown artist. Examining the results of these analyses it was concluded, that linseed oil was used as the binder in the paint mixture. Therefore, both developed derivatization procedures showed the capacity for an effective analysis of small paint samples.

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ABSTRACT P.01.18

CONFOCAL MICRO-RAMAN SPECTROSCOPY FOR THE STUDY OF NATURAL FIBRES

Rousaki A.[1], Braem B.[1], Moens L.[1], Vandenabeele P.*[2]

Keywords: micro-Raman spectroscopy, biomolecules, natural fibers, non-destructive analysis, spectral interpretation

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Micro-Raman spectroscopy is a powerful tool for performing non-destructive analysis on organic and inorganic materials. Some of the advantages of the technique are the minimum or absent sample preparation, the small spectral footprint (down to 1 µm), the ability to perform mappings in order to associate the chemical information with its spatial distribution etc. The operator can have full control over the focusing procedure and spectra recordings by changing the objectives, concluding in the proper measuring conditions that will result in a good signal to noise ratio, choosing the correct laser that will enhance the Raman signal and will suppress fluorescence and finally determine the laser power that will not alter the measured material.

A set of natural fibres of both, plant and animal origin, were investigated by the means of micro-Raman spectroscopy. These natural fibres were selected as they can be encountered in works of art. The aim of this study is to be able to differentiate between related chemical structures and thus, create a detailed library. The latter is performed by using two micro-Raman spectrometers, namely a Bruker Senterra spectrometer (785 nm and 532 nm) and a Kaiser System Hololab 5000R (785 nm). The recorded spectra were interpreted based on band assignments of organic molecules, and chemometrics was used to facilitate discrimination between highly similar structures.

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

ABSTRACT P.01.19

CONTACTLESS APPROACH TO IDENTIFY BINDERS OF GERMAN AND ITALIAN MODERN PAINTINGS THROUGH PORTABLE VIBRATIONAL SPECTROSCOPY TECHNIQUES

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Keywords: contactless SR-IR/Raman, portable, binders, Modern Paintings, museum

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The aim of this work is to identify binders through a contactless approach used in 2D and 3D Modern paintings on-site at the "Galleria Nazionale d'Arte Moderna e Contemporanea" of Rome. Paintings studied, dating from the second half of the XXth century, have been created with commercial paints by German and

Italian artists (J. Albers, A. Bonalumi, L. Boille, T. Scialoja and M. Schifano). With respect to artworks of the past, post-industrial revolution artists have experimented new products based on industrial polymers, leading to a diversification of materials and their aesthetic appearance. Their precise identification is then not straightforward whereas needed for studying the history of artistic techniques and to establish conservation or restoration policies.

Indeed, binders of studied artworks were previously attributed to acrylic, vinylic, tempera, oil, and enamel polymer families on the basis of visual analysis and art history research by conservation and restoration professionals*. Nevertheless, the precision of such informations were to be confirmed with analytical approaches which respect the artwork authenticity.

In this work, we explore the potential of non-invasive analyses implemented in the museum: infrared in specular reflectance mode and Raman spectroscopies.

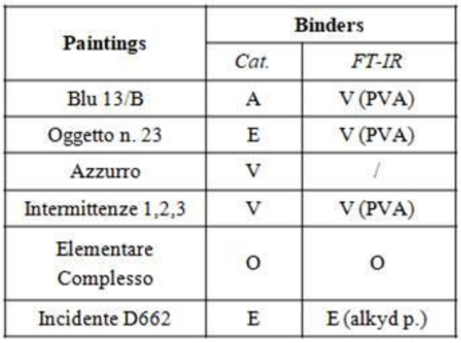
In a first step, an Attenuated Total Reflection (ATR, i.e. involving contact) mode using an Alpha® portable infrared spectrometer was applied on commercial paints (references) to compare the obtained results with contactless measures by Specular Reflectance (SR) IR mode. Reflectance-spectra were transformed using the KKT algorithm in Pseudo-absorbance spectra. Both analyses gave FTIR spectra with polymer classical patterns underlining the validity of measurements in Specular Reflectance mode.

In a second step, the contactless Specular Reflectance analysis was performed in the museum environment on a selection of paintings illustrating a period of artistic productions, a diversity of materials, and implementations. Whereas on-site analyses were sometime difficult to perform due to the characteristics of surfaces (roughness/smoothness, opacity/brilliance etc.) and irregularities of shapes (particularly for some 3D paintings), the pseudo-absorbance spectra obtained could be attributed to the various families of binders thanks to the previously references and to the scientific literature. The pictorial techniques of the paintings are therefore analytically characterized, confirming or not, or specifying, the hypothesized attributions* (Table 1).

The obtained IR spectra also underline the complex composition of the paintings studied including pigments or dyes, binders, additives etc.

To complete the study of each painting components, additional non-invasive Raman spectroscopy analyses (lasers source at 785 nm and 532 nm) were performed. Results emphasize that Raman spectroscopy was more suitable for pigments and dyes characterization, while the SR- IR spectroscopy was more performant for identifying binders.

The SR-IR and Raman spectroscopies are promising contactless and portable analytical approaches, easy to implement, that could provide straight identifications of materials, especially useful in the case of contemporary art where a wide range of possibilities exists.



Paintings	Binders	
	Cat.	*FT-IR*
Blu 13/B	A	V (PVA)
Oggetto n. 23	E	V (PVA)
Azzurro	V	/
Intermittenze 1,2,3	V	V (PVA)
Elementare Complesso	O	O
Incidente D662	E	E (alkyd p.)

Table 1: The binder media as identified by the Catalogue (Cat.) and the FT-IR analyses: A (acrylic), E (enamel), V (vinylic) and O (oil).

*S. Frezzotti, C. Italiano and A. Rorro, Galleria Nazionale d'Arte Moderna & MAXXI: Le collezioni 1958-2008, Electa, 2009.

ABSTRACT P.01.20

DETERMINATION OF GILDING THICKNESS USING X- RAY FLUORESCENCE AND MONTE CARLO SIMULATION

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Keywords: XRF, Monte Carlo, Gold leaf thickness, panel paintings, Goa

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X Ray Fluorescence (XRF) spectrometry is one of the most powerful tools in material characterization studies of Cultural Heritage, due to user friendly features and quick qualitative interpretation of the spectra. Moreover, its non-destructive nature is of paramount importance when dealing with Cultural Heritage objects, due to the availability of portable setups enabling analysis to occur in the controlled Museum environment and avoiding the collection of samples. However, these materials analyzed are seldom homogeneous and often present stratigraphy with more or less complexity. In this way, Monte Carlo simulation methods have proven suitable for the evaluation of the spectra and interpretation of the composition of each layer. In this work we present the determination of the thickness of the gildings applied in three panel paintings belonging to the Museum of Christian Art (MOCA) in Goa: two paintings from the 18th century, pertaining to the same series but different themes: Our Lady of Sorrows and Our Lady of Seven Sorrows and a third panel entitled Monstrance, attributed to the 17th century. The obtained results determined that thicker gold leaf was used in the older painting, in consonance with the belief that the experience acquired during the ages of leaf beating technology resulted in thinner leaf in later times.

M.Manso, N.Schiavon, I. Queralt, A.M.Arruda, J.M.Sampaio, A.Brunetti, Alloy characterization of a 7th Century BC archeological bronze vase — Overcoming patina constraints using Monte Carlo simulations, Spectrochimica Acta B, 107 (2015) 93-96

ABSTRACT P.01.21

DEVELOPMENT OF A METHODICAL APPROACH FOR IN-SITU ANALYSIS OF MODERN REVERSE PAINTINGS ON GLASS (1905-1955)

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Keywords: Reverse painting on glass, in-situ analysis, non-invasive, synthetic organic pigment, modern art

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The technique of painting on the reverse side of glass was rediscovered by artists in the early 20th century and gained great popularity, especially in Germany. In contrast to other paint techniques (e.g. panel and mural painting), the paint layers are applied in reverse succession starting with the foremost paint layer and ending with the primer (backmost layer). The paintings are viewed in reflected light, thus revealing an impressive gloss, luminosity and depth of colour [1].

Scientific investigation of the material provides important information for appropriate conservation concepts. Transport of the precious and fragile objects to the lab is often not feasible. Therefore, in-situ, non-invasive analysis is necessary to analyse colorants and binders. However, some analytical problems need to be considered: due to the reverse paint stratigraphy in reverse paintings on glass, the measured layer is always the backmost one. The analytical possibilities are extremely reduced, when the back is covered by a metal foil (or by paper, carton etc.). However, measurements through the glass (using Raman and VIS) can still yield information on the colourants of the front layer.

When the paint layer is accessible, we start our procedure using X-ray fluorescence (Tracer III-SD, Bruker AXS Microanalysis GmbH, 40 kV, 15 µA) and VIS reflectance spectroscopy (SPM 100, Gretag-Imaging AG). Both techniques provide first information on the inorganic colourants. Raman measurements (i-Raman®Plus, Bwtek inc., 785 nm, 50× objective, resolution 4 cm^{-1}) are then carried out to clarify uncertain XRF measurements and to identify synthetic organic pigments (SOP). Diffuse Reflection-Infrared-Fourier-Transform Spectroscopy (DRIFTS; ExoScan, Agilent GmbH, 4000–650 cm^{-1}, 500 scans, spectral resolution 4 cm^{-1}) is used for the classification of the binders. Moreover, it may help to identify SOP, when fluorescence dominates the Raman signal. This analytical sequence yields the best results, when time is the limiting factor.

We present two in-situ studies of the paintings “Kreuzabnahme” (1914-15) by Carlo Mense and “Stadt am Morgen” (1921) by Walter Dexel. The painting “Kreuzabnahme” is an outstanding piece in Mense’s œuvre, because the glass plate was painted on both sides (Fig. 1). The results of the back-side show mainly inorganic pigments: basic lead white, talc, red and brown ochre, cinnabar, chrome yellow, viridian, ultramarine blue, Prussian blue and bone black. The classification of binding media using DRIFTS yields positive results for drying oil. Acrylic resin could be identified in two areas, resulting from a previous

restauration treatment. For the front side painting, Mense used basic lead white, cinnabar, chrome yellow and umbra as pigments and oil as binder.
Measurements of the abstract painting “Stadt am Morgen” (Fig. 1) by Walter Dexel show zinc white, basic lead white, chalk, cinnabar, red lead, strontium yellow, cadmium yellow, cobalt blue, Prussian blue, ultramarine blue, brown ochre and bone black as pigments. Moreover, synthetic alizarin (PR83) was identified as dark red colorant. The results of DRIFTS classify oil as binding media.
We conclude that, the use of complementary spectroscopic methods yields the best results for in-situ analysis of reverse paintings on glass.

Fig. 1: “Stadt am Morgen” by Walter Dexel, left (top): front side, left (bottom): reverse side, Von der Heydt-Museum Wuppertal. “Kreuzabnahme” by Carlo Mense, middle: front side, right: reverse side, private collection. © Simone Bretz.

[1] G. Geiger, S. Bretz, Heinrich Campendonk Die Hinterglasbilder, Wienand Verlag: Köln, 2017

ABSTRACT P.01.22

DIGITAL MANUFACTURING OF FINE ART REPRODUCTIONS FOR APPEARANCE: CURRENT STATE AND LOOKING AHEAD

Elkhuizen W.[1], Doubrosvki Z.[1], Van Apeldoorn N.[1], Essers T.*[1], Geraedts J.[1]

Keywords: digital manufacturing, 3D printing, 3D scanning, cultural heritage, fine art

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3D scanning and Additive Manufacturing (AM, a.k.a. 3D Printing) provide new opportunities for fine art reproduction. (Digitally created) fine art reproductions have a wide range of applications [1]. However, depending on the artefact, different appearance modalities of the artefact need to be scanned and fabricated [2], [3], such as colour, relief, gloss and translucency.

A limited number of 3D printers can now fabricate full colour objects [4], but it remains a challenge to

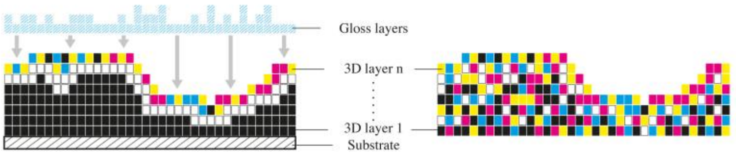
create a life-like reproductions. First, adequate multi-modal scanning methods are lacking that capture the needed modalities at the required detail. Second, new methods need to be developed to process the scanned data into printable files. Furthermore, 3D printers themselves and the print materials need to be developed further to allow for a wider range of visual appearances.

In this work, we evaluate the applicability and required workflow of two different state-of-the-art material jetting systems [5]. While the two printers build up the geometry in a comparable manner, the principle of obtaining colour and appearance differs significantly. To evaluate the suitability of the two approaches for appearance reproduction, we present a reproduction workflow for three types of fine art artefacts: an oil painting, a carved wooden furniture element, and stone bas-relief [6].

Two types of 3D printers were used: a surface-based system (fig. 1a) and a volume-based system (fig 1b). Both printers use 5 base colours: CMYK and White. The surface-based colour system prints on a substrate, the inner volume is built up with ink, the surface has several white intermediate layers and a coloured outer layer. Optionally, layers of transparent ink can be printed on top of the colour, to vary the surface gloss [7]. In the volume-based system the inks are translucent [8]. The colour is created through consecutive layers of pixels, requiring 3D halftoning. For this, a multi-channel 3D error diffusion algorithm was developed. 2D image data can be used as input and projected through the volume or volumetric colour data can be used.

The reproductions, although impressive, show differences to the original (fig. 2-7). Both systems are able to accurately reproduce the shape and surface relief (fig. 2, 6, 7). The surface-based system is more accurate in terms of colour. The volume-based reproductions show blurring of fine details, a consequence of the translucent inks. Oil painting: Fig. 3 shows a difference in gloss for both systems. This shows more likeness when gloss layers are added with the surface-based system (fig. 4). The translucency of the volume-based reproduction is very different from the original (fig. 5). Overall, the surface-based reproduction appears most like-like. Wooden artefact: The limited colour gamut of volume-based system is less of a problem – wood does not have such a wide colour range (fig.6). Since wood itself is slightly translucent, the volume-based system appears to be better in reproducing its appearance. Bas-relief: The most noticeable difference in appearance is the surface gloss (fig.7). Fig. 7c shows a print made using a ZCrop binder jetting system. Although this print has a rougher surface the colour gamut and printing accuracy is much lower.

We found that the characteristics of the print materials have a large influence on the life-likeness of reproductions, although artifacts like image blurring can be minimized in printing [9]. As the number of available full-colour AM systems is increasing, it becomes important to be able to match the specifications of a reproduction to the capabilities of the AM system. Choosing the right reproduction system should involve considering all modalities of an artifacts’ appearance. This work is a first step towards such an overview. A more systematic investigation is needed into capturing and fabricating all appearance modalities and linking the two parts of the workflow.



1(a) Surface-based colour reproduction, with the option to apply transparent layers to create surface gloss variation, *Océ Technologies High Resolution 3D Printing*

(b) Volume-based colour reproduction, *Stratasys Connex3 (3 colour channels) and J750 (5 colour channels)*

2. Grazing angle illumination
(a) Original painting: '*Sunflowers in the style of Van Gogh*'

(b) Surface based colour reproduction using *Océ Technologies High Resolution 3D printing*

(c) Volume-based colour reproduction using Stratasys J750

3. Mirror angle illumination
a) Original painting: *Sunflowers in the style of Van Gogh*

(b) Surface based colour reproduction using *Océ Technologies High Resolution 3D printing*

(c) Volume-based colour reproduction using *Stratasys J750*

4(a) Surface based colour reproduction with spatially-varying surface gloss, using *Océ Technologies High Resolution 3D printing*

6(a) Original part: *Part of traditional Chinese table*

(b) Volume-based colour reproduction using *Stratasys Connex3*

5. Backlight illumination
(a) Original painting: ‘*Sunflowers in the style of Van Gogh’*

(b) Surface based colour reproduction using *Océ Technologies High Resolution 3D printing*

(c) Volume-based colour reproduction using *Stratasys J750*

7(a) Original bas-relief: *Assyrian reliefs of the Southwest Palace of Sennacherib in Niniveh*
(original photograph Copyright of l’Istituto Superiore per la Conservazione ed il Restauro and the Centro Ricerche Archeologiche e Scavi di Torin)

(b) Surface-based colour reproduction using *Océ Technologies High Resolution 3D printing*

(c) Reproduction with *ZCorp full color sandstone*

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ABSTRACT P.01.23

DOUBLE-LOOPED PALSTAVES WITH CASTING JET FROM WESTERN IBERIA. AN ANALYTICAL APPROACH

Bottaini C.[2], Vilaça R.[1], Montero-Ruiz I.[3], Armada X.[4], Brunetti A.*[5]

Keywords: EDXRF, Double-looped palstaves, Monte Carlo simulation, LBA/EIA, Western Iberia

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In this study, a collection of double-looped palstaves with casting jet from the Late Bronze Age (LBA)/Early Iron Age (EIA) (approximately the first half of the I millennium BC) of Western Iberia was analysed through a non-destructive analytical protocol which combined Energy Dispersive X-Ray Fluorescence (EDXRF) Spectroscopy with a Monte Carlo (MC) simulation algorithm named XRMC [1].

