RAA
2015

8TH CONGRESS ON APPLICATION OF RAMAN SPECTROSCOPY IN ART AND ARCHAEOLOGY

Book of Abstracts

Wroclaw, 1-5 September 2015

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Dear Participants of the RAA2015

On behalf of the Scientific and Organizing Committee of the 8th Congress on Application of Raman Spectroscopy in Art and Archaeology (RAA 2015) we would like to welcome all guests and participants in Wrocław. It is a great honor and pleasure to host the RAA2015 meeting in Poland at the Faculty of Chemistry, University of Wrocław.

This year two types of the invited presentations were introduced into the program: trendsetting speeches by prominent experts in the field and congress lectures meant to broaden the experience of participants. Based on the proposals for oral and poster presentations the program of the congress was divided in fourteen scientific session. The presentations are focused on studies from diverse areas and represent dedicated works on the use of Raman spectroscopy technique in connection to art-history, archaeology, paleontology, conservation and restoration, museology, degradation of cultural heritage, archaeometry etc. Furthermore, the development of new instrumentation, especially for non-invasive measurements will be presented during the congress.

We are also honored to host the ARCHMAT Summer School with the Thesis Proposal session for the 2014-2016 edition of the ARCHMAT Master (http://www.erasmusmundus-archmat.uevora.pt).

The 8th Congress on Application of Raman Spectroscopy in Art and Archaeology is involved as a celebrating event in the program of International Year of Light 2015 organized by UNESCO.

The Patronage of RAA2015 was graciously accepted by the Rector of the University of Wrocław, Governor of Lower Silesia, Marshal of the Dolnośląskie, President of the City of Wroclaw Voivodeship and the Polish Chemical Society.

We want to express our sincere thanks to all authors and members of the scientific committee for their unmatched support and commitment to make the RAA2015 a successful meeting.

Last but not least the Organizing Committee expresses its gratitude to Platinum Sponsor – company Renishaw and to two Silver Sponsor companies: B&W Tek, Inc. and WITec GmbH, as well as to the exhibitors present at the conference: ABE IPS and Metrohm, Polska.

We wish you a pleasant conference and nice stay in Wroclaw.

On behalf of the Organizing Committee

Barbara Łydżba-Kopczyńska

Chair of the RAA2015

History of Congress on Application of Raman Spectroscopy in Art and Archaeology

Since the beginning the RAA conferences promote Raman spectroscopy and play an important role in increasing the field of its application in Art and Archaeology. The RAA is an established biennial international event. Previously they were held in London (2001), Ghent (2003), Paris (2005), Modena (2007), Bilbao (2009), Parma (2011), and Ljubljana (2013).

RAA2015 will provide the international platform for presentation and discussion on the application of Raman spectroscopy in the fields of art, history, archaeology, conservation, restoration and museology:

- Material characterization and degradation processes (pigments, inks, plastic materials, photographic materials, gemstones, stones, precious stones, glass, ceramics, contemporary materials etc.),
- Conservation issues affecting cultural heritage (decaying, corrosion, etc.),
- Raman spectroscopy of biological and organic materials (resins, fibers, ancient organic compounds, etc.),
- Surface enhanced Raman spectroscopy (dyes, organic pigments, etc.),
- Chemometrics in Raman spectroscopy,
- Development of Raman techniques,
- New Raman instrumentation and applications in cultural heritage objects investigations;
- Raman spectroscopy in paleontology, paleoenvironment and archeology,
- Forensic applications in art and archaeology (e.g. forensic archeology,

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The Birth of RAA: RAA1

Howell G.M. Edwards[1] and Ian C. Freestone[2]

[1]Emeritus Professor of Molecular Spectroscopy , School of Life Sciences , University of Bradford , Richmond Road , Bradford BD7 1DP, UK.

[2] Professor of Archaeological Materials and Technology , Wolfson Archaeological Science Laboratories , Institute of Archaeology , University College London , 31-34 Gordon Square , London WC1H 0PY , UK.