From an archaeological point of view, double-looped palstaves with casting jet present a strong morphological standardization. Even in most of cases they have unknown archaeological context, they are generally found in multiple and monotypological hoards which are a distinctive mark of the LBA/EIA from the Northwest of the Iberian Peninsula.

The palstaves selected for this paper have been analysed with a forefront analytical protocol combining EDXRF for the analysis of the artefacts and MC simulation for the data processing and quantification process. This protocol has already proven to be able to reproduce the chemical composition of the bulk alloy of a multilayered artefact, such as archaeological metals, with no need of removing or cleaning the more superficial layers [2,3]. This analytical approach has represented an undoubted advantage in the analysis of the selected palstaves, both because sampling of the artefacts was not allowed and for the possibility of analysing different points for each palstave in a completely non-destructive way.

According to previous studies, double-looped palstaves with casting jet are usually associated to a high-leaded tin bronze metallurgical tradition, being characterised by a high and unpredictable Pb concentration [4,5]. However, more recent studies have shown that double looped palstaves with casting jet with lower Pb concentration were produced as well [6,7]. The determination of the Pb concentration is a central issue for the archaeological interpretation of this type of artefacts, since Pb affects the mechanical properties of an alloy: indeed, higher Pb values led to the formation of segregations that make the metal weakness, thus theoretically not suitable for activities requiring high mechanical stress.

The preliminary results carried out on the double-looped palstaves with casting jet selected for this paper seems to support this trend, also confirming the reliability of the EDXRF/MC as a non-destructive tool able to address and solve specific archaeological issues.

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ABSTRACT P.01.24

EVALUATION OF ICE-DRY BLASTING INVASIVENESS INDUCED ON BRONZE SAMPLES COATED WITH DIFFERENT TYPES OF PATINA

Basile S.*[1], Bersani D.[2], Cagnini A.[3], Galeotti M.[3], Porcinai S.[3], Santagostino Barbone A.[3]

Keywords: Cleaning, Bronze, Ice-dry blasting, Patina, Spectroscopy

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Ice-dry blasting exploits the properties of solid state CO_2 to clean different types of material.
Recently, this method has been proposed as an effective tool for cleaning metal art objects. Its main advantage consists in sublimation of CO_2 when it meets a surface, with no release of moisture onto the surface. Nevertheless, it is of utmost importance to check the invasiveness in terms of morphological and chemical changes.

For this purpose, bronze samples with different types of patina were prepared by an art foundry.
Green and black artificial patinas were applied on two set of 4 samples each. Some other samples were gilded with the fire gilding technique.

Before treating the samples, a deep knowledge of the features of chemical patinas and gilding is required for evaluating possible changes occurring with cleaning. In this contribution, a protocol based on µRaman, SEM-EDX and FT-IR ATR spectroscopy is applied to the samples to provide a full chemical characterization of patinas. Spectroscopic data, together with those obtained by roughness, color and gloss measurements, are acquired before and after preliminary ice-blasting tests for monitoring the response of bronze surface to CO_2 pellets impact.

ABSTRACT P.01.25

GOAN OR EUROPEAN MANNERISM STYLE OF PRODUCTION? TECHNICAL AND MATERIAL CHARACTERIZATION OF A PAIR OF PAINTINGS FROM 17TH CENTURY

Antunes V.[1], Serrão V.[2], Candeias A.*[3], Mirão J.[4], Cardoso A.[4], Carvalho M.L.[5], Manso M.[6]

Keywords: painting, mannerism, technique, materials, analitical techniques

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In this work is addressed the technical and material characterization of a pair of paintings from the beginning of the 17th century. The paintings were inspired by engravings made by Hieronymus Wierix after Bernardino Passeri, published in the celebrated work Evangelicae Historiae Imagines by Father Jerónimo Nadal (ed. Antwerp, 1593) [1], a well-known edition of those who commissioned these artworks. These paintings are placed in Dona Paula, Goa, in the church belonging to Palácio do Cabo, built among the 16th and 17th century in the former Portuguese India, being nowadays the Government house (Raj Bhavan). The paintings, with themes "Flagellatur Christus" (The Flagellation) and "The Christi Sepultura"(The entombment) are in this work materially compared to other Goan and Portuguese paintings under the same themes and influences of mannerism style in order to determine the material influence of European materials and technique in Goan Art for this period - a Goan or an European mannerism style of production?

The methods used to answer this question were Infrared reflectography (IRR), optical microscopy (OM), besides the analitical techniques of Energy Dispersive X-ray Fluorescence spectroscopy (EDXRF), micro-Raman spectroscopy (µ-Raman), micro-X-ray Diffraction (µ-XRD), scanning electron microscopy - energy dispersive spectroscopy (SEM-EDS) and micro-Fourier Transform Infrared spectroscopy (µ-FTIR).

Conclusions drawn from data observation allowed finding scientific confirmation for the identification and origins of the paintings and bring new data for its conservation resolutions.

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ABSTRACT P.01.26

GRAFFITI CHARACTERIZATION PRIOR AN INTERVENTION: IN-SITU RAMAN SPECTROSCOPY AT THE SERVICE OF RESTORATION

Lama E.*[1], Madariaga I.[1], Prieto-Taboada N.[1], Rodriguez Laso M.D.[1], Madariaga J.M.[1]

Keywords: Grafittis, Characterization, Raman spectroscopy, Restoration, Database

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Punta Begoña Galleries are located in the township of Getxo (Bizkaia). In the main hall of the galleries, there are several mural paintings that reflect the passage of the different historical moments that have happened in the Basque Country since the beginning of the 20th century. The Galleries are currently in process of restoration and conservation because they have been abandoned for many years. For that reason, a large number of graffities, which affect directly the reading of wall paintings, appears in most of their walls with different inks, in a total of 20 different colors. Moreover, the graffities are some superposed to others, becoming up to 7 different layers which makes more difficult their removal. For all of these, the chemical characterization of these pigments is a priority to optimize the cleaning and consolidation treatments of wall paintings.

The chemical characterization of pigments used in the graffities is also crucial for the conservation and restoration of urban art, which has been increased in the last years in our cities and for the recovery of degraded heritage by anthropogenic factors (vandalism). In this sense, one of the most interesting techniques which avoid the sampling is the in-situ Raman Spectroscopy.

The first step for the characterization of pigments by Raman spectroscopy involves the need of a valuable database to compare the results. This fact becomes more important bearing in mind the fast development in the graffiti industry. Thus, a complete and updated database is required. In literature is possible to find some databases, but the major of them are not open-access which limits the possibility to exchange the information and join forces. Anyway, there are some interesting open-access databases as the Royal Institute for Cultural Heritage database (KIK-IRPA), although these reference spectra have been limited to a certain number of pigments. For that reason, the databases of graffities, because of their nature, must be completed and updated to be useful. In summary, the aim of this work was to complete and update the existing databases in an open-access way as the first step in the characterization of the graffities that cover the Punta Begoña Galleries.

Thus, two innoRam spectrometers from B&WTEKINC (USA), providing a 785-nm and 514-nm excitation lasers were used. First of all, different samples of mortar were painted with 16 different sprays and measured after dry to complete the databases. After this, an in-situ analysis was carried out in order to characterize the different pigments and inks observed in the Galleries.

Thanks to all of this, it was updated the existing databases. Moreover, in the Galleries it was observed the presence of several pigments derived from phthalocyanine, such as blue or green. Regarding inorganic compounds, orange or red inks corresponded with the pigment chrome yellow orange. Thus, the selection of the best removing process could be carried out in the most effective treatment avoiding the “try and error” classical practice.

This project has been funded by the MADyLIN project (ref BIA2017-87063-P) funded by the Spanish Ministry of Economy and Competitiveness (MINECO) and the European Regional Development Fund (FEDER).

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ABSTRACT P.01.27

HISTORICAL AND ARCHEOMETRIC CHARACTERIZATION OF A UNIQUE SIX-COLOUR RELIEF PRINT

Sodo A.*[1], Savage E.[2], Ridolfi S.[3], Ruggiero L.[1], Valbonetti L.[4], Ricci M.A.[1]

Keywords: Relief print, Raman spectroscopy, XRF, UV fluorescence, dating

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A private collector recently acquired the unique impression of a historical single-sheet relief print depicting Charlemagne enthroned in Aachen Cathedral (fig.1A). It was printed on parchment from six colours: red, yellow, blue, green, black and 'gold' inks (the order of printing cannot be determined). It is undescribed, undated and unsigned. The print was tentatively dated to the 16th century based on the style and iconography. The use of prestige materials (parchment) and novel materials (colour inks) indicate this was created as an exceptional production and the use of six colour inks would make it one of the most important colour prints of the first 350 years of printing (from Gutenberg's invention of printing around 1450 until Le Blon's invention of trichromatic process printing around 1700). This study offers a revised dating based on stylistic analysis of the design and on elemental and molecular analysis of the inks. The style of the design and unusual aspects of the manufacture of the impression both suggest a 19th century origin. Stylistic analysis reveals that many elements of the design derive from sixteenth-century sources, especially prints by Albrecht Dürer (1471–1528). However, they arranged in a pastiche, a form of imitation that was uncommon in the 16th century but relatively common in the mid-to-late 19th century. The antiquarian revival of late medieval/early Renaissance forms is linked to the neo-Gothic movement, which took hold in Germany especially after unification in the 1870s. The treatment of figures, particularly facial profiles, shows influences of the English pre-Raphaelite movement of the 1850s through the 1890s. Analysis of the parchment treatment and printing inks was required to refine this re-dating. Parchment and inks were suitable for analysis because they were in good condition, excepting discolouration (especially visible on the verso) and a cut to the lower margin. A non-destructive approach was required, given the significance of this object. Preliminary unaided visual analysis, UV fluorescence and IR reflectography were used to investigate the surface and condition of the impression and to select the most promising areas for further analysis. Raman spectroscopy and XRF were used to identify pigments and treatments. Our results show that the parchment support is in good condition. The pigments of all six inks have been identified. The red ink combines cinnabar and minium (Fig.1B) and the black ink is carbon black. These three pigments have been used since antiquity and do not suggest a date of production. However, the other colours were produced from synthetic pigments or later recipes. The yellow ink is from chrome yellow, which was first

synthetized in 1809 [1]; the blue ink is Prussian Blue, a synthetic pigment that was introduced in 1724 [2]; and the green ink combines the two. The 'gold' ink is a false, made by cheaper elements like Cu, Zn and Pb. The printing inks reveal that the impression cannot have been printed before 1809. Raman spectra showed that the parchment had been treated with a cellulose based compound with a Zn compound (probably zinc white, which was manufactured from 1850 [3]). While this could have been applied at any point after the impression had been printed, for example during conservation, it was likely applied to prepare the parchment for printing. Analysis of the support reinforces the later dating and suggests that the impression was printed after 1850. The results of the art historical and chemical analyses suggest that this impression was printed after 1850 and before c.1900. In its conception and production, this artwork used then-modern methods and materials to pay homage to the styles and production techniques of the earliest German colour woodcuts.

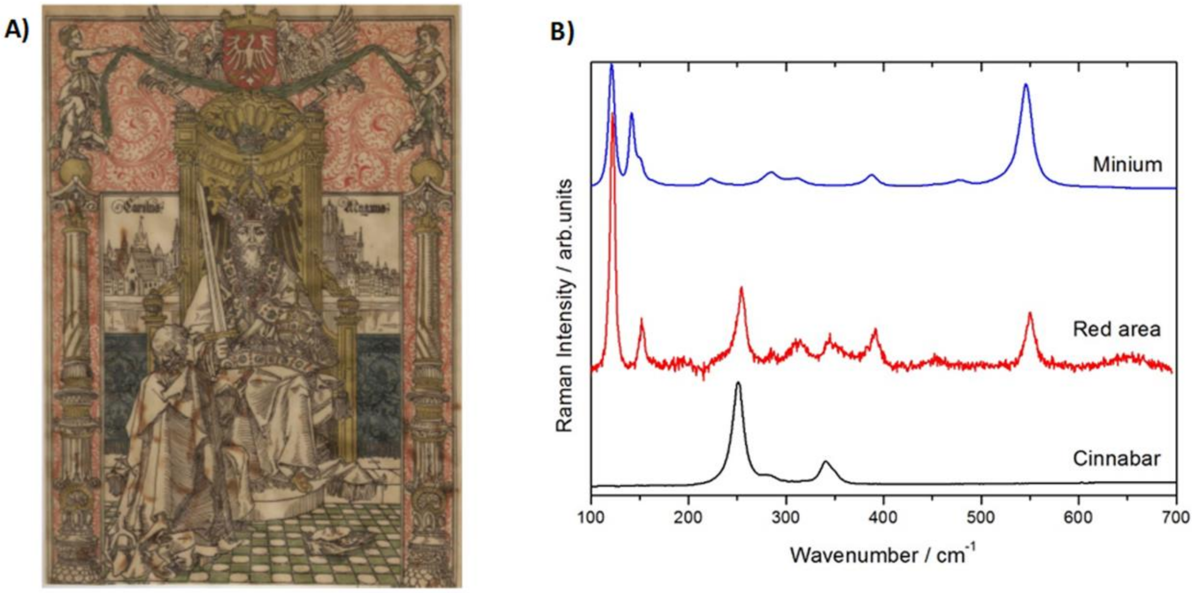

Figure 1: A) Anonymous, *Carolus Magnus*, relief print (21x29.3 cm) from six colours, private collection); B) Raman spectra of the red ink (red line) compared with Raman spectra of standard Minium (blue line) and cinnabar (black line).

[1] http://www.webexhibits.org/pigments/indiv/history/cryellow.html
[2] http://www.webexhibits.org/pigments/indiv/history/prussblue.html
[3] http://www.webexhibits.org/pigments/indiv/history/zincwhite.html

ABSTRACT P.01.28
IDENTIFICATION OF NATURAL RESINS BY FTIR-ATR SPECTROSCOPY ON CLEANING SWABS

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Keywords: FTIR, Resin, Varnish, ATR, Painting

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The identification of varnishes present on paintings is usually a complex task, due to the minimal invasivity required in the art analysis field. In addition, some of the most used portable contactless analytical techniques, such as Raman and X-ray fluorescence (XRF), often fails in this particular case; Raman, because of the strong fluorescence always present in the signal of aged varnishes, XRF because of the absence of characteristic elements allowing to identify the varnish.

The aim of the present research is the characterization of paint varnish by FTIR-ATR (Fourier-transform infrared absorption spectroscopy in attenuated total reflection geometry) performed directly on cleaning swabs. The very small amount of varnish present on the swabs can be identified, even when solvents are presents, reducing the invasivity of the method. No additional samplings are required, the only analyzed material being that removed during the cleaning process. The method has been deeply tested through the use of reference resins like amber, mastic, dammar and sandarac resins; they are used on their own and also in mixture with wax (as in the case of mastic and dammar resins) and oil (for amber resin). Spectral subtraction procedures has been applied in order to enhance the finish varnish spectra in the analysis of cleaning swabs used on the important 16th century oil painting Madonna col Bambino, San Giovannino e angeli, executed by Pomponio Allegri and from its 19th gilded picture frame. The method allowed the identification of the class of natural resins (diterpenoid and triterpenoid) and the presence of wax and oil in mixture with the natural resins.

ABSTRACT P.01.29
IDENTYFICATION OF BLACK PIGMENTS OF THE WORKS OF SZYMON CZECHOWICZ (1689-1775)

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Keywords: Szymon Czechowicz, XVIIIth century painting materials, Raman Spectroscopy, oil paintings, black pigments

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Szymon Czechowicz is the most important Polish painter of the 18th century. He commenced his artistic education at the court of Franciszek Maksymilian Ossoliński, who sent him for further studies to Rome around 1711. In 1716 he took part in the prestigious Clementine competition organized by the St Luke's Academy, winning the 3rd prize in second class for a drawing of Samson Killing the Lion and Victorious

Return from a Campaign. In Italy he also copied the works of famous painters, including Raphael, Reni, Rubens or Barocci. In 1731 the painter returned to Warszawa. He was a very productive "independent" artist, working for various patrons, both church and lay. He specialized mainly in religious themes but was also able at painting portraits of his patrons and state officials. Szymon Czechowicz had a large studio and taught numerous students. He left several hundred paintings which are mostly in churches, monasteries and museums in today's Poland, Lithuania and Ukraine.

Interdyscyplinary researches are a part of large project concerning characterisation of oeuvre, techniques and a technology used by Szymon Czechowicz and his students (1). In the period from 2012 to 2017, 50 paintings of the artist from the Polish, Lithuanian, and the Ukrainian collection were subject to IRFC, UV, RTG and IR tests. Samples were also taken for specialist tests such as XRPD, SEM-EDS, ATR-FTIR and RS.

Preliminary study of black pigments were done with SEM-EDS. Black points were analyzed in cross sections. These analyzes showed the presence of various kinds of carbons originating from soot, plant, but above all, bone. In certain cross sections there were identified both pure carbon and apatite, suggesting the use of different blacks in mixtures. Current literature does not discuss the use of such blends, as opposed to pigments of different colors or a mixture of different color pigments to obtain specific colors. There is some simplification in the interpretation of the results of conservation studies, which is to identify one dominant type of black pigment. To confirm the assumption of blending of different black by the artist, we have employed Raman spectroscopy. The spectra were measured with the microRaman, Senterra, Bruker Optik 200 spectrometer. The spectral parameters were as follows: laser power 1-10 mW at 785 nm, resolution 9-15 cm^{-1}, CCD temperature 223 K, laser spot of 2 µm, objective 50× and total integration time 1000 s (50 × 20 s). The spectra were collected and analyzed in order to identify composition of black pigments in all Szymon Czechowicz art activities. For the correct interpretation of the research results, we have made black patterns, which we have obtained by historical methods described in the treatises of the epoch. We also researched commercial products. For recognition of carbons we used ID/IG ratio, which is a recognized, major factor for distinguishing types of coals used.