The first conference dedicated to the application of Raman spectroscopy to art and archaeology (RAA1) was organised by Professor Howell Edwards of the University of Bradford and Dr Ian Freestone of the British Museum Research Laboratories on 20th November , 2001 in the BP Lecture Theatre of the British Museum , London .From the first successful Raman spectroscopic characterisation of mineral art pigments in the 1970s , a growing interest in this application parallelled instrumentation development which facilitated the interrogation of artworks using long wavelength excitation and microscopic sample illumination. RAA1 brought together for the first time 120 experts from 17 countries in analytical Raman spectroscopy, museum science , conservators and archaeologists who enjoyed 13 oral papers and 17 posters: at the closing reception it was realised that the impetus achieved must be maintained and the challenge was successfully taken up by Peter Vandenabeele in the University of Ghent in 2003 with the launch of RAA2 .

Since RAA1, Raman spectroscopy has now been established firmly in the analytical armoury and repertoire of laboratories in museums and devotees of the technique have been brought together at the arts/science interface to solve problems involving significant intellectual and practical challenges in the derivation , recording and interpretation of spectroscopic data . From the outset , a major challenge involved non-destructive sampling or minimally directed sample removal from valuable artefacts , in contrast to the first experimental analytical chemical data from wall painting specimens from Pompeii reported by Sir Humphry Davy in 1815, which was nevertheless achieved only by the complete destruction of the valuable specimens available at that time.

In the intervening years since RAA1, the acceleration of this area of study has made RAA a well-established biennial conference which provides a much-needed directional focus in art and archaeology alongside other major analytical spectroscopic meetings such as FACSS/SciX , EUCMOS , IRUG , ICORS and GeoRaman . Sir Chandrasekhar Venkata Raman , who was awarded the Nobel Prize for the discovery which bears his name in 1930, maintained that "*Raman Spectroscopy is an Art and not a Science*" , highlighting the scientific artistry he believed was necessary to obtain Raman spectra historically; the RAA series of meetings illuminates historical mysteries and provides novel information relating to ancient technologies , the use of pigments and art materials and the degradation of artefacts in burial environments – hence, demonstrating unambiguously that Raman spectroscopy must be truly both a *Science* AND an *Art* for the practitioners of RAA who work at this challenging Science/Art interface !

Raman Spectroscopy in Art and Archaeology, Ghent (Belgium), 2003

Peter Vandenabeele

In 2003, we organised the first multi-day conference on Raman Spectroscopy in Art and Archaeology. The conference was hosted in ‘Het Pand’, an old Dominican monastery, in the centre of Ghent. The first day, an opening reception was given at the Ghent city hall. The conference consisted of 4 full days of presentations, with in the middle an excursion to Bruges. During this excursion, attendees could learn about the history of this mediaeval town, visit the most important museums and churches, and a lunch and visit (with sampling) was provided at a local brewery.

We hosted ca. 120 guests during this conference. The scientific topics were on the one hand organised according to the materials that were studied (pigments, glass, corrosion products, ceramics, minerals, etc.) and according to the approach on the other hand (SERS, instrumental developments, data-processing, etc.). For our research group, this conference has a special value, as on this conference our brand new developed mobile Raman instrument (MArtA) was presented. Next to the many oral presentations, two poster sessions were scheduled. During these sessions the sponsors could also exhibit their instruments, and the participants could sample a series of Belgian beers: from the first ideas in the organisation of the conference, we aimed to encourage interaction between the participants.

The logo of the conference was a gryphon (a mythical creature that ate men), which was stylised after a mediaeval manuscript that was previously examined with Raman spectroscopy.

Raman Spectroscopy in Art and Archaeology, Paris (France), 2005

Bellot-Gurlet L., Pagès-Camagna S. and Coupry

RAMAN
in ART
& ARCHAEO
PARIS 1-4 SEPT. 2005

The 3rd International Conference on the Application of Raman Spectroscopy in Art and Archaeology was held in 2005 in Paris at the Université Pierre et Marie Curie - UPMC / Paris 6 (August 31-September 3). It was organised by Ludovic Bellot-Gurlet and Claude Coupry from the Laboratoire de Dynamique, Interactions et Réactivité (LADIR, UMR 7075 CNRS-Université Pierre et Marie Curie, Paris 6 ; now became MONARIS UMR 8233 UPMC/CNRS) and Sandrine Pagès-Camagna from the Centre de Recherche et de Restauration des Musées de France (Ministère de la Culture et de la Communication).