It is well known that different I_D/I_G values mean different materials. The lower the value, the higher the contribution of graphite C (sp^2) and the smaller amount of amorphous carbon (sp^3). Black color research showed that the artist to use black did not use the only one type of black, but mixtures of two even three different black pigments.

The project was financed by the Polish National Science Centre under Decision DEC-2013/11/B/HS2/02585.

ABSTRACT P.01.30

IN SITU RAMAN SPECTROSCOPY OF MICROBIAL PIGMENTS FOR THE IDENTIFICATION OF BIOCOLONISATIONS ON ART OBJECTS

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Keywords: Carotenoids, Resonant Raman Spectroscopy, Mobile spectroscopy, Biodeteriogens, Biocolonization

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Many previous studies showed how Raman Spectroscopy can be successfully used as a micro-organisms investigation technique through the identification of carotenoids chains vibrational modes [1]. The studies were devoted mostly on the detection of bio-organisms in extreme environmental conditions (very low or very high temperatures, high salinity, lack of water, etc…) in view of space exploration missions. The intensity of the Raman spectrum of carotenoids under green or blue excitation is particularly high due to a resonance effect, making it a good candidate for the detection of many forms of life producing them, including bacteria, algae and lichens.

This work aims to apply this type of study to the field of cultural heritage, investigating the biodeteriogens present on stone and metal sculptures by P. Sciola, V. Ferrari and G. Spagnulo which are situated in the outdoor courtyard of the Study Centre and Communication Archive (CSAC) in Parma (Italy). In particular, most of the analysis were carried out on the surface of the opera semi della terra (earth seeds) realized by the Italian sculptor Pinuccio Sciola in 2008 on basalt. Other analysed sculptures are made by different materials such as trachyte and weathering steel.

This research wants to evaluate Raman spectroscopy possibilities and limits within the microorganisms characterization using carotenoids signals. The analysis have been carried out using a portable (handheld) Raman spectrometer (EnSpectr RaPort) with excitation laser line at 532 nm , suitable to obtain resonance Raman scattering from carotenoids, and a laboratory micro-Raman spectrometer (Horiba Labram) using the blue line of a doubled Nd:YAG laser at 473.1 nm, in order to compare the results and thus to estimate the possibility about the in situ study of biodeterioration.

[1] Jan Jehlička, Howell G. M. Edwards and Aharon Oren, Appl. Environ. Microbiol. 2014, 80(11):3286. DOI:10.1128/AEM.00699-14.

ABSTRACT P.01.31

INFLUENCE OF DISINFECTANTS ON NATURAL TEXTILE FIBRES

Drabkova K.*[1], **Krejci J.**[1], **Skrdlantova M.**[1], **Bacilkova B.**[2]

Keywords: textile disinfection, ethylene oxide, glutaraldehyde, Bacillol AF, Septonex

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Textile objects frequently occur in historical collections, archaeological findings as well as a part of archives. Cultural heritage objects are often contaminated by microorganisms. Therefore the disinfection is one of the most important steps during the conservation treatment with regard to occupational health and safety and also in terms of cultural heritage preservation.

Disinfection agents can be classified according to their effectiveness, to the means of application (immersion, spraying, gassing...) or according to the mechanism of the action (physical, chemical and physical-chemical).[1] Physical disinfection methods include, e.g. gamma radiation, controlled atmosphere of N_2 or CO_2, deep freezing. Chemical disinfectants utilize the action of various types of chemicals – e.g. alcohols, phenols, aldehydes, quaternary ammonium salts, epoxides, or metal nanoparticles.[1,2]

This work is concerned with studying the effect of different disinfectants on natural textile fibres (cellulosic and proteinaceous). The textile samples (cotton and silk) were artificially preaged before disinfection to simulate the treatment of old textile objects. Tested disinfectants were following: gamma radiation (doses 1.7, 4.5, 6.6 and 10.1 kGy), ethylene oxide, Septonex (karbethopendecinium bromide), silver nanoparticles, glutaraldehyde, Chiroseptol (glyoxal, glutaraldehyde, quaternary ammonium salts and alcohol ethoxylates), Bacillol AF (1-propanol, 2-propanol and ethanol) and butanol vapour. The dosage of the disinfectants was chosen according to the literature [3-6] or material safety data sheets. In case of glutaraldehyde and silver nanoparticles the dosage was estimated according to the testing of their antimicrobial effectiveness by disc diffusion test in National archive. The long-term stability of disinfected samples was also studied during an artificial ageing by moist heat, dry heat and light (imitation of day light).

Properties of textiles were measured before and after artificial ageing for disinfected and non-disinfected samples. Degradation changes were determined by means of viscometry, colorimetry, UV/VIS spectroscopy and tensile strength measurement.

There are only slight differences in results for cotton and silk. Gamma radiation significantly damaged both types of fibres; therefore it is necessary to find an alternative for mass disinfection. Application of the ethylene oxide seems to be the way, because we did not observe any substantial changes in the fibres structure. Silver nanoparticles (in tested form), glutaraldehyde and Chiroseptol are not suitable for disinfection of historical textiles because they cause considerable colour changes in treated materials. Also the changes in fibres chemical structure were observed in case of glutaraldehyde. Certain changes were noticed after treatment by Septonex, thus this disinfectant is feasible to use only in special cases (e. g. microorganisms sensitivity). Disinfectants based on alcohols (Bacillol AF, butanol vapour) are suitable for historical textiles conservation.

This work was supported by project of Ministry of Culture NAKI II (DG16P02R040).

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ABSTRACT P.01.32

INORGANIC-ORGANIC HYBRID COATINGS BASED ON AMIDOAMINE POLYMERS FOR BIOCIDAL ACTIVITY AGAINST CHLORELLA VULGARIS AND SCENEDESMUS ACUTUS ON TRAVERTINE STONE

Spina E.[1], Bergamonti L.*[2], Di Maggio R.[3], Graiff C.[1], Lottici P.P.[4], Predieri G.[1]

Keywords: polyamidoamines, biocidal activity, hybrid polymers, biocorrosion, Travertine stone

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Stone materials exposed outdoors or in high humidity conditions are subject to various forms of degradation, including the biological deterioration caused by various microorganisms such as bacteria, fungi and algae.

Inorganic–organic hybrid coatings based on polyamidoamines (PAAs) functionalized with hydroxyl and siloxane groups are here proposed as biocidal treatment for stone protection.

The polyamidoamines are characterized by the presence of amide and tertiary amino groups regularly distributed in the main chain. PAAs are obtained by polyaddition of bis-acrylamides with primary and secondary di-amines in protic polar solvents. The mechanism of addition of the amine to the acrylamide double bond is a nucleophilic addition 1-4 to the α, β unsaturated carbonyl compound according to Michael reaction [1].

Polymers are synthesized by reaction between N,N-methylenebisacrylamide (MBA) and ethanolamine (EtA) or aminopropyltriethoxysilane (APTES) and N,N dimethyl-1,6-hexanediamine (N2C6) as chain extender, at different molar ratios. For the biocidal tests the pH of polymers was controlled adding ethylenediaminetetraacetic acid (EDTA).

The products were characterized by Raman and FTIR spectroscopies, following the disappearance of the C=C bond stretching peak of bisacrylamide at 1629 cm^{-1} and by NMR spectroscopy following the appearance of the aliphatic CH_2 signals in the product.

The harmlessness of the treatment was tested on Travertine, the most famous Roman stone. Stone samples coated with different formulations were subjected to water capillary absorption and colorimetric tests, according to UNI EN 15801:2010 and UNI EN 15866:2010, respectively. The water capillary absorption considerably decreases and no changes in the appearance of the stone is observed. The mechanical properties investigated by compressive strength method and by freezing/thawing cycles evidenced an overall improvement after the treatments.

The biocidal activity of PAA was evaluated against two species of algae between the most frequently found on Travertine monuments, Chlorella vulgaris and Scenedesmus acutus. The C. vulgaris growth is inhibited with the PAA treatment at pH = 7.2. The result was confirmed by the recovery test. In cultural medium, S. acutus shows an evident inhibition of cell division in presence of the PAA without formation of coenobia but after recovery test about 80-90% of the cells resume their biological activity.

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ABSTRACT P.01.33

IN-SITU CHARACTERIZATION OF WALL MIRRORS FROM POMPEII BY MEANS OF LIBS AND RAMAN PORTABLE INSTRUMENTS

Veneranda M.[1], Fdez-Ortiz De Vallejuelo S.[1], Prieto-Taboada N.*[1], Marcaida I.[1], Maguregui M.[2], Morillas H.[1], Martellone A.[3], De Nigris B.[3], Osanna M.[3], Madariaga J.M.[1]

Keywords: Mirror, Pompeii, LIBS, Raman, Cultural heritage

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The house of the Gilded Cupids represents one of the most outstanding examples of patrician residence that can be found in the archaeological site of Pompeii (Italy). Thanks to the excavations started in the 20th century AD, several artworks and artefacts of inestimable value were discovered. Among them, the resumption of two wall mirrors attached to the east wall of the peristyle is particularly important due to the fact that, together with those recovered from the House of Efebo and the Domus of Euplia, are the only one conserved in Pompei.

In spite of the rarity of these objects, the hypotheses proposed so far about their composition and conservation issues have never been supported by specific analytical studies. In order to overcome this lack, portable analytical systems were used in situ with the purpose of analyze original and decay materials while avoiding sampling activity.

Concretely, molecular analysis were performed by means of an InnoRamTM-785S Raman spectrometer equipped with a 785 nm red laser (maximum power of 300 mW). Regarding elemental analysis an EasyLIBS IVEA (model Easy 2C) LIBS system was used. This instrument employs a pulsed Nd:YAG laser emitting at the fundamental wavelength of 1064 nm and is coupled to three spectrometers, covering the 196-1000 nm spectral range.

Raman spectra collected from the not degraded areas of the two mirrors provided equivalent vibrational profiles, consisting in an intense broad band between 1200 and 1650 cm^{-1} together with two weak signals at 795 and 1097 cm^{-1}.

According to bibliography, the broad band centred at 1350 cm^{-1} is a typical luminescence effect provided by glassy materials, while the band around 800 cm^{-1} and a massif between 950 and 1150 cm^{-1} are characteristic of obsidians.

The remarkable amounts of Ca, K Al and Na detected by LIBS analysis agree with Raman results. Indeed, high concentrations of those elements are characteristic obsidians and areresponsible for their brown-black colour[1].

In addition to those, hydrogen was alsodetected. After a deep bibliographic review, it was deduced that the presence of H is symptomatic ofthe obsidian hydration process. Indeed, is it well known that obsidian is a metastable igneous rock that reacts with atmospheric humidityleading to the formation of hydrated phases (such as perlite)[2].To verifythis hypothesis, the LIBS system was used. Considering that LIBS analysis generates a crater with an approximate depth of about 5 microns, multiple shot on the same point were performed to remove the hydrated layer until reaching the inner part of the obsidian.

As shown in figure 1, the intensity of the main hydrogen emission line decreased systematically until the 8th shot. The observed trendindicates that a hydration layer waspresent and, shot after shot, it was completely ablated (the remaining hydrogen signal represent the contribution of atmospheric water).

This project has been funded by the MADyLIN project (ref BIA2017-87063-P) funded by the Spanish Ministry of Economy and Competitiveness (MINECO) and the European Regional Development Fund (FEDER).

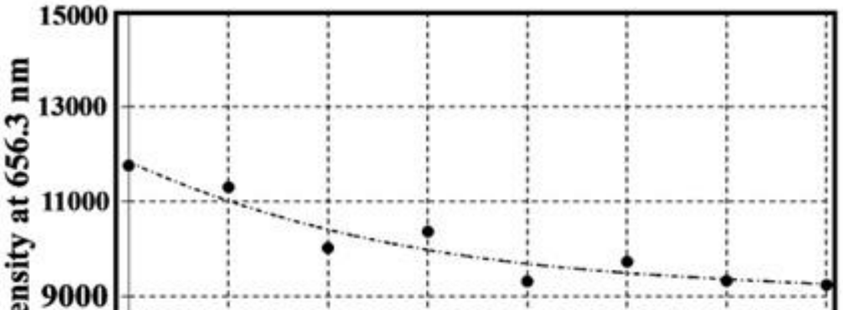

Figure 1: Graph showing how the intensity of the main hydrogen LIBS emission line decreases as a function of the number of laser shots.

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ABSTRACT P.01.34

LOCKED IN A COPPER BOX? THE MYSTERIOUS STORY OF THE GREEN MUMMY OF BOLOGNA

Bridelli M.G.*[1], **Bersani D.**[1], **Saragoni L.**[2], **Mazzotti M.C.**[3], **Fersini F.**[3], **Pelotti S.**[3], **Luiselli D.**[4], **Traversari M.**[5]

Keywords: green mummy, copper box, histology, Infrared and Raman spectroscopy, SEM-EDX

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In this paper are described the preliminary results of the analyses performed on a naturally mummified body found in the basement of an ancient mansion in Bologna and currently stored in the museum Centre of the Forensic Medicine section of the University of Bologna. The skeletal and soft tissues of the fortuitous recovery are all green colored but a leg. The remains were therefore identified as the “green mummy”. This feature, in addition to the body posture, displaying the neck bent ahead on the chest and the legs folded back, suggested hints to hypothesize that the body could have been pushed and pressed in a copper box or urn. The “green mummy” is the body of a teenager (11-14) as gathered from both the ossification and the teeth. The skin tissues are preserved only in some body districts, such as the thorax and the left leg. The mummy displays some other soft tissues in a quite good preservation state, such as spinal cord, pleura, ligaments, trachea, vessels, and, extraordinarily the brain. The TC scanned images of the body helped to exclude osseous pathologies and the genetic analyses are in progress to define sex and health conditions [1]. Histological analyses on soft tissues revealed that they are fairly preserved. In particular, the mesenchymal structures and their alterations are recognizable, while an important cell lysis is present, which, however, does not prevent the recognition of histogenesis. The nuclei appear hyperchromatic and immersed in a diffuse cytoplasmic rhyme due to the phenomena of cell lysis. Fourier Transform InfraRed (FTIR) spectroscopy was applied to the various tissue fragments collected from different body districts. The wave number region between 1800 and 1000 cm^{-1} was used as a fingerprint for skin proteins and lipids. The characteristic protein bands Amide I and II appear shifted and enlarged, revealing a partial deterioration of the collagen component of the tissue [2]. The protein degradation is associated with the presence of the fatty acids bands in the high wave number region (2850, 2886 cm^{-1}, CH stretching), at 1750 (C=O), at 1576 cm^{-1} (calcium salt of fatty acids) and 1310 cm^{-1} (CH bending) mainly attributable to the early stage of adipocere development on the tissue during the starting post-mortem phases. SEM measurements confirm FTIR results. The fibrous structure of collagen fibers is only locally apparent in areas floating within a flake and blob surface typical for lipid accumulation. EDX analysis showed the presence on the surface of significant amount of Ca, K, and P, testifying the presence of fatty acids and a large amount of Copper, responsible for the green coloration of the mummy tissues. Raman measurements revealed the presence of Copper smeared on the skin surface [3]. Various crystalline forms were detected, like Malachite and Sampleite. The preliminar results suggest that the body, locked in the Cu-box could have started the degradation processes developing the adipocere formation, before beginning the mummification processes. Such compounds conveyed Cu ions of the holder to the body tissues, where they crystallized on the soft tissues and penetrated into the bones.

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ABSTRACT P.01.35

MASS SPECTROMETRY TO INVESTIGATE DEGRADATION PHENOMENA OF MODERN OIL PAINTINGS IN JPI PROJECT: "CMOP-CLEANING OF MODERN OIL PAINT"

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Keywords: Mass spectrometry, Chromatography, Modern Oil Paint, JPi Project, Analysis

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The aims of the Heritage+ JPI project: "CMOP-Cleaning of Modern Oil Paint" (2015-2018) [1] include advancing our knowledge on the molecular causes and mechanisms related to the condition of unvarnished modern oil paintings.

Traditionally, oil paints were prepared by hand in artists' ateliers: raw materials were purchased and paints were prepared according to traditional recipes. The industrial revolution brought technological changes that affected the production and quality of artists' materials. Manufacturers' paint formulations developed, to include a wider range of pigments and oil binders, and incorporating additives. Modern oil paint included both traditional drying oils, and new drying and semi-drying oils in the formulation, together with industrial oleo-chemicals such as hydrogenated or partially transesterified drying oils. Metallic salts, metal soaps, and a variety of dispersion agents, plasticizers, fillers, surfactants could also be added to paint formulations, to achieve and modulate different properties such as viscosity, drying rate, working properties and shelf-life.

The diversity of artists' uses of oil paint from the 20th century including thickly applied impasto and diluted paint media, together with the preference for display of unvarnished paintings left the surface exposed and vulnerable to deterioration from environmental influences.

Modern paintings made in oil media present specific conservation problems due to phys-ical and chemical degradation of the paint [2]. These include colour change, formation of medium skins on paint surfaces, efflorescence, protrusions, dripping paint and paint delami-nation. During surface cleaning by conservators, these paintings can also exhibit water- and solvent-sensitivity, however the causes of these phenomena are not yet fully understood.

The present investigation of the organic composition of modern oil paints is aimed to characterize the chemical composition of paints that exhibit water sensitivity during cleaning using water. New analytical

methods employing a combination of gas chromatography/mass spectrometry (GC/MS) [3] and liquid chromatography/mass spectrometry (HPLC/MS2) [4] were developed for the characterization of mixtures of free fatty acids, glycerides and metal soaps in paint samples. These methods proved suitable to provide detailed data on changes in the molecular composition of oil paints constituents upon curing and ageing.
GC/MS and HPLC/MS2 together with direct infusion electrospray ionization mass spec-trometry (ESI-MS) were used to investigate oil binders in selected oil paintings, in paint from Talens, Old-Holland and Winsor & Newton naturally aged for 10 years and submitted to arti-ficial ageing, and in water sensitive Winsor & Newton paint swatches from 1945-2003 [5].
The results showed that the processes involved in paint curing, oxidation and polymeri-sation, including their dependence on the pigment and the particle size, as well as hydrolysis and saponification, all appear to play a fundamental role in determining the water sensitivity of modern oil paints.

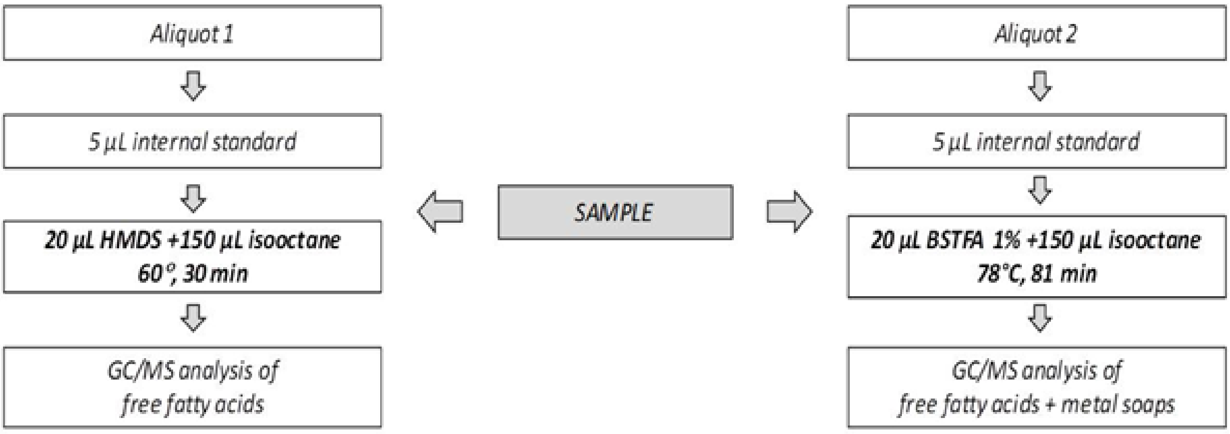

Figure 1 –Procedures for the characterization of free fatty acids and metal soap by GC/MS analysis [3]

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ABSTRACT P.01.36

MICRO-INVASIVE AND NON-INVASIVE APPROACHES TO DETECT MADDER LAKE IN FINISHING LAYERS OF BOWED STRING INSTRUMENTS

Fiocco G.*[1], Rovetta T.[1], Gulmini M.[2], Piccirillo A.[3], Canevari C.[4], Licchelli M.[1], Malagodi M.[1]

Keywords: Musical instruments, Madder, Varnish, FTIR, FORS

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Madder extracts from Rubia spp. have been widely used over time as both mordant dyes for textiles and lake pigments in paintings [1]. The possibility of obtaining a number of red and brown shades and a remarkable ease of use have made madder one of the most popular materials used by various artists. On these grounds, the analytical characterization of madder represents one of the most interesting and significant topic in the domain of Cultural Heritage diagnostics. On the other hand, identifying the presence of madder lake in a complex multi-material and multi-layered system could be a challenge. Some experimental procedures have been already carried out on several artworks [2], although in the field of historical musical instruments research, the results concerning the characterization of madder lake still made room for hypothesis, due to photodegradation processes [3] and to the low concentration of the pigment dispersed in the varnish.

In order to reproduce real situations, model samples of madder lake dispersed in different organic binders have been prepared according to historical recipes for musical instruments [4] and artificially aged in a solar-box up to 520 hours. The study of the considered materials has been carried out by means of non-invasive and micro-invasive analytical approaches. The multi-technique investigation has involved UV-Induced Fluorescence imaging, FORS, colorimetry, µFTIR, XRF, Optical Microscopy and SEM-EDX with the aim of obtaining information on the characteristic features of the madder lake pigment dispersed in different organic binders, before and after the aging treatment.

As expected, significant variations between t=0h (Figure 1a) and t=520h (Figure 1b) have been observed under the optical microscope with visible and UV illumination: the lake particles dispersed in proteinaceous and oily binders have mostly changed their colour from bright red to white. The characteristic FORS signals for madder at 510–515 nm and at 540–545 nm were detected only on model samples aged up to t=72h. On the other hand, characteristic IR bands of madder at 1644 cm^{-1} (C=C aromatic bands) and 1415 cm^{-1} (C-H bending bands) (Figure 1c_1) have been observed not only in the spectrum measured at t=0 (Fig1c_3) but even at the end of the ageing process (t=520h, Fig1c_2) although their intensity has been slightly modified. Sulphates bands of the alum substrate (potassium-aluminum sulphate) has been identified at 1115 cm^{-1} and 984 cm^{-1}. The Al, S, K, Ca peak intensities collected by XRF (analysis spot 1,2 mm) could be considered qualitatively comparable between t=0h and t=520h; similar results were highlighted by the single lake grain analysis through SEM-EDX (Figure 1d).

In conclusion, the results obtained by combining non-invasive and micro-invasive approaches allowed us to identify and characterize the madder lake in several models samples. From this point, the spectroscopic multi-analytical results, extended to some real case studies, may represent a reference for the investigation of finishing treatments on musical instruments and, possibly, on other wooden artworks.

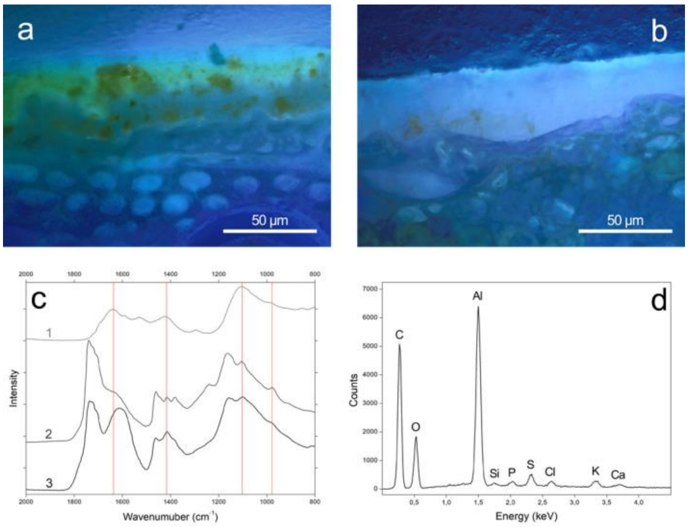

Fig. 1

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ABSTRACT P.01.37

MIXED-MODE SPE FOLLOWED BY GC-MS ANALYSIS TO DETERMINE WATER SOLUBLE ORGANIC COMPOUNDS IN AEROSOL AND HISTORICAL MORTARS AFFECTED BY MARINE ATMOSPHERE

Blanco-Zubiaguirre L.[1], Cabezas A.[1], Carrero J.A.[1], Fernández L.Á.[1], Olivares M.[1], Castro K.*[1], Prieto-Taboada N.[1], Madariaga J.M.[1]

Keywords: GC-MS, Mixed SPE, Air pollution, Dicarboxilic acids, Aerosol

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The unquestionable value of Cultural Heritage has brought the scientific community to make significant efforts to slow down the decaying processes that these materials can suffer. Atmospheric pollutants present in marine aerosol such as water soluble organic compounds (WSOCs) can be the chief factor of the decay of these materials. Nevertheless, the matrix complexity together with their chemical nature and low concentration levels make the determination and quantification of these compounds a scientific challenge. This work describes the development of an analytical procedure for the determination of short chain dicarboxylic acids (C_2-C_{10}) both in aqueous and solid matrices such as mortars. The developed and validated methodology was based on the preconcentration of compounds by means of mixed-mode solid phase extraction and gas chromatography-mass spectrometry, regardless the analyzed samples. In the case of solid samples, a prior extraction of target compounds using focused ultrasound solid-liquid extraction was required. The method was applied to detect dicarboxylic acids in marine aerosol water samples and in mortars of a 20th century historical building placed in a coastal environment (Punta Begoña, Getxo, Biscay, Basque Country). According to the results, harbor activities may have an effect in the concentrations of dicarboxylic acids found in both matrices since the side exposed to the harbor appears to be more contaminated.

ABSTRACT P.01.38

MUSTIDISCIPLINARY STUDY OF LISBON EARTHQUAKE OF 1755 CANVAS PAINTING BY PORTUGUESE PAINTER JOÃO GLAMA STRÖBERLE

Valadas S.*[1], **Machado A.**[2], **Serra E Moura T.**[3], **Cardoso A.**[1], **Manhita A.**[1], **Candeias A.**[1]

Keywords: 18th century Portuguese canvas painting, Material characterization, µ-FTIR, SEM-EDS, Py-GC-MS

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João Glama Ströberle, a Portuguese-born painter (1708 - 1792) of German descent, started his artistic career in Lisbon studying with painter Vieira Lusitano and other portuguese painters. In 1734 he left for Rome where he integrated the famous Academy of St. Luke and became member of the Arcadia Romana. João Glama returned to Portugal seven years later and was in charge of several artistic projects (e.g. mural paintings of the Royal Theater of the Paço). However, it was through his last work, the unique painting in the world allusive to Lisbon Earthquake of 1755 (a catastrophic moment that he witnessed) that he gained a reputation. This painting, belonging to the Nacional Ancient Art Museum deposit, received new attention during an intervention process supported by surface examination, allowing to underline remaining questions related to the technical aspects of artistic production, the motifs represented in the painting and the historical facts of the catastrophe. Complementary micro-analytical research was performed by combining stratigraphic analysis related to representative areas of painting (giving information about layers built-up, pigments' mixtures and granulometry) with high sensitive laboratory chemical analysis. Relevant information about pigments and binders used in this painting was obtained by micro-Fourier transform infrared spectroscopy (µ-FTIR), scanning electron microscopy coupled to energy dispersive X-ray spectrometry (SEM-EDS), and Pyrolysis–Gas Chromatography/Mass Spectrometry (Py-GC/MS). The combined state-of-art analytical tools revealed that over the canvas support, on twill linen, the artist applied two layers of a grayish preparation, composed mainly by calcite and smaller additions of lead white, yellow ochre and carbon black bounded in linseed oil. The artist´s palette includes: lead white, calcite, yellow, red and brown ochres, lead antimonate yellow (Naples yellow), vermillion, Umber, Prussian blue, green earth, carbon black and ivory black. Integrated research revealed that changes of composition / non-homogeneous pigment mixtures / layers build-up are related to different stages of painting execution - the painter´s last and unfinished work. The study of this iconic painting is fundamental for comparison with

other works from the initial period in order to understand the evolution of the technique of his artistic production and the influences of artistic context (Portugal vs Italy). On the other hand, the study of this painter’s work is essential to understand the profound changes that occurred in the Portuguese art during the Baroque period.

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ABSTRACT P.01.39

NEW CONSOLIDANTS BASED ON CNC FOR DECAYED WOOD

Basile R.*[1], Bergamonti L.[2], Fernandez F.[1], Graiff C.[3], Haghighi A.[4], Isca C.[3], Lottici P.P.[5], Pizzo B.[6], Predieri G.[3]

Keywords: Cellulose Nanocrystals, Wood degradation, Wood consolidant, XRD, Dynamic Mechanical Analysis (DMA)

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Wood, thanks to its particular aesthetic characteristics and mechanical properties, is one of the oldest materials used in a large variety of human artefacts. Wood is very sensitive to physical, chemical and biological degradative processes. Current treatments adopted for historical wood conservation often have undesirable side-effects which can have an impact on the aesthetical and mechanical characteristics.

This work is an attempt to obtain new consolidants based on cellulose, naturally compatible with wooden substrates. Cellulose nanocrystals (CNC) were selected as nanoscale constituent for renewable reinforcing agents for decayed ancient Norway spruce (Picea abies L.) wood.

Suspensions of cellulose nanocrystals (CNCs) were prepared by typical sulfuric acid hydrolysis starting from α-cellulose. The crystalline nature of nanocellulose was confirmed by XRD analysis and Raman spectroscopy.

The coatings tested were CNC and CNC mixed with lignin and/or PDMS. The evaluation of the consolidant efficacy of the CNC based products on rotted wood samples was tested by means of Dynamic Mechanical Analysis (DMA)

The CNC sol was applied on wood sample by total impregnation, under vacuum. The mechanical tests results confirm the consolidant efficiency of the CNC appreciably improving the stiffness properties of the decayed wood.

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ABSTRACT P.01.40

NON DESTRUCTIVE CHARACTERIZATION STUDY OF PICENES GLASS BEADS

De Ferri L.*[1], Mezzadri F.[2], Falcone R.[3], Quagliani V.[4], Milazzo F.[5], Pojana G.[1]

Keywords: Iron age, Raman spectroscopy, beads, XRD, FORS

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Studies carried out in the last decades defined that two main ethnic groups existed along the Italian Adriatic coast from the beginning of the Iron Age to the Romans conquest: Japigi and Sabelli, which were in turn divided into various tribes, including Picenes, living in the current coastal area of the Marche and of the northern Abruzzo regions between the 1st millennium B.C. and the 3rd century A.D.

The excavations of two Picene necropolises in Novilara (9th-7th century B.C, PU) and Matelica (9th-6th century B.C., MC) uncovered various grave goods including many colored glass, shell and bone-based beads.

A non-invasive characterization these beads has been performed by means of analytical techniques such as Reflectance and Raman spectroscopy and X-Ray diffraction.

Raman spectroscopy resulted particularly useful in the characterization of shell and bone based beads, displaying the typical spectra of calcite and Ca-phosphate, respectively, parallel reflectance spectroscopy gave information about the use of different chromophores in blue glass beads: as expected spectra of the darker samples contain the typical features of tetrahedral Co^{2+} ions, while data obtained from the two light blue beads available, coming from the Matelica necropolis, showed no traces of this metal but only the spectral profile deriving from the presence of Cu^{2+} ions. As known from literature, turquoise glass was commonly used during the Bronze Age, while cobalt started to be employed as a colorant during the Final Bronze Age in association with copper and then became the dominant metal to obtain dark hues due to its high colouring efficiency.

Both Reflectance and Raman Spectroscopy allowed the identification of hematite as the colouring agent of the only red bead available, coming from the Novilara necropolis. This is a very peculiar result, since no literature data have been reported so far, to the best of our knowledge, about the use of hematite in glassy beads dated to the Iron Age.

White and yellow samples were mainly studied by XRD: in both cases the use of traditional opacifiers such as Ca and Pb antimonates was demonstrated. Yellow samples in particular displayed the presence of lead pyroantimonate ($Pb_2Sb_2O_7$), whose diffraction peaks could be well distinguished over the broad glass structure; on the contrary, the collection of patterns from white samples, exhibiting a black surface decorative coating, gave results that were more difficult to interpret.

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ABSTRACT P.01.41

NON-INVASIVE FTIR STUDY ON EXPERIMENTALLY HEATED BONES AND CREMATED HUMAN REMAINS FROM ARCHAEOLOGICAL SITES

Legan L.*[1], Leskovar T.[2], Crešnar M.[2], Cavalli F.[3], Innocenti D.[3], Ropret P.[1]

Keywords: Bone, Reflection FTIR spectroscopy, Non-invasive analysis, Thermal degradation, Archaeology

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Bones from archaeological contexts can reveal valuable information about the various aspects of life in the past. Degradation of bones starts with the death of an organism and can be accelerated by different factors, as funeral practices (e.g. cremation on pyre), burial environment (e.g. acidic soil conditions), post depositional changes etc. Whatever the way, degradation processes are unavoidable and have a strong impact on the chemical and morphological structure of bone. [1]

In this work, non-invasive reflection FTIR spectroscopy was utilised in order to investigate its ability for determination of chemical composition and degradation phases of bones exposed to heat. For that purpose, pieces of unaltered fresh bovine femur were exposed to different temperatures ranging from 300°C to 1200°C using 300°C temperature increments. At each temperature interval (300°C, 600°C, 900°C and 1200°C), four pieces were heated for 30 to 120 minutes using 30 minutes time steps.

As expected, the non-invasively obtained reflection spectra were distorted by specular and diffuse components of reflection light, therefore, the comparison with standard ATR modality was necessary. Moreover, total reflection spectra of bovine femurs were transformed also by Kramers-Kronig (KK) algorithm to correct specular reflection anomalies. However, comparison of band position in k – index and in ATR spectrum shows large deviations in band shifting (more than 25 cm^{-1}), which indicates a large contribution of diffuse reflection.