The Paris RAA conference welcomed about 120 participants representing 18 countries who submitted 88 abstracts selected for presentation. Following, the Journal of Raman Spectroscopy special issue (vol. 37, issue 10) dedicated to RAA 2015 has 33 papers which could be classified in four main topics: technical developments, mobile measurements, colours, pigments and technologies and studies dealing with degradation processes (Bellot-Gurlet *et al.*, 2006). Being the third edition, this one emphasise an increasing of participation, with a wider international representation, which underline in the middle of the years 2000 the advances in the use of Raman spectroscopy in studies related to Cultural Heritage.

Further than the scientific program itself, guided visits were organised to highlight some Cultural Heritage places or collections. In Paris it concerns: the Louvre Museum and Bibliothèque Mazarine, and in the surroundings the Château d'Ecouen which house the Musée National de la Renaissance, and the Château de Chantilly with its painting collections and its park.

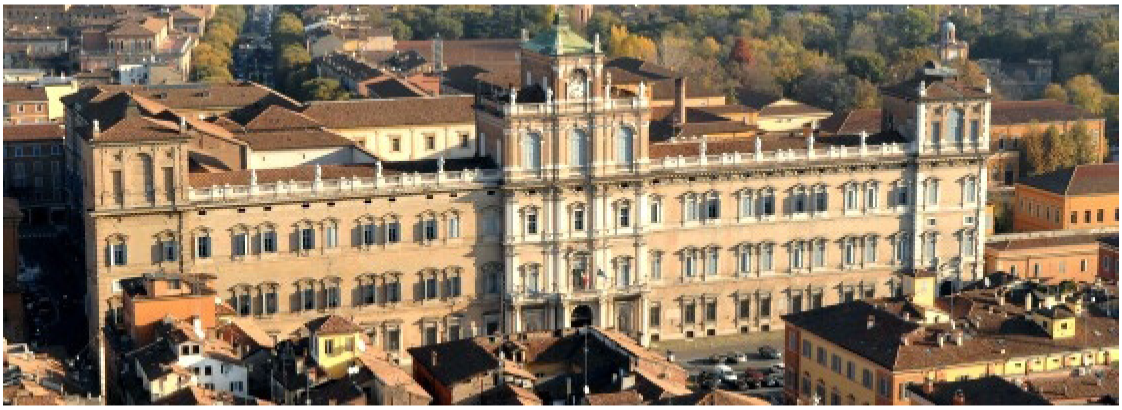
Reference:

Bellot-Gurlet L., Pagès-Camagna S. and Coupry C. (2006) Raman spectroscopy in Art and Archaeology, *Journal of Raman Spectroscopy*, **37**, 962-965.

Raman Spectroscopy in Art and Archaeology, Modena (Italy), 2007

Pietro Baraldi

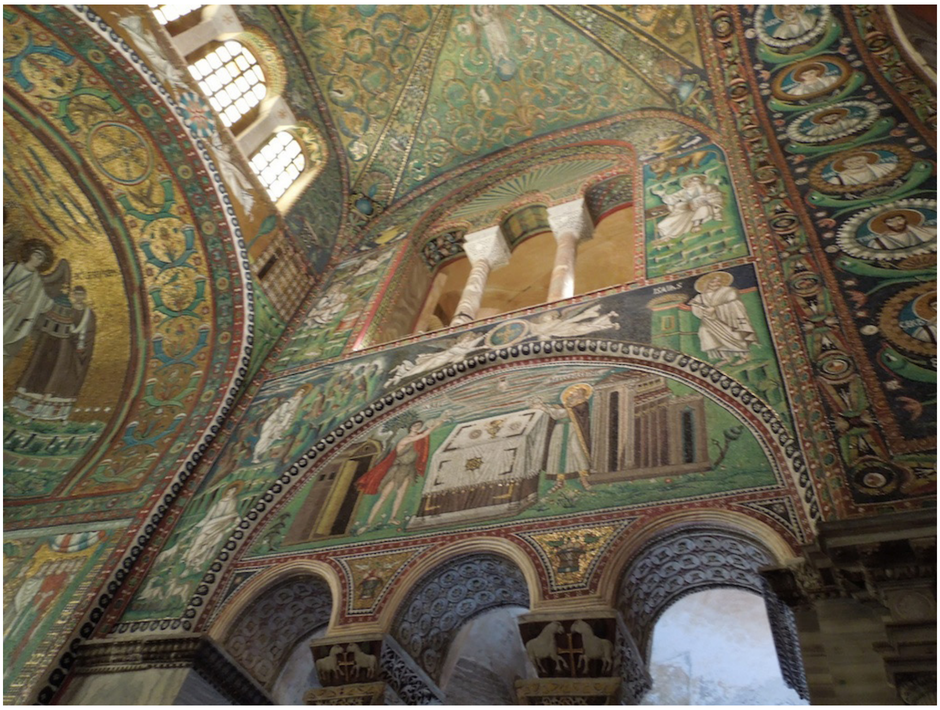
The IV International Congress on the Application of Raman Spectroscopy in Art and Archaeology was held in Modena (Italy) with the participation of about one hundred persons. The 2007 edition took place in September 5 – 8th and was hosted in the Ducal Palace, where also the Military Academy exerts its activity. The first session was opened with Rocco Mazzeo lecture on the application of spectroscopic methods to Cultural Heritage problems and was followed by many talks about prehistoric materials, classical civilizations remains and especially paintings. In the afternoon some reports were about illuminated manuscripts coming from many countries of the world. The second day was opened with the sad news about the death of famous tenor Luciano Pavarotti, who was a honorable citizen of Modena. The lectures were continued with some research on inks and manuscripts and their alteration followed by Raman measurements. After lunch some characterizations of ceramic materials were exposed. On Friday morning the research was centered on the spectroscopy of glasses and on the corrosion and degradation studies about cultural heritage materials. In the afternoon the participants were transferred to Maranello for a visit to the Ferrari cars Museum and then to Vignola where, after the visit to the castle, a social dinner in the twilights of the night occurred. A concert of popular Renaissance music was performed. The Saturday morning was reserved to the social excursion to the monuments of Ravenna, the ancient byzantine city of the Middle Ages.



The Duke's Palace, seat of the Congress

The party in the Castle of Vignola in the twilights of the evening, after a visit to the Ferrari Museum in Maranello

Visiting Ravenna byzantine churches with their mosaics



Raman Spectroscopy in Art and Archaeology, Bilbao (Spain), 2009

Juan Manuel Madariaga

The **5th International Congress on the Application of Raman Spectroscopy in Art and Archaeology (RAA2009)** was held in the Fine Arts Museum of Bilbao (Spain) from 14-18 of September 2009. The scientific contributions were arranged in 5 Plenary Lectures, 42 Oral Presentations and 65 Posters, with a total number of 408 authors, of which 146 were attendees. Among the 112 scientific works presented at RAA2009, 23 of them were selected as part of the special issue by the Journal of Raman Spectroscopy (vol. 41, No. 11, 2010) devoted to the RAA2009 Congress.

The Scientific Committee decided to include in this 5th edition a new topic, "the applicability of Raman spectroscopy to study the environmental impacts on Cultural Heritage assets", maintaining of course the classical subjects of past RAA editions. The acceptation of the new topic was excellent because 27% of the accepted works were proposed for this new topic.

The especial issue of Journal of Raman Spectroscopy published 23 scientific papers and a Editorial on the current status and future trends of Raman Spectroscopy in the field of Art and Archaeology. The scientific contributions were grouped in four main topics:

a.- **The Impacts of the Environment**, with a total of 8 works covering natural and anthropogenic impacts on rock art, roman wall paintings, medieval wall paintings, archaeological remains, illuminated manuscripts and Monuments of the Built Heritage

b.- **New Methods and Techniques for Complex Mixtures**, with a total of 6 works dedicated to solve problems on real samples using novel analytical procedures (SERS methods) and instruments (Raman image)

c.- **Artworks Materials and Techniques**, included 4 works of which two discovered painted fakes attributed to the Flemish Master Jan van Eick and the Russian painter Liubov Popova, a representative of the avant-garde school.

d.- **Archaeological Materials and Findings**, with a total of 5 papers of which 3 were related to ceramics (pottery) assets from the roman times till the Renaissance

The impact of this special issue can be considered very important. The last four years (2011-2014) we have received an average of 72 cites/year (288 in total). If we take into account the 24 papers in that special issue, an Impact Factor of 3.0 is obtained, a little bit higher than the Impact Factor of the whole Journal of Raman Spectroscopy. And the h-index of the special issue is nowadays 11, and it will increase in the next months for sure.