Furthermore, the presence of volume reflection in total reflection spectra of bones exposed to heat gives rise also to diffuse-enhanced spectral features such as combination bands and overtones.[2] These undistorted bands are increased in the reflection mode spectra and provide additional information about chemical composition of examined bones (i.e. combinations and overtones of $PO_4^{3-}$and CO_3^{2-} modes). In this spectral range (1900 – 2700 cm^{-1}), also v_3 stretching vibration bands of cyanate (NCO-) and cyan amide (NCN^{2-}) [3] ions are visible that arise after the thermal treatment of bones (see Figure 1).

It was found that the total reflection spectra give much more vibrational features, e.g. due to dehydroxylation of thermally degraded bones, than ATR. All these additional information was then successfully used for characterisation of archaeological bones excavated from different Slovenian archaeological sites.

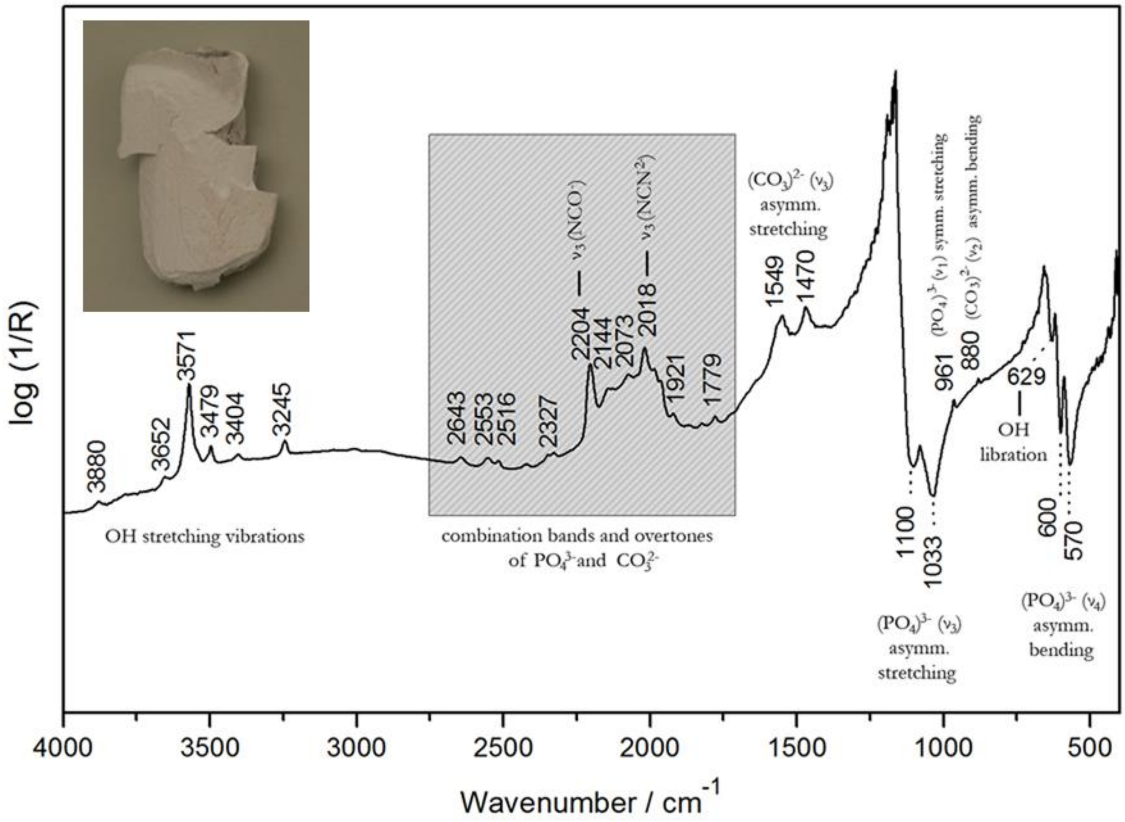

Figure 1: Example of reflection FTIR spectrum of thermally degraded bone (T = 1200 °C, t = 30 min). The inset shows the image of thermally degraded bone.

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ABSTRACT P.01.42

NON-INVASIVE SCIENTIFIC ANALYSIS OF DESIGNS FOR WOVEN SILK AT THE VICTORIA AND ALBERT MUSEUM

Manca R.*[1], Burgio L.[2], Button V.[2], Rutherston J.[2], Horsfall Turner O.[2], Browne C.[2]

Keywords: Non-invasive analysis, In situ analysis, Imaging, Multianalythical approach, Pigment identification

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The Victoria and Albert Museum (V&A, London) has recently promoted the multidisciplinary study of the a set of designs for woven silk - the so-called Leman Album - relying on the synergy between curators, conservators and scientists.

The Leman Album designs were produced in London in the first half of the 18th century and represent one of the earliest surviving examples of designs for woven silk [1]. They were painted with watercolours and body-colours on paper and are almost always signed by James Leman, a renowned weaver and designer of the period [2].

The identification of the pigments and dyes used in the Leman Album designs was the main objective of the scientific analysis undertaken. Moreover, the research focused on obtaining information on the degradation processes suffered by the colouring materials and, in general, on the techniques and materials used. Finally, an attempt was made to decipher some of the autograph inscriptions by James Lemans, which are not readable since they are written on the reverse of the designs, which in turn are glued on a paper support.

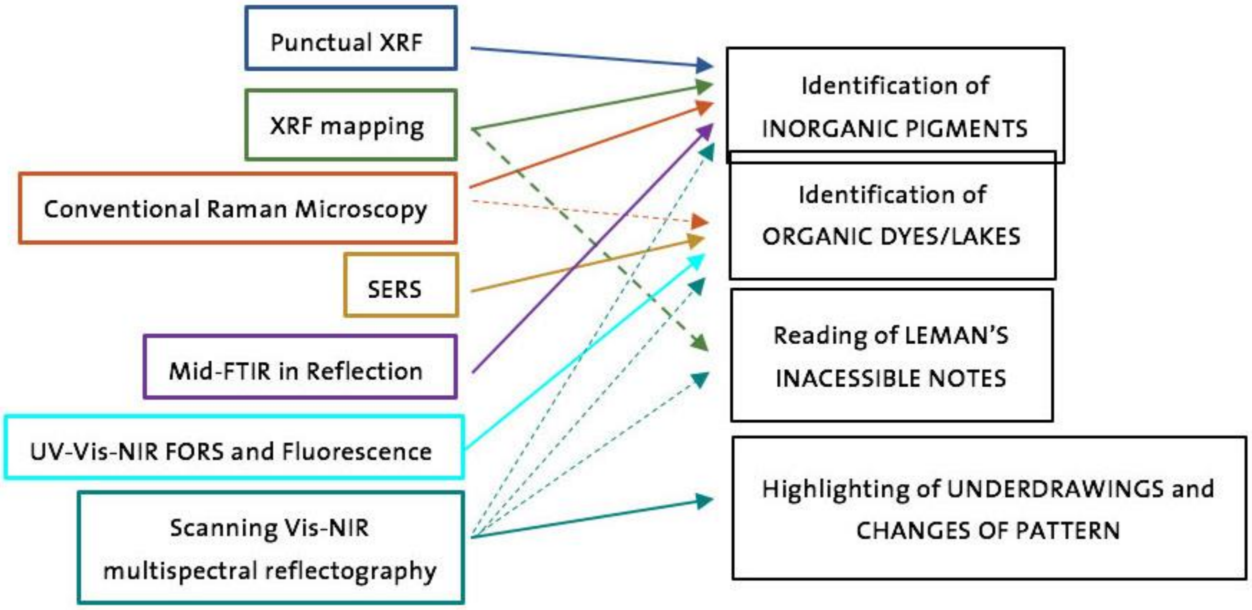
An extensive, non-invasive analysis campaign was conducted inside the museum, thanks to the availability of the equipment present in the scientific laboratories of the V&A, as well as the intervention of MOLAB, a mobile laboratory for the analysis of cultural heritage [3]. The analytical methods used were optical and Raman microscopy, SERS, punctual and scanning XRF spectroscopy, Fourier-transform infrared, UV-Vis-NIR reflectance and Vis-NIR emission spectroscopy, scanning Vis-NIR multispectral and NIR hyperspectral reflectography (Figure 1). The use of non-invasive techniques - or minimally micro-destructive ones in the case of SERS – yielded a comprehensive set of complementary data which strengthened each other. The multi-analytical approach adopted has proven extremely successful: some of the limitations of the individual techniques could be counterbalanced and most of the colouring materials used, as well as some degradation products, were identified. In many instances, the results obtained from different analyses corroborated each other and could, therefore, be considered as more reliable.It was also possible to obtain some technical information on the paper and glues used in the Leman Album.

The legibility of Leman's handwritten notes on the reverse of some of the designs was significantly increased by means of multispectral reflectography. However, the proper deciphering of the text is still rather arduous. The inks used for the notes were identified as iron-gall inks. In addition to this, multispectral reflectography enabled to highlight interesting characteristics of the pencil underdrawings and the presence of pentimenti.

In conclusion, this study represents a valuable scientific contribution to the investigation of the Leman Album, also considering that this is the first time that such a complete diagnostic study is performed on objects of this kind. A wide range of analytical results were obtained and will help in classifying better the Leman Album textile designs from a material point of view and in gaining new information on the

availability of pigments and dyes in eighteenth-century London. They will also assist in the conservation of the designs.

Access to Research Infrastructures activity in the H2020 Programme of the EU (IPERION CH Grant Agreement n. 654028) are gratefully acknowledged.



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ABSTRACT P.01.43

ON THE FOOTSTEPS OF THE ANCIENT GLASS MAKERS: TOWARD AN EXPERIMENTAL GLASS CLASSIFICATION BY USING RAMAN SIGNATURE BASED ON ROMAN GLASS REPLICAS

Raneri S.*[1], Masotta M.[1], Fornasini L.[2], Marino M.[2], Barone G.[3], Mazzoleni P.[3], Lezzerini M.[1], Lottici P.P.[2], Bersani D.[2]

Keywords: Raman spectroscopy, ancient glass and replicas, experimental petrology, Raman signature, non-destructive methods

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In the last decade, Raman spectroscopy has been applied successfully to non-invasive characterization of ancient glass, allowing to differentiate composition and toexploreaspects as glass maker technology and dating [1-3]. One of the most used methods in the field of art and archaeology, proposed for the first time by Colomban et al. [4], is based on the relation between the structure of silica glass and its Raman signature. In particular, the band arearatio (A500/A1000) of the Si–O bending - at 500 cm^{-1} - and stretching - about 1000 cm^{-1} - was proposed as polymerization index. Further information is obtained by the analysis of the wavenumberand relative amplitude of the different Si–O stretching components, related to the Q_n units constituting the glass. The method has been widely and successfully applied on numerous ancient glass [4 and references therein], providingan empirical approach to classify different "glassy silicate families".

The aim of this work is to investigate the dependence of the Raman spectra of silica glasses on their compositions, fabrication procedures (fluxing agents and quenching environment) and on the experimental setup (kind of spectrometer and, mostly, excitation laser line). Their influence on the polymerization index and on the apparent changes on the Q_n stretching bands is evaluated. For this scope, we created and analyzed a series of artificial glass samples (named SR1-14) resembling ancient Roman ones, with a compositional rangeshown in Fig. 1.

The compositional data have been determined by EMPA analysis. Micro-Raman measurements have been performed on artificial glass by using different laboratory micro-Raman apparatus, with 632 to 473 nm excitation wavelengths, and a portable Raman with 532 nm excitation. Spectra have been processed in order to determine parameters as the polymerization index and Si–O bands frequencies and intensities. The obtained results have been therefore compared with reference glassand discussed on the basis of compositional data.

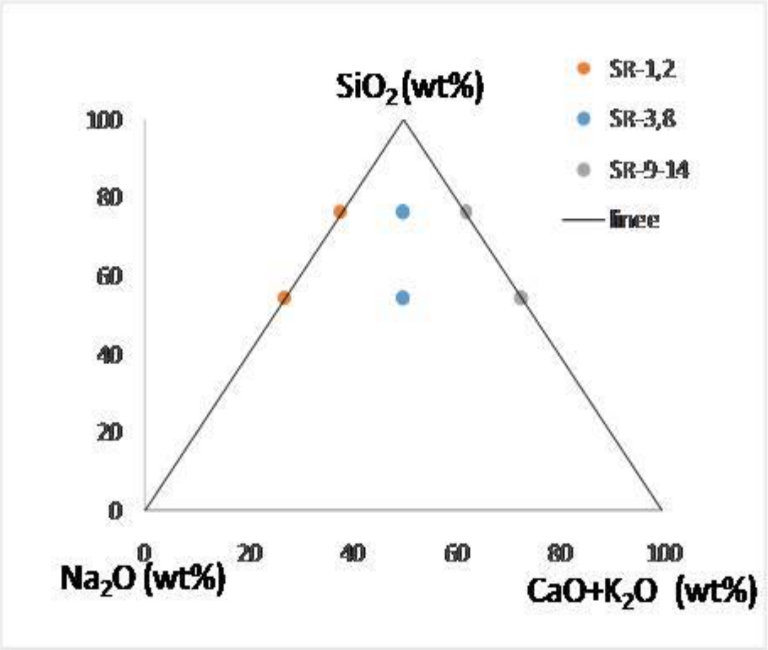

Figure 1. Composition of artificial glass made resembling Roman ancient glass. SR1-2 : Na_2O >>CaO + K_2O; SR3-8:Na_2O = CaO + K_2O; SR 9-14: Na_2O <<CaO + K_2O. Quenching in oxidizing conditions.

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ABSTRACT P.01.44

PIGMENT ANALYSIS AS DATING TOOL: MULTI-ANALYTICAL STUDY OF THE PAINTING FIORI (OIL ON CANVAS, 20TH CENTURY), ALLEGED TO FILIPPO DE PISIS

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Keywords: dating, pigments, fake/counterfeit, SEM/EDS, MicroRaman

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In the field of dating and authentication of artworks, the opinions of art experts have long been a crucial role in the final judgment. The study on authenticity has usually been based on the comparison of the style and the artistic technique of investigated painting with that of originals artworks attributed to the artist [1]. Since the 20th century, scientific disciplines have increasingly played an important role in these researches and, though they cannot prove alone the authenticity, they can sometimes disprove an early dating and/or support the case for authenticity [2-4]. In fact, the identification of artistic techniques and materials provides useful information not only for conservative purpose and restoration projects but also it can reveal the presence of anachronistic pigments. The possible presence of these pigments may be easy detected by traditional pigments analysis in ancient paintings but it encounters new and complex problems in Modern and Contemporary paintings, which are mainly constituted by artificial pigments, commonly considered as “dating”. For this reason, in depth pigments analysis is required: the study of the morphology of pigments particles, chemical – mineralogical composition, etc. allows to better understand the origin of pigments (natural or artificial, ancient or modern, etc.), exploiting therefore the pigments’ timelines for dating purpose [5]. The present work shows results of dating studies on “Fiori” (Flowers), a painting attributed to Filippo De Pisis (1896-1956), renowned Italian artist. The painting (oil on plywood) was accompanied by an expertise of Giovanni Commisso, but the date of realization is unknown. In addition to identify artist palette and technique, preliminary diagnostic survey (diagnostic by imaging, optical microscopy) and X-ray fluorescence spectrometry were performed in order to select areas for in depth investigation and for samples collection. Results by optical and electron microscopy, crossed with Micro-Raman spectroscopy data, confirmed that the pigments used in this artwork are compatible with the period of artist (1896-1956), suggesting a painting’s achievement between 1923 and 1957. The author thanks Professor Carmela Vaccaro (University of Ferrara, Italy) for providing unlimited access to analytical facilities and contact with owners of the studied painting. Thanks are also due to the owner of the paintings. Financial support for the study was provided by University of Ferrara - Laboratory TekneHub - Physics and Earth Science department (Ferrara, Italy), grant Tit. III, Cl.11 - N.79 – Prot. N. 1485 (2011).

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ABSTRACT P.01.45

POLYAMIDOAMINES AS PRESERVATIVES OF RESTORATION ADHESIVES FOR PAPER

Antonazzo V.*[1], Bergamonti L.[2], Branchi M.[3], Isca C.[1], Lottici P.P.[4], Ossiprandi M.C.[5], Predieri G.[1], Reverberi C.[5], Tireni L.[6], Zanella F.[3], Bondioli F.[2]

Keywords: Paper adhesives, Polyamidoamines, Biocidal activity, Bacteria, Fungi

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Traditionally, adhesives of natural origin are used to repair and adhere paper-based materials: starch paste, cellulose ether, arabic gum, and animal glue or gelatine. Rice starch and cellulose ether, thanks to their affinity with paper substrate, are widely employed in paper restoration. Rice starch is preferred by restorers because of its high adhesive properties, but it shows low stability against biodeteriogens, insects and molds. To improve the resistance of the adhesives to biodeteriogen attack, rice starch and cellulose ether were mixed to polyamidoamine (PAA), whose biostatic activity both against insects and molds is known. Polyamidoamine (PAA) is synthesized by Michael reaction, adding ethanolamine to methylenebisacrylamide in water. The PAA solution was mixed with rice starch (RS/PAA) and Klucel G (K/PAA), a cellulose ether, at concentration of 4% (w/V). Samples were studied as films or applied to different kinds of paper: straw paper as support for modern paper (Art graphics BM), Fabriano paper as support for "collage" paper and tracing paper. The viscosity of RS/PAA decreases with increasing PAA content while the opposite is observed for K/PAA. Thanks to the deacidification properties of PAA , both papers glued with functionalized adhesives gave neutral/basic pH. Paper samples were subjected to accelerated ageing under Osram Vitalux lamp irradiation. Raman spectra show that the addition of PAA gives no oxidation features after ageing. The biological tests were made on pure adhesives and on glued paper applying the Kirby-Bauer method. Different bacterial species (Pseudomonas aeruginosa, Vibrio fluvialis, Bacillus subtilis, Sarcina lutea, Actinomyces naeslundii and Capnocytophaga spp) and fungal species (Aspergillus niger and Penicilium spp) were tested. The results on pure adhesive show that Pseudomonas aeruginosa, one the most resistant bacterial species, was inhibited by the presence of PAA in the adhesives whereas the other bacterial species are resistant to the PAA addition to adhesives. Aspergillus niger and Penicilium spp. were also sensitive to PAA biocidal effect. Tests on glued paper were conducted with Aspergillus niger and Penicilium spp. Paper samples pasted with PAA-functionalized adhesives show fungal growth slightly lower than pure paper. This result may be explained by the fact the adhesives do not migrate on the upper surface of the paper layer (or in negligible manner), as confirmed by Raman spectroscopy. The polyamidoamines are therefore useful to preserve the adhesives used in paper restoration from the biological attack. They can also be employed to prevent the biodeterioration on cellulosic materials as well as paper artifacts.