To increase the participation of young people, the Congress offered inscription grants. A total amount of 22 pre-doc students applied and were funded. Moreover, the Congress gave a daily award to the better poster where a pre-doc student was the first author, and also an award to the best Oral Presentation by a pre-doc student was granted.

Raman Spectroscopy in Art and Archaeology, Parma (Italy), 2011

Danilo Bersani

The Sixth edition of the International Congress on the Application of Raman Spectroscopy in Art and Archeology (RAA 2011) was held in Parma (Italy) from 5 to 8 september 2011, following the tradition of biennial conferences started in London (2001)[1]. The following editions were held in Ghent (2003)[2], Paris (2005)[3], Modena (2007)[4] and Bilbao (2009)[5].

As in the previous editions, the scientific program was focused on the analysis by means of Raman spectroscopy of materials related to cultural heritage and archaeology (pigments, dyes, inks, paper, polymers, glass, ceramics, resins, fibers, corrosion products) including topics related to natural heritage (gemstones, minerals, fossils) and some aspects involving forensic science. In this edition, particular attention was put on the new techniques (CARS, SERS, resonance) and on the recent developments in Raman data interpretation (chemometrics, simulation of Raman spectra, imaging and mapping).

These studies were presented along 5 Plenary Lectures, 45 Oral Presentations and 83 Poster Presentations. The number of active participants was 130 delegates from 26 countries among the 502 authors that presented at least one work to the Congress. Some of those contributions are collected in this special issue, starting with a critical review by Colomban [6] on the story of the evolution from laboratory Raman instrument to transportable, mobile and ultramobile ones, enhancing the drawbacks and success of on-site/remote Raman analysis in cultural heritage studies and associated fields.

Due to the increasing need for well defined and quickly available reference spectra, the congress was completed by a round table about the most important criteria and requirements for the building of a public database of standard Raman spectra of compounds related to cultural heritage and archaeology.

During the conference it was organized a guided visit to the national archaeological museum, a cocktail at the Biblioteca Palatina, a conference excursion including the guided visit to the castle of Soragna, the guided visit to the village and the castle of Fontanellato and the visit to the cistercian abbey of Fontevivo.

Raman Spectroscopy in Art and Archaeology, Ljubljana (Slovenia), 2013

Polonca Ropret

The RAA 2013 conference, held in Ljubljana (2 – 6 September 2013), was organised by Research institute of The Institute for the Protection of Cultural Heritage of Slovenia. The conference received over 100 high quality contributions from different research laboratories all over the world, presenting their latest advancements. 5 plenary lectures, 40 oral presentations and 60 posters offered insights in the latest research on studies of deterioration induced by different environmental factors, such as biodeterioration, pollution, light and humidity exposure; the characterisation of traditional organic colorants by introducing new solutions for Surface enhanced Raman spectroscopic studies; the advancements in metals characterisation for understanding of their corrosion processes and/or deliberate patinations by artists; archaeometry research, from characterisation of ancient artefacts, their degradation processes, to finding possible solutions for their preservation; gemstones characterisation, provenance, authenticity research, and furthermore, forensics applications. The latest innovations in Raman instrumentation were presented by well – known companies in the field of Raman instruments, with a special emphasis in the development of portable, non-invasive instruments. The diversity of contributions attested of the wide applicability of Raman spectroscopy. The RAA 2013 edition featured keynote speakers from Howell G. M. Edwards (University of Bradford), presenting “Raman Spectroscopy of Extremophilic Biodeterioration : An Interface Between Archaeology and the Preservation of Cultural Heritage”; Costanza Miliani (Istituto CNR di Scienze e Technologie Molecolari, Perugia), introducing “The Art of non-invasive in situ Raman spectroscopy: identification of chromate pigments on Van Gogh paintings”; Marco Leona (The Metropolitan Museum of Art, New York), introducing “Surface-enhanced Raman spectroscopy in art and archaeology”; Juan Manuel Madariaga (Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country, Spain), presenting “The contribution of Archaeometry to understand the effects of past and future Changes in the World Heritage site of Pompeii (Italy)”; to Marcello Picollo (“Nello Carrara” Institute of Applied Physics - National Research Council, Florence), giving introduction to “The Infrared and Raman Users Group Web-based Raman Spectral Database”. RAA 2013 also gave important emphasis to support young scientists, as a special award was given to the best younger scientist’s poster by the Molecular Spectroscopy Group of the Royal Society of Chemistry, London.