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ABSTRACT P.01.46

PRESERVING THE COLOR OF CONTEMPORARY ART: IDENTIFICATION OF COLORANTS IN PLASTIC MATERIALS

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Keywords: Contemporary art, in situ techniques, plastics, multi-analytical approach, colorant identification

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The molecular characterization of colorants in plastics represents a fundamental step in supporting the conservation of plastic artworks. In fact, the chemical structure of chromophore and its chemical surrounding play a key role in assessing the stability of colorants in plastic.

Following exposure to light, colorants (pigments and dyes) can degrade which may result in a change of colour. In works of art made of plastic, this phenomenon is able to dramatically affect appearance and perception. Discoloration of plastic artefacts has been observed and reported as sign of alteration by the conservation community [1]. Although photochemical mechanisms to explain the fading of dyed and pigmented polymers have been proposed [2], a systematic study on degradation mechanisms is needed. The objective of this work is the characterisation of colorants in plastics.

To provide color, very small amounts of colorants were added during plastic formulation (0.5%-5%) [3] making their characterization a methodological and analytical challenge. In the conservation science pioneering studies by de Groot [4-5] report the suitable combination of Raman spectroscopy and Py-GC/MS analysis on microsamples for the identification of organic pigments in plastic objects. In this work, preliminary results of colorant characterization by using in situ molecular and elemental techniques (without micro-sampling) are presented. This first step of colorant identification supports the further investigation of discoloration in plastic artefacts providing new insight into their molecular photodegredation mechanisms in well-defined experimental research design.

Coloured acrylic and cellulose acetate samples belonged to the major Portuguese artists of the 20th century, Ângelo de Souza (1938-2011), Lourdes Castro (1930-) and José Escada (1934-1980), were selected as case studies and analysed through a multi-analytical approach. µ-EDXRF analysis permitted the distinction between organic and inorganic colorants, while Raman microscopy was employed for the molecular characterization at the micrometre scale of the colorant in the plastic medium (Fig.1). In addition, Fibre optic reflectance spectroscopy (FORS) in the 350-2200 nm range was used to study the reflectance profile of the colorants. Given the influence of the chemical environment in the colorant stability, microspectrofluorimetry was used to investigate the luminescence of the colorants and their condition by comparing results from acrylic and cellulose acetate. The potential, efficacy and limits of the methods used will be discussed together with consideration of the inherent complexity of the system studied.

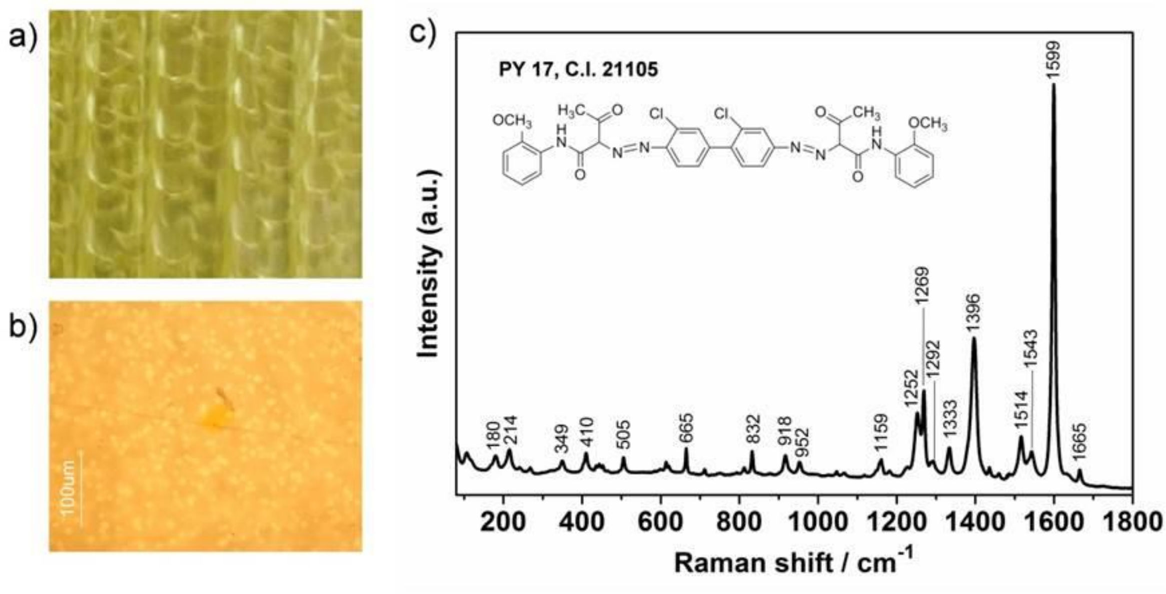

Fig.1 – a) yellow acrylic remnant found in the studio of Ângelo de Souza; b) reflected light microscopy in bright field of yellow particle in the acrylic sample; c) Raman spectrum of the yellow particle (laser 632.8 nm). The Raman bands found accordance with the vibrational pattern of diarylide yellow PY 17 (C.I. 21105).

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ABSTRACT P.01.47
PROVENANCE OF THE EUROPEAN GLASS BEADS OF LUMBU (MBANZA KONGO, ANGOLA)

Costa M.[1], Barrulas P.[2], Dias L.[2], Lopes M.D.C.[3], Barreira J.[4], Clist B.[5], Karklins K.[6], De Jesus M.D.P.[7], Da Silva Domingos S.[7], Moens L.[8], Vandenabeele P.*[9], Mirão J.[10]

Keywords: Mbanza Kongo, Kongo Kingdom, glass beads, provenance, colorants and opacifiers

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Glass beads, often in large quantities, have been found in many archaeological sites in central and southern Africa. These beads, used as adornments and currency, weren't produced locally, but introduced initially via the Islamic mercantile network and the Indian Ocean trade, and later (since the 15th century) by European traders [1–4]. Based on morphological and chemical analysis, glass beads assemblages have been attributed to distinct production centers, allowing a better understanding of the consumption patterns and economic interactions in place in the region throughout time.

This study focusses on the chemical characterization of the European trade glass beads found in Lumbu (Mbanza Kongo, Angola). Located in the capital of the Kongo Kingdom, Lumbu is thought to be either the site of the Royal palace, or an area used by the King to hold public audiences when important state matters were being decided. The archaeological excavations carried out in 2014, uncovered glass beads and pottery and pipe fragments.

Thirty-three glass beads, subdivided into 19 distinct typologies were studied by means of a multi-analytical minimally invasive methodology, which included handheld X-ray fluorescence (hXRF), variable pressure scanning electron microscope coupled with energy dispersive X-ray spectrometry (VP-SEM-EDS), micro-Raman spectroscopy, micro X-ray diffraction (μ-XRD) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS).

The determination of the raw materials used and probable provenance were the main aims of this study. The process of glass coloring and opacification was also studied in an attempt to determine the technology available in the production of these artefacts.

Acknowledgments

The authors would like to thank the Angolan Government for funding the archaeological excavations carried out in the city of Mbanza Kongo during 2014 and the archaeological laboratory work conducted in 2015.

This work has been financially supported by a Concerted Research Action (GOA) of Ghent University, by Starting Grant No. 284126 of the European Research Council awarded to Koen Bostoen and by the Special Research Fund of Ghent University. The financial support of the Fundação para a Ciência e Tecnologia's (FCT) project UID/Multi/04449/2013, and the financial support given by the FEDER funds through the COMPETE 2020 project POCI-01-0145-FEDER-007649, is also acknowledged.

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ABSTRACT P.01.48

REACTIVITY OF FATTY AND TERPENIC ACIDS AS A POSSIBLE INTERPRETATION OF DRYING OILS AND NATURAL RESINS INTERACTION IN REAL PAINTINGS

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Keywords: metal soaps, smalt, resins, potassium hydroxide, abietate

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Metal soaps formation in paintings is a well-known phenomenon related to many degradation processes [1]. Those compounds are the result of interactions between cations from pigments and free organic acids from binding media and varnishes [2]. Despite their diffusion, their formation mechanism is not fully understood. Metal carboxylate formation is often related to oil-based paintings, but few cases of metal soaps formation in egg yolk and resins are reported. An aspect that hasn't been investigate yet is the formation of metal soaps in mixed binding media, like the ones obtained by mixing a siccative oil and a natural resin, where a variety of different fatty and terpenic acids is available. In order to investigate this aspect, we set up some simple reactions of saponification involving a cation (here represented by potassium, from potassium hydroxide (KOH)) and two different organic acids: palmitic acid and abietic acid. The first, a saturated fatty acid, is contained in drying oils, the second one is the main component of colophony, a natural resin [3]. The course of each considered reaction has been monitored for 12 hours through the acquisition of 50 (one every 15 minutes) ATR-FT-IR spectra. The experimental set-up consisted in 5 systems: a mixture of abietic acid and KOH (1:2 in weight-mixture A), a mixture of palmitic acid and KOH (1:2 in weight-mixture B), a mixture containing all the three reactants together (0,5:0,5:2 in weight-mixture C), a system obtained by adding abietic acid to mixture C after 24 hours (1:1:2 in weight-mixture D) and a system obtained by adding palmitic acid to mixture A after 24 hours (1:1:2 in weight-mixture E). The two neo-formed metal carboxylate involving a single acid (abietic and palmitic) showed two well-defined carboxylic bands at 1541 cm^{-1} and 1561 cm^{-1}, respectively. As predictable, when the two acids were simultaneously put in contact with the KOH, both the previously observed bands arose. The amount of KOH

was enough to react with both the acids. A different reactivity occurred when an acid was added to a previously formed carboxylate. In mixture D, after the addition of abietic acid to palmitate, the band at 1561 cm^{-1} disappeared in 15 minutes and a sharp band centered on 1541 cm^{-1} appeared instead: abietic acid subtracted the K^+ cation from palmitate. In mixture E, after the addition of palmitic acid to abietate, the carboxylic band split in a doublet (1537 cm^{-1} and 1545 cm^{-1}) and a new one, with a lower value of absorbance, appeared as a shoulder at 1561 cm^{-1}: palmitic acid reacted with the remaining KOH and showed no ability in subtracting K^+ from abietate. However, the splitting of the abietate carboxylic band underlined a probable interference in the organization of the previously formed carboxylate. This means that natural resin can form metal soaps reacting directly with pigments, as previously assessed, but also that in real painting layers metal soaps migrating to the surface can further react with the varnishes to form new molecular aggregates. This behaviour is very interesting since, differently than in our simplified experimental setup, in real samples it's almost impossible to distinguish the bands of potassium carboxylates (for examples coming from smalt layers) arising from fatty acid (drying oil) and the ones coming from terpenic acids (natural varnishes). This difficulty is due the broadening of the carboxylate bands reflecting the higher complexity of a painting system (pigments particle size, ageing of binders or varnishes, heterogeneous composition of drying oils and natural resins). Further analysis will investigate on this aspect, since loss of potassium is one of the main causes of degradation of an important artistic blue: the smalt pigment [4] .

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ABSTRACT P.01.49

RESEARCH AND MAINTENANCE OF ICONS WITH GILDING AND PUNCTURING KNOWLEDGE OF ANCIENT PAINTING TECHNIQUES IN THE ASPECT OF SUSTAINABLE DEVELOPMENT

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Keywords: Icons, puncturing, non invasive research techniques, sustainable development, gold

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The scientific objective of the research task is to carry out the interdisciplinary research on the writing workshop of the icon of St. Mitrofan Bishop from Voronezh, the examination of all technological layers, analysis of technique and technology, and documentation of the reconstruction of the "Icon Painter" workshop.

Dr K. Wantuch-Jarkiewicz, dr M. Wachowiak performed X-ray fluorescence (XRF) method

- non-invasive method for painting layers on wooden substrate portable by XRF spectrometer.

The results of the XRF study showed that the icon was painted on chalky soils, on which gilding was made(a silver-gold flake called a bipedal, used in iconic painting since the 14th century) on a red background - bolus, lead white, with the addition of baryte white with the use of red iron, gnats, umbras and cinnabar. Blues were painted by using ultramarine, Prussian blue, organic blue.

Analysis of samples taken from the icon were made by Anna Nowicka, MA. Elżbieta Jeżewska, MSc. (wood sample analysis) and Marek Wróbel ,MA. (SEM-EDS analysis).

Studies have shown that the paint layer contains chromate green (mixture of Prussian blue and chromate yellow - lead chromate) with white pigment, presumably white barium (indicated by the shape and size of the grain). The paint layer contains cinnabar, presumably artificially obtained, and organic red. Microscopic examination showed that the wood was made of alder (sp Alnus). The filler used in the mortar is plaster.

Recognizing the icon's content and how it is written, we get valuable information about the workshop and the period in which the work was created. The results of our research and knowledge of art history deepen the knowledge of the artist's workshop. The results of the study are certainly helpful in the attribution and dating of similar art monuments.

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ABSTRACT P.01.50

REVEALING THE ANCIENT POLYCHROMY OF TWO ZODIACAL TABLETS (2ND CENTURY AD) USING X-RAY FLUORESCENCE MAPPING

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Keywords: ancient polychromy, X-ray fluorescence mapping, reconstitution, alteration, conservation treatments

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The diptych is composed of two zodiacal tablets dated from the 2nd century AD and conserved with their lids at the departmental museum of Epinal (inventory number 2013.0.217). They were deliberately broken and thrown in a well in Grand in France. They were discovered during an archeological excavation in 1967-1968 with an other zodiacal diptych now conserved in the national archaeology museum of Saint-Germain-en-Laye in France, and several heterogeneous objects dated from the end of the 2nd century. These two only knows diptychs could have been used for the astrological divination and medical healing in the prestigious Gallo-Roman sanctuary of Grand. The tablets were made in large elephant defenses, engraved with sharp tools and colored. Helios and Selene are visible at the center of the diptych. They are surrounded by the twelve signs of the Zodiac probably made from an Egyptian model, letters in Greek alphabet, Egyptian divinities named in old Coptic. Finally, winged creatures are represented in the corners. Conservation treatments done in 1968 on the damaged tablets, have regrettably induced a significant loss of polychromy and a whitish deposit. The aim of the present study was therefore to identify the nature of the constituent materials, their origins and their states of preservation in order to propose a reconstitution of the ancient polychromy.

Scanning X-ray fluorescence analyses were achieved using a prototype developed at the C2RMF with a Mo X-ray tube and a SDD detector (Eveno et al. 2014, Ravaud et al. 2016). The system is mounted on an X-Y motorized translation table. Taking into account the fragility of the diptych, analyses were exceptionally performed with a horizontal configuration and the set-up was securely fixed over the tablets. Datas were acquired using a current of 40 kV and an intensity of 1000 µA, with a spatial resolution of 200 µm and an exposure time of 200 ms. For each pixel, fluorescence spectra were then treated using the PYMCA software to get elemental maps (Solé et al. 2007). Additionally analyses were performed on four micro-samples prepared as cross-section by scanning electron microscopy coupled with energy dispersive spectroscopy.

The complementary use of elemental distribution images, cross-section analyses and scientific photographs enabled us to distinguish the original polychromy, altered components, as well as conservation products. Regarding the original polychromy, black areas are mainly composed of galena, red areas of vermilion and beige areas of orpiment. Few traces of gold were also detected. The blue grey areas are however not original. They have been identified as vivianite, an iron phosphate containing traces amount of magnesium and manganese. As ivory is composed of calcium phosphate, the formation of iron phosphate may result from an ionic substitution of calcium by iron. During the conservation treatments of 1968, lacunas were

fulfill with walnut panel and a brown putty composed of lithopone and a ferrous compound. The whitish deposit are probably plaster residues coming from a plaster mould made after the excavation. All these results enabled us to purpose a restitution of the ancient polychromy that will undoubtedly help conservators and historians to study the iconographical and stylistic composition (figure 1). This case study demonstrates that scanning macro X-ray fluorescence is a useful technique to recover original polychromies.

Figure 1 : Tablet of the Moon. (left) Visible light photography of the actual state of preservation. (right) Ancient original polychromy reconstitution. Traces of gold are not represented.