List of accepted works with corresponding authors

PL: Plenary Lecture
OP: Oral Presentation
TS: Trendsetting Speech
P: Poster Presentiation

Tuesday, September 1st, 2015

Mobile Raman Spectroscopy in Art and Archaeology: Challenges and Opportunities	Peter Vandenabeele	**10:00 - 10:50**	**PL1**	**27**
Chair	Peter Vandenabeele			
From past to future possibilities on the Application of Raman spectroscopy in Art and Archaeology	Juan Manuel Madariaga	**11:20 - 12:00**	**TS1**	**28**
An Insight into the spectroscopic properties and metal coordination of artistic logwood inks	Silvia A. Centeno	**12:00 - 12:20**	**OP1**	**30**
Application of Raman Microscopy to Analysis of Paper in Documents and Works of Art	Enrico Pigorsch	**12:20 - 12:40**	**OP2**	**32**
A Comprehensive Investigation of Paul Gauguin’s Graphic Works on Paper	Celine Daher	**12:40 - 13:00**	**OP3**	**34**
Chair	Polonca Ropret			
Back to basics: from materials science to conservation.	Danilo Bersani	**14:00 - 14:40**	**TS2**	**36**
Micro-Raman Spectroscopy for the Archaeology of the Iberians	Alberto Sánchez	**14:40 - 15:00**	**OP4**	**38**
Spectroscopic characterization of carbon based pigments used for decoration of prehistoric ceramic	Barbara Łydżba-Kopczyńska	**15:00 - 15:20**	**OP5**	**40**
Characterization of natural, synthetic and imitation opals	Annalaura C. Municchia	**15:20 - 15:40**	**OP6**	**42**
Discovery and characterization of challacolloite, an uncommon chloride on a fifteenthcentury polychrome terracotta relief by Michele da Firenze	Jens Stenger	**15:40 - 16:00**	**OP7**	**44**
Chair	Danilo Bersani			
Revealing the chemistry of ancient medicinal or cosmetic preparations containing heavy metals	Marlene Aubin	**16:30 - 16:50**	**OP8**	**46**
Studying the degradation of arsenic sulfide pigments by the use of tandem Raman spectroscopy-electrochemistry	Marc Vermeulen	**16:50 - 17:10**	**OP9**	**47**
The green paints in the paradise wing of the triptych The Last Judgement by Hieronymus Bosch in the Paintings Gallery of the Academy of Fine Arts Vienna	Federica Cappa	**17:10 - 17:30**	**OP10**	**48**

Comparative Pallet Characterization in easel paintings of Two Well-Known 19th Century Colombian Artists by Confocal Raman Spectroscopy	Diego Badillo	**17:30 - 17:50**	**OP11**	**50**
Raman microspectroscopy and laser ablation of old paper samples with foxings	Irina Balakhnina	**17:50 - 18:10**	**OP12**	**51**