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ABSTRACT P.01.51

SISSI@ELETTRA: AN INFRARED SYNCHROTRON LIGHT ON CULTURAL HERITAGE

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Keywords: Synchrotron Light, FTIR Spectroscopy, SISSI beamline, Microscopy, Cultural Heritage

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The use of Synchrotron Radiation (SR) for the investigation of samples of historical and artistic importance has been increasing over the past years, and experiments related to Cultural Heritage have been routinely performed at many beamlines of Elettra, the Italian synchrotron radiation facility, covering almost 12% of the total submitted proposals. In this poster presentation we aim to present to InArt2018 interdisciplinary audience the capabilities and advantages of infrared synchrotron radiation for FTIR spectroscopy and microscopy in the field of Cultural Heritage, potentially in combination with other SR techniques such as X-ray fluorescence and UV-resonant Raman spectroscopy. We will introduce the infrared beamline at Elettra, SISSI (Synchrotron Infrared Source for Spectroscopy and Imaging), and specifically instrumentation available at the SISSI-Chemical and Life Sciences branchline: a Bruker VERTEX 70v FTIR spectrometer coupled with the Hyperion 3000 Vis/IR microscope equipped with MCT or FPA detectors for single-point analyses and chemical images respectively, and FIR-MIR setup for FTIR analysis on the entire IR spectral range in one shot [1]. Special emphasis will be given to the sampling in diamond anvil cell (DAC), without any additional embedding of the material. This technique, often applied in our laboratory for Cultural Heritage samples, enabled us to obtain maximum transmission of the IR radiation through formally thick and hard samples, without the need of slicing and/or polishing.

Through a series of examples, taken from experiments of our users, we will demonstrate the performances of the laboratory for the investigation of a plethora of samples, from different cultural and historical contexts. By exploiting SISSI laboratory capabilities we could obtain information on the chemical composition of prehistoric chewing gum and roman inks [2], on the paining techniques of ancient Greek frescoes [3], [4], on the degradation processes undergone by pigments, ancient parchments and sacred books, as well as on the nature of minute food remains on prehistoric grinding stones.

The upcoming upgrade of the IR beamline with an infrared spectroscopy endstation able to provide chemical details with nanometric resolution will be also disclosed, highlighting the extraordinary impact that it could have for revealing chemical and morphological heterogeneity with unprecedented spatial resolution.

Figure 1: panel A: bird's eye view of SISSI – Chemical and Life Sciences branchline (Photo courtesy of CERIC-ERIC, Photographer: Roberto Barnabà); Panel B: Diamond anvil cell sample preparation.

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ABSTRACT P.01.52

SPECTROPHOTOMETRIC STUDY OF EARLY MEDIEVAL TILES AND BEDDING MORTARS FROM NONANTOLA (MODENA, ITALY) EXCAVATIONS

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Keywords: Tiles, FT-IR spectroscopy, Mortars, Raman spectroscopy, Surface alteration

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A large amount of cover bricks, mainly tiles of various sizes, were found during archaeological excavations carried out in the courtyard of San Silvestro Abbey in Nonantola (Modena, Italy). Recovered tiles were adapted for flooring the room of a monastic building belonging to the second half of the IX century and excavated in 2004, 2006 and 2009. A second, smaller and less homogeneous, group of tiles was found in the drainage pits of a IX century furnace containing thermo-modified fragments, other fragments employed to cover a burial tomb and 5 elements re-used to build a drainage duct of late medieval structures.

Many fragments exhibited peculiar characteristics, such as the presence of a grayish-white granular material on the lateral parts (the so-called wings) and on the back of some tiles, and chromatic differences on the surface of some findings. These aspects were investigated by means of vibrational techniques such as FTIR-ATR and Raman spectroscopy comparing spectra of the granular encrusting material to those of residual bedding mortars: while in some cases matching of data indicated the use of the same kind of coarse lime-clay-sand mortar used to locate tiles on the floor, in other cases the encrusted material was positioned on the side constituting the floor surface, and resulted enriched in calcite in both coarse and fine fractions. As a consequence, this material was interpreted as due to the production process and it was sprinkled with sand or, as in this case, lime coarse powder, probably to avoid adherence of the ceramic clay to the formwork.

Cross sections were realized in order to investigate chromatic difference of tiles surfaces, and fragments could be classified into two groups. The first group displayed a gradual lightening from the ceramic body to the surface, also resulting lowered in clay minerals and enriched in calcite, quartz and feldspars. This different distribution of the components within the internal and the external parts could be due to the surface treatment with a spatula, aimed to smooth the surfaces, and such process was probably accompanied by the adding of a liquid component, possibly diluted lime.

The second, more in-homogenous, group showed a surface layer clearly distinguishable from the ceramic body, and compositional differences within the samples concerning both surface layers and ceramic bodies could be detected. Diversities regarded mainly the amount of calcite: taking into account excavation data, evidencing two hearts on the floor, it can be supposed that the prolonged contact with flames lead to the disappearance/reduction of calcite from some tiles, whose layers were probably obtained similarly to the so-called barbottina technique. It involved the use of a mixture of water, clay and small amounts of lime applied on the ceramic body before smoothing through a spatula. This surface treatment could be aimed to different goals, such as a peculiar chromatic effect on the roofing of buildings, or the protection from atmospheric agents, showing this layer only the tiles exposed surfaces.

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ABSTRACT P.01.53

SPECTROSCOPIC CHARACTERIZATION OF MURAL PAINTINGS SAMPLES FROM THE PAESTUM NECROPOLIS (ITALY)

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Keywords: Raman, Pigment, Cross-section, Necropolis, Wallpaintings

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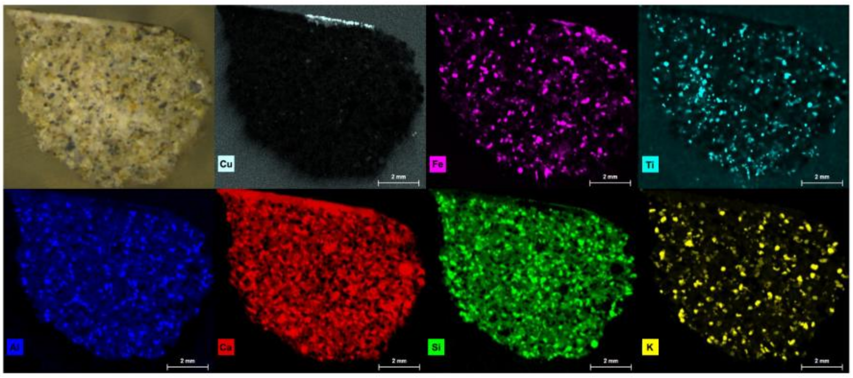
The present work concerns the study of 13 samples from the necropolis of the archaeological site of Paestum located in the centre of Italy. The samples analysed were taken from painted slabs that covered the burials, currently preserved in the National Archaeological Museum of Paestum. They are datable between the 6th century B.C. to the first decades of the 3rd century. The excavations have been carried out since the 1980s and they have revealed a corpus of tombstones of Lucan funerary art, which is one of the most important example of pre-Roman mural painting in Italy.

The samples, representative of the various tones, were analysed in the form of cross-section using Raman spectroscopy and X-ray microfluorescence with the aim to identify the original materials used for the mural paintings. The palette of the artist’s pigments was fairly limited: Raman analyses showed the features of iron oxides, hematite and goethite, Egyptian blue, anatase, and black bones . The green tone was given by the mixture of a yellow and a blue pigment as no green pigment has been identified. In addition, quartz, rutile and augite were found in the plaster. Although most of the wall paintings have been made with fresco technique, in the pictorial layer of a dark sample, the presence of beeswax was identified as binding

medium. Elemental analysis obtained by X-ray microfluorescence was compared with the molecular information from Raman spectroscopy. In particular, they have been useful for the characterization of samples where a thick layer of plaster is also visible: the elemental maps of the pictorial layer and mortar confirmed the results obtained by Raman spectroscopy showing the presence of different mineral phases.



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ABSTRACT P.01.54

SPECTROSCOPIC METHODS AND STATISTICAL ANALYSIS APPLIED ON ARTIFICIALLY AGED SAMPLES OF AMBER

Badea G.I.*[1], Caggiani M.C.[2], Mangone A.[2], Colomban P.[3], Teodor E. D.[1], Teodor E. S.[4], Rudu G.L.[5]

Keywords: FT-Raman, ageing experiment, statistical analysis, amber, FTIR

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Amber is a fossil resin, with special colors and textures, appreciated for its beauty and used as jewelry or in curative purposes since early times. There are many well-known species of amber: Baltic amber, Dominican amber, Sicilian amber (simetit) and the amber from Romanian Carpathians (Rumanite or Romanite).

In the present work, we report the experimental results that refer to spectroscopic methods applied on two categories of artificially aged sample of amber (Baltic and Romanian) and the statistical interpretation of data using principal component analysis (PCA).

Infrared and Raman spectroscopy are extremely powerful analytical techniques, for both qualitative and semi-quantitative analysis, which offer the possibility to identify inorganic and organic molecular species, therefore, any kind of sample, large or small, optically perfect or imperfect, colorless or colored.The key advantage of Raman spectroscopy is that requires little to no sample preparation, while the Fourier transform infrared (FT-IR) method has constraints on sample thickness, uniformity, and dilution to avoid saturation. In Raman technique water does not cause interference and the spectra can be collected from a small volume (1- 50 µm in diameter). Combining two complementary techniques, such as IR and Raman spectroscopy, can lead to a decrease in uncertainty of a single analysis and becomes a powerful tool in performing materials characterization. In this case, due to the great similarity between Baltic and Romanian amber, both spectroscopic methods were employed and data were processed by means of statistical analysis allowing the establishment of criteria for distinguishing between the two varieties of resins.

Ten geological samples (five from each source—Romanian and Baltic amber), in duplicate, were subjected to artificially ageing experiments in five different media (air, water, saline, acid and basic) for 12 weeks. The samples were analyzed before and after the alteration experiment and the acquired spectra were statistically processed by multivariate data analysis (PCA).

The statistical analysis applied successfully confirmed that the two categories of amber have different behavior in terms of direction and degree of alteration during the experiments, and Romanian amber is the most affected by the hostile environment when compared to Baltic samples. During the ageing experiment the Baltic amber turns into something very close to our definitions for romanite. This observation confirms the hypothesis of Stout et al. that romanite is thermally altered Baltic amber. That alteration can occur not only in geological strata but also during thermal treatment applied while crafting amber artefacts. For Baltic samples the alteration of the spectra results less evident and the differences between the spectra are attenuated with respect to romanite.

The optimized FT- Raman technique (laser 1064 nm, power on sample ~ 190 mW and 2000 scans per sample) coupled with statistical analysis represent a promising set of tools for amber artefacts analysis. The results of the experiment are useful in giving a better picture of how to discriminate between archaeological amber artefacts.

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ABSTRACT P.01.55

SYNTHESIS, CHARACTERIZATION AND BIOCIDAL ACTIVITY OF SILVER NANOPARTICLES FOR CULTURAL HERITAGE APPLICATIONS

Alfieri I.[1], Bergamonti L.[2], Fernandez F.[3], Lazzarini L.[4], Lorenzi A.[1], Lottici P.P.[5], Potenza M.*[1], Predieri G.[1], Sambo L.[1], Sanangelantoni A.M.[1]

Keywords: Ag nanoparticles, biocidal actiity, biological attack, biocorrosion, Lecce stone

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The deterioration processes of stone monuments exposed in outdoor conditions are determined by physical, chemical and biological causes. The biodeteriogens produce the formation of surface-covering biofilms that, besides the aesthetical damage, promote even the alteration of the mineral structure of the material thanks to the mechanical pressure due to the shrinking and swelling of the biofilm. In addition, the biocorrosion processes act as precursors for the formation of black crusts [1]. Silver nanoparticles, ions or salts are known to possess antibacterial and antimicrobial activity and are applied in medicine as a medium for antibiotic delivery, to synthesize composites for use as disinfecting filters and coating materials. The biocidal properties of Ag-nanoparticles depend on their stability in the growth medium that guarantees high retention times for bacterium–nanoparticle interaction. Here, silver nanoparticle sols are proposed as preservatives against biological attack for the application in cultural Heritage field.

Ag nanosol was synthesized in water at room temperature starting from silver nitrate ($AgNO_3$) using Allium cepa extract as reducing agent and compared with Ag nanosols obtained by Lee–Meisel method by thermal reduction of $AgNO_3$ with sodium citrate or sodium borohydride. All the synthesized silver nanosols exhibit pale to dark yellow colour. The sols monitored for 6 months are stable as confirmed by UV/Vis absorption spectra: the peak at 416 nm is compatible with nanoparticle size of about 10 nm. Spherical nanoparticles of 10-15 nm are indeed revealed by TEM.

The biocidal activity of Ag nanosols was tested in microplates on Gram-positive and Gram-negative bacteria (Escherichia coli and Bacillus subtilis), fungi (Aspergillus niger and Saccharomyces cerevisiae) and algae (Selenastrum capricornutum). Minimum Inhibitory Concentration (MIC) was determined: E. coli was inhibited at low concentration of Ag nanoparticles (6 µM), whereas growth inhibitory effects on B. subtilis, fungi and algae are observed for slightly higher concentration. Observations by the Scanning Electron Microscope show evident cracks in the cellular membrane and dehydration due to silver nanoparticles action on E. coli cells.

The nanosols were applied on plaster and Lecce stone as inhibitors of microbial growth. Tests performed on S. capricornutum and A .niger demonstrate their biocidal efficiency: on treated stone surface no fungal or algal growth was registered, whereas on uncoated stone after 24h the biofilm formation was evidenced.

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ABSTRACT P.01.56

TEXTILE TAGS OF HISTORICAL SEALS MADE OF BLACK DYED SILK AND POSSIBILITIES OF ITS STABILIZATION

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Keywords: textile tag, black dye, silk, stabilization, seal

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Textile tags made of dyed silk yarns were often used to attach seals on historical documents. They were often made of tabby woven ribbons or of braided cords varying in thickness and colours. The black dyed ones have usually been damaged more than those of different colours. They are very frequently in such bad condition that the seal is nearly detached from the document which would result in its invalidity. The fibres of such badly damaged textile tags are fragile, they chalk and there is ultimate need for preservation intervention.

The dyeing process

Mordant dyes (including tannins as the basic substance) were often used to dye silk to achieve black shades. There were many different sources of tannins used for dyeing. Tannins are present most frequently in plant tissues, particularly in bark, fruit skin and damaged parts of plants.

Mordants facilitate the bonding of the dye to the fabric via metal cations that might however later catalyse degradation of the textile. The most frequent mordant used to dye silk was iron(II) sulphate.

Damaging silk during the dyeing process

Increased temperature during the dyeing process can cause partial hydrolysis of silk fibres. Iron that was brought to the system by the mordant oxidizes during the dyeing process and binds to the compound in its +3 oxidation number.

Acidic conditions or just increased humidity can cause decomposition of the compound and release of Fe ions that can subsequently catalyse radical oxidation and degradation of the material. The process of acid hydrolysis can occur simultaneously.

Possibilities of black dyed silk stabilization

Stabilization of damaged black dyed silk has been explored to a much lesser extent than stabilization of iron gall ink on paper. Possibilities of chemical stabilization include neutralization and application of antioxidants. In case of paper documents, neutralization results in removing the acids present in the material and an ‘alkaline reserve’ is deposited in the material – usually in the form of calcium carbonate or magnesium carbonate. Application of antioxidants is run through peroxide decomposition or metal binding to the compounds.

Unlike cellulose materials, silk is more resistant to acidic conditions than basic conditions. As most stabilization procedures have been developed for cellulose materials, they use the ‘alkaline reserve’ and their suitability for silk is yet to be confirmed.

Influence of pH on silk stability

In order to discover the possibilities of stabilization, influence of different pH values on silk was investigated. Samples of unbleached silk were exposed to pH values 3, 5, 7 and 8 for the periods of 1, 2 and

3 weeks. The experiment monitored changes in colour, thread tensile strength and limiting viscosity number of silk. The results indicate that solutions of different pH values have not had particularly harmful effects on silk fabrics. Only samples of silk that were exposed to border pH values manifested slightly higher changes in colour. In these cases, the total colour difference was 0.8 and 0.9 for pH values 3 and 8 respectively. However, such changes have not been significant.

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ABSTRACT P.01.57
THE COLOURS OF "BARBABLÙ"

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The topic of this work deals with the scientific results obtained thanks to a diagnostic campaign, which was carried out, through non-invasive and non-destructive methodologies, on the famous "head of Hades" popular also as Barbablù. The sculpture is conserved at the Museo Archeologico di Morgantina in Aidone, a town in Southern Sicily and its name derives from the colour of the beard. The head, belonging to a statue of human dimension, is dated, on stylistic basis, to hellenistic age (400-300 B.C.) and it represents the god of underworld. It seems that its original collocation was the sanctuary of Demeter, site in Saint Francesco Bisconti in Morgantina [1]. Different techniques were performed in situ on the coloured surfaces and they allowed the pigments identification.

After the return to Sicily of the terracotta head representing the god Hades by the Getty Museum [2,3], the sculpture was object of a characterization study aimed to identification of pigments. Among the polychrome archaeological finds saved at the Museo di Morgantina, Barbablù represents an unicum with respect to the technical production [4] and for the exceptional conservation status of the original polychromy. In the Haden's head, the blue traces of the original colours of the beard, together with the red ones of both hair and lips, are in fact visible to the naked eye.
The scientific analyses are focused on the characterization of the painting materials after a first step carried out using UV light in order to identify the original painted areas. By Raman spectrometry the red pigment was then identified as hematite and the blue one of the beard as Egyptian Blue. Colorimetric measurements performed with spectrophotometric and spectroradiometric methods allowed the colour specification.

The analyses represent an integration of the study made by the conservators of the Getty Museum through microscopy, microchemical investigation and X-Ray Fluorescence [5]. Our results confirm the presence of the rare Egyptian blue pigment found by the Getty Museum conservators. So, as supposed, the head could be then part of a statue that depicts a god since “The unnatural colouring of the hair and beard contributes to the impression of a supernatural figure” [5].

The research, besides analysing polychromy of this masterpiece of Greek coroplastic collection, represents a contribution in a wider methodological work aimed to optimise the in situ analyses involving different methodologies. Since the multidisciplinary approach to the cultural heritage study is fundamental, the use of several techniques is necessary to achieve an exhaustive and deepened knowledge of artworks. In this context, from the methodological point of view, the knowledge of potentialities and limits of each technique is also essential.

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ABSTRACT P.01.58

THE IDENTIFICATION OF THE ORIGINAL PICTORIAL LAYER OF THE ETRUSCAN SARCOPHAGUS HASTI AFUNEI BY RAMAN AND SERS ANALYSES

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Keywords: pictorial layer, Etruscan, sarcophagus, SERS analyses, Egyptian blue

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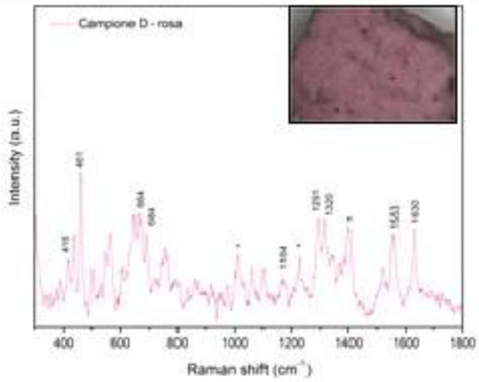
The sarcophagus of Hasti Afunei is a large Etruscan urn made up of two chalky alabaster monoliths of the last quarter of the third century BC, found in 1826 in the small town of Chiusi (Tuscany- località il Colle) by a landowner, Pietro Bonci Casuccini (Fig. 1) [1-2].

The noble owner's collection was sold in 1865 to the Royal Museum of Palermo, actually the Antonino Salinas Regional Archaeological Museum, where it is still exposed. The sarcophagus is characterized by a complex iconography that is meticulously illustrated with an excellent sculptural technique, despite it has been subjected to anthropic degradation and numerous restorative works. During the restoration work carried out between 2016 and 2017 [3-5], a targeted diagnostic campaign was carried out to identify the constituent materials of the artefact, paintings, executive technique and the various criticalities present. By Optical Light Microscope reflex analysis, and by FTIR, SEM-EDS and XRD it was possible to identify the

composition of constituent materials and of the various alterations and degradations suffered (chalky alabaster, chalky neoformation, dendritic veins). By the physical examination techniques (endoscope and pacometer), the presence of brackets and metal braces inserted in the urn, in order to ensure its structural stability, has been determined. The NMR technique was used to identify the protectors of the surface, which allowed the detection of characteristic peaks of animal and synthetic waxes (beeswax and paraffin waxes).
By XRF, Raman and SERS spectroscopy [6], red ocher and yellow ocher, black coal, Egyptian blue and the madder lake, pigments compatible with the historical period of the work, were identified. Furthermore, other modern pigments (green Paris, chrome orange, barium yellow, blue monastral) used in the eighteenth and twentieth century restorations were detected (Fig. 2).



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ABSTRACT P.01.59

THE POTENTIAL OF INTERCONNECTED X-RAY TECHNIQUES IN THE ATTRIBUTION INVESTIGATION - THE ECSTASY OF SAINT FRANCIS BY EL GRECO

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Keywords: attribution investigation, X ray imaging, XRF, SEM-EDS, El Greco

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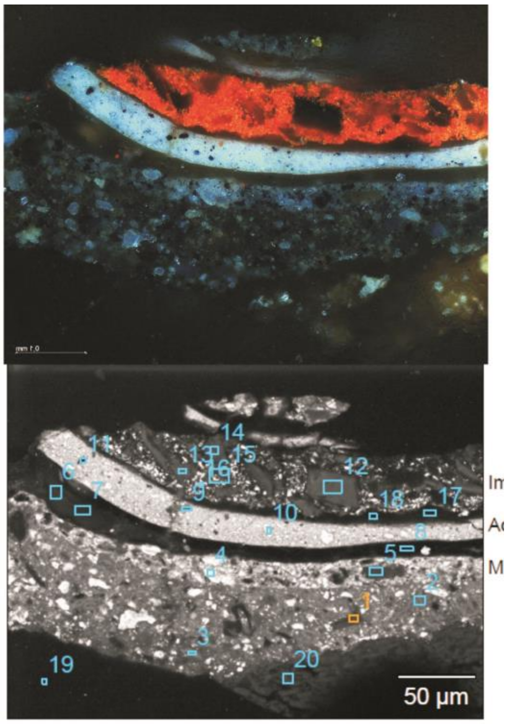
The techniques based on the X-ray radiation are widely applied in the attribution investigations due to the possibility for in-depth examination of objects. in the thirthies of the last centurycentury X-ray photography was introduced to the examination of the paintings [1]. Today, X-ray based techniques like XRF, macro XRF and SEM-EDS today are fundamental methods of non-destructive examination of art objects. They enable us to collect information of the whole investigated area and, furthermore, macro XRF scanning gives also access to XRF spectra of selected points or areas. The results are visualized as a map of element distribution which makes the analysis more precise and user-friendly. Unfortunately, there are some disadvantages of XRF techniques - especially in the case of paintings, as they provide information of all layers of the painting. Nevertheless, XRF and macro XRF became techniques preferred by curators and conservators because they do not demand sampling, which is especially important in the case of valuable art objects.

One of the most valuable paintings in Poland and the only work by El Greco in a Polish museum collection, The Ecstasy of Saint Francis (Fig. 1), was lent to the National Musem in Kraków to undergo a conservation process, highly connected with comprehensive physicochemical investigations. The reason for this decision was its unacceptable state of preservation. The layer of varnish that covered the picture was significantly darkened and yellowed, causing the distortion of the original colors, so typical of images of St. Francis painted by the Master of Toledo.

An interdisciplinary team made up of conservators, physicists, chemists and art historians conducted examinations and a museum conservation process which took nearly six months. They started with a comprehensive physicochemical analysis, which was followed by conservation and restoration works on the painting based on the examination results and the needs arising from the evaluation of the state of its preservation. A completed parametrized documentations of the current state of preservation based on noninvasive analysisis (VIS, UV, IR and X-ray imaging) will allow in the future to monitor the changes that may affect the condition of the painting. The methodology, incorporating various X-ray techniques, like X-ray imaging, XRF and macro XRF, as well as SEM-EDS supported by IR, UV analysis and optical microscopy, was applied in these attribution investigations. The results presented the details of the painting technique and also provided information about later alternations introduced to the composition. The analysis of the stratigraphy of the cross-sections supported by SEM-EDS analysis revealed that the stigma on the habit (Fig. 2) was a later addition originally absent from the image. Moreover, the SEM-EDS analysis allowed us to identify the use of the smalt pigment not detected in the macro XRF measurements.

The comprehensive analysis of the presented project proved both the potential and the limitations of X-ray techniques in the attribution investigations of objects of art.



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ABSTRACT P.01.60

THE SURFACE COATINGS OF 19TH CENTURY PLASTER CASTS AND THEIR CONSERVATION. TECHNIQUES AND CONSERVATION WITH A SPECIAL INSIGHT AT THE V&A‘S COLLECTION

Risdonne V.*[1], Theodorakopoulos C.[2], Hubbard C.[1], Theodorakopoulos C.[2]

Keywords: Plaster Casts, V&A Cast Courts, Art Technological Reconstruction, Cleaning Tests, PhD research

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The Art and Humanities Research Council (AHRC) supports this PhD research as part of a Collaborative Doctoral Partnership (CDP) between Northumbria University’s (NU) Department of Art and Department of Applied Science and the Victoria and Albert Museum’s (V&A) Department of Conservation and Sculpture. The study aims to investigate the iconic V&A collection of the 19th century plaster casts through the analysis of their coatings, as a means to understand the materials and methods of the Victorian cast makers. It also aims at a comparative study of a number of conservation treatments which will enable the development of a safe and effective method for the removal of retained soils on their surface, which will obtained a desired appearance and durability. The understanding of the materials and the techniques of the 19th century makers and a glance at the coeval plaster casts’ collection, in Europe and in the world, are fundamental to achieve these objectives.

The research is well framed in the respective fields of expertise of the NU’s and V&A’s supervisors and it is proceeding in a very exciting moment for the V&A’s Casts Courts. The Weston cast court (Gallery 46b, also known as Italian Cast Court) was recently renovated (from 2010 to 2014) and the twin Gallery 46a is currently under refurbishment (due to be completed in late 2018). The recent renovation of the galleries has enabled new studies and it will lead to ad-hoc conservation of the collection with in-depth examinations. This opportunity for a systematic research into the techniques of casts, surface coatings, finishes and mould making, joint to a review of novel conservation contributions and scientific techniques constitute the backbone of this PhD research.

During this study the coating layers exclusively are going to be analysed, but migration of compounds from the plaster and other similar phenomena that affects the condition of the coating will be considered). A decision on whether to add or remove later added materials will be made as soon as the composition and the originality of the stratified layers will be determined. Any conservation treatment will be carefully designed in order to minimize the possible reaction of subsurface layers with various reagents, which will lead to the disruption of the object’s surface. Changes will have occurred under the influence of time, air, light and heat. These variables will be taken into account. Moreover, even if not in itself the object of this study, the porous nature of substrate, must be considered. The ultimate aim of this research is to understand the coatings and to propose a future plan for the conservation of relevant objects.

Due to the early stage of my research and in light of the unexpected, which could range from unexpected findings to the breakdown of a specimen, the following is indicative and therefore open to changes and revision. (valentina.risdonne@northumbria.ac.uk)

Additional information will be collected by the conservators about the conservation state of the objects and the conservation treatment applied from now on. These data will aid a statistic comprehension of the degradation occurring in the Casts Court. Hypotheses for the reasons behind the degradation processes could be made in consideration of all the data collected.

The methodology in developing and testing conservation treatments has become standard these days and commonly proceed as follow:

1. Analysis of all the layers of the real object
2. Recreating the stratigraphy of the object
3. Ageing, natural and artificial
4. Cleaning tests
5. Cleaning assessment (post-treatment surface assessment and assessment after consequent ageing)

The experimental and scientific strategy of the whole project is being tested and refined on selected object case studies.

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ABSTRACT P.01.61

TIME-RESOLVED PHOTOLUMINESCENCE OF HISTORICAL CADMIUM PIGMENTS: SHEDDING LIGHT ON IMPERFECT SYNTHESIS PROCESSES BY MEASURING EMISSION FROM TRAP STATES

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Keywords: cadmium pigments, time-resolved photoluminescence spectroscopy and microscopy, trap state emission, pigment synthesis processes, crystal defects

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Cadmium sulphides (CdS) are inorganic pigments widely employed by artists after their introduction in colourman's catalogue in the 1840s [1]. Cd-based pigments are highly popular thanks to their availability in a wide range of shades (from yellow to red), their intense and bright colouration, high covering power and extended applications. Despite their good reputation, several studies are now demonstrating the instability of these pigments [1,2]. To investigate whether the causes of deterioration can be associated with an imperfect synthesis process (which favours pigment's oxidation), in this study we employed photoluminescence (PL) spectroscopy and microscopy methods to reveal differences in the crystalline structure of the pigments. The analyses are further supported by FTIR and Raman spectroscopy.

CdS is a semiconductor of the IIb-IVa group: when excited by light at a suitable wavelength exhibits a characteristic PL emission that can be classified in two types. i) The band-to-band transition, determined by pigments composition and crystal structure, is characterized by a fast decay kinetic with a lifetime in the order of picoseconds and an emission spectrum centred in the blue/green spectral region. ii) The trap state emission, which depends on the presence and nature of impurities and defects, exhibits a longer lifetime (hundreds of nanoseconds to microseconds) and occurs at longer wavelengths (red/ near infrared) [3]. While band-to-band and trap state spectral emissions have been deeply investigated [4,5], decay kinetics has been less studied [3]. In this work we propose a time-resolved PL approach, using both time-correlated single photon counting and time-resolved PL (TRPL) spectroscopy, to investigate the PL emission spectrum and the decay kinetics of six historical cadmium yellow based pigments, dated between 1851 and 1949 and conserved in the archival collection of the Courtauld Institute of Art.

The characteristic emission of these samples was compared with the one of commercial samples, produced with modern synthesis methods. The comparison highlights how the band-to-band emission is strictly related with the composition of the samples, with a similar emission for historical and commercial pigments. Conversely, the emission from trap state levels in historical pigments is substantially different from the one detected in commercial pigments. These observations suggest that in historical cadmium pigments there exist crystal defects different than the ones typically formed in the CdS pigments produced with standardized modern synthesis processes. We ascribe the existence of these peculiar defects to the imperfect synthesis processes available in the past. Once evaluated the spectral and kinetic properties of pigments, the micro-TRPL approach has been used to highlight spatial heterogeneities of the band-to-band and trap state emissions in the historical pigments, revealing the complex nature of these samples.

Whereas the identification of the nature of crystal defects in the CdS historical pigments is not straightforward and would require further analytical measurements, such as those based on electron paramagnetic resonance (EPR) spectroscopy and X-ray photoelectron spectroscopy (XPS), we confirmed the strong sensitivity of PL to the presence of defects in crystal solids, thus providing support in favour of a multi-analytical approach in the analysis of this type of samples.

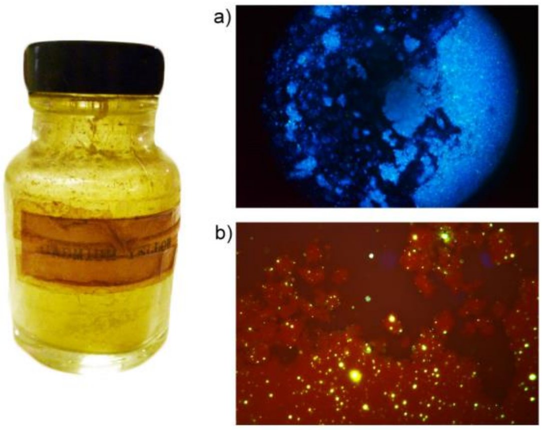

Figure 1: Example of microscopy PL images of historical cadmium powder following band to band (a) and trap state (b) recombination. The bottom PL image shows clearly the heterogeneities present in trap state emission.

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ABSTRACT P.01.62

UNDERSTANDING AUTHENTICITY: A MINERALOGICAL APPROACH TO AN ARCHAEOLOGICAL BRONZE ARTEFACT

Mantovani L.*[1], Tribaudino M.[1], Bersani D.[2], Lottici P.P.[2], Facchinetti G.[3]

Keywords: bronze statue, Roman Age, XRD, optical and electron microscope, 14C-AMS dating

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The results of a mineralogical investigation, aimed to determine whether a bronze statue coming from judicial seizure is authentic or fake are the subject of this case of study.

The bronze statue represents a sylvan deity holding in his left hand a snake. The artefact was in bad state of conservation, with clear signs of corrosion, covered with a light green patina; the right arm was missing and there were signs of fractures on the legs. Two main questions had to be addressed: 1) the provenance of the artefact and, 2) the historical period of production. The iconological aspects, colours, patina and conservation state are strictly compatible with ancient bronze production in Imperial Roman age but a doubt on the authenticity was cast by the presence of nineteenth and twentieth century copies of original Herculaneum statues produced by Chiurazzi smelter. Small pieces of soil between the draperies, clay-core (the soil used before the casting), fibres inside the hole of a missing arm and little chips of bronze were taken and analysed at optical and electron microscope (SEM-EDS) and by powder X-ray diffraction.

The small pieces of soil attached to the external bronze showed the presence of sanidine, phlogopite, analcime, and sometimes phillipsite: such mineralogical association, together with the observation of pumice, could support a provenance from the Vesuvius area. The green patina of alteration of the bronze was mainly formed by copper chlorides, in particular paratacamite and botallackite, which suggested a burial of the bronze statue close to the seashore. To note, a well-developed and stratified alteration patina was found, suggesting a natural patinaformed over long periods.

However further analysis showed that the artefact is actually a forgery. The residuals of the clays-core highlighted the presence of quartz and gypsum, and the absence of clay minerals, which are instead found in imperial clays-cores; in addition, the fibres used for the casting were tissues, differently from the straws or plant residues used in the Roman period.

The alloy formed by copper, zinc and tin was heterogeneous, with some areas very rich in zinc. An high Zn content is unusual for statues from the Roman age, but common from Renaissance onwards. A ^{14}C dating was performed on charred tissues found in the broken arm allowing to determine three possible dates, not before the 1640±30 AD. The above evidences indicate that, given appropriate conditions, a well-developed alteration patina can be formed also over relatively short periods, but it cannot be taken as decisive criterion of authenticity.

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