Wednesday, September 2nd, 2015

Chair	Ludovic Bellot-Gurlet			
Raman spectroscopy for Art and Archaeology: 30 years of pushing the envelope in cultural heritage studies	Francesca Casadio	**9:00 – 9:40**	**TS3**	**55**
FT-Raman analyses of dyes and lac pigments in folk arts and crafts in the interiors of Decorative Farmhouses of Hälsingland, Sweden, UNESCO World Heritage	Ingalill Nyström	**9:40 - 10:00**	**OP13**	**56**
New frontiers of Raman spectroscopy in conservation science	Agnieszka Sozańska	**10:00 - 10:20**	**OP14**	**58**
Chair	Juan Manuel Madariaga			
Raman spectroscopy: from Museum to archaeological excavations	Sandrine Pagès-Camagna	**11:00 - 11:40**	**TS4**	**59**
Multi-analytical approach to the study of archaeological iron corrosion products	Nick Schiavon	**11:40 - 12:00**	**OP15**	**60**
A new insight into polyurethane foams degradation – the use of Raman spectroscopy for the evaluation of long-term storage conditions	Susana França de Sá	**12:00 - 12:20**	**OP16**	**62**
Multidisciplinary approach to characterize an unusual blackish patina on the Neang Khmau temple- Archaeological Khmer area (Cambodia)	Annalaura C. Municchia	**12:20 - 12:40**	**OP17**	**64**
Chair	Bruno Brunetti			
Extension of Spatially Offset Raman Spectroscopy to the Microscale for Conservation Science	Claudia Conti	**13:40 - 14:20**	**TS5**	**66**
Combined spectroscopic analysis of beads from the tombs of Kindoki, MbanzaNsundi, Lower Congo	Alessia Coccato	**14:20 - 14:40**	**OP18**	**68**
Combined spectroscopic and paleobiologic approach to the provenance investigation of painting materials	Monika Czarnecka	**14:40 - 15:00**	**OP19**	**70**
Micro-Raman analysis of prehistoric rock art in Patagonia (Argentina)	Anastasia Rousaki	**15:00 - 15:20**	**OP20**	**72**
Famous Historic Chrysoprase Deposit in Szklary, Poland: Raman Characterisation of Nibearing Minerals	Zdeňka Čermáková	**15:20 - 15:40**	**OP21**	**73**

Thursday, September 3rd, 2015

Chair	Francesca Casadio			
Exploiting Raman abilities: from spectra recording to advanced data treatment. Focuses on natural organic substances involved in cultural heritage studies	Ludovic Bellot-Gurlet	**9:00 - 9:50**	**PL2**	**77**
Automatic Classification System of Raman Spectra Applied to Pigments Analysis	J. J. González-Vidal	**9:50 - 10:10**	**OP22**	**78**
Suitability of DFT Modelling for Raman spectral Interpretation of Copper Complexes	Elena Platania	**10:10 - 10:30**	**OP23**	**76**
Chair	Silvia A. Centeno			
Going beyond single colorant identification with surface-enhanced Raman spectroscopy (SERS): a systematic study of natural red dyes in mixtures	Francesca Casadio	**11:10 - 11:30**	**OP24**	**80**
Multi-analytical approach combining conventional Raman and SERS with fluorescence lifetime spectroscopy and HPLC for the study of twenty historical lake pigments	Francesca Gabrieli	**11:30 - 11:50**	**OP25**	**84**
Portable SERS analysis assisted with additional techniques to characterize the ancient recipe used to prepare Pompeian pink and purple pigments	Maite Maguregui	**11:50 - 12:10**	**OP26**	**86**
SERS identification of orchil and folium mixtures on purple codices: a methodological approach on model samples	Monica Gulmini	**12:10 - 12:30**	**OP27**	**88**
Chair	Nick Schiavon			
Raman forbronze characterization: case studies and treatments	Polonca Ropret	**13:40 - 14:10**	**TS6**	**89**
Raman investigation of surface layers on copper cargo from XV c. ship wreck excavated in the Gdańsk Bay - contribution to study of the trade routing in medieval Europe	Katarzyna Schaefer	**14:10 - 14:30**	**OP28**	**92**
Deterioration of Iron Nails from Historical Structures Exposed to Coastal Town Atmosphere: Investigation of Corrosion Layers by Micro-Raman Spectroscopy	Nurdan Yucel	**14:30 - 14:50**	**OP29**	**94**

Identification of salts from deteriorated stone of historical monuments using microRaman spectroscopy, X-ray diffraction and SEM-EDS	Mariola Marszałek	**14:50 - 15:10**	**OP30**	**96**
Chair	Barbara Łydżba-Kopczyńska			
Uncomon pigments and dyes identified through Raman microscop	Pietro Baraldi	**15:40 - 16:20**	**TS7**	**98**
Smalt characterization with Raman spectroscopy	Sylwia Pawełkowicz	**16:20 - 16:40**	**OP31**	**100**
Raman and infrared spectroscopy of megafauna and human ancient bones recovered from submerged caves in Yucatan, Mexico	María A. Mondragón	**16:40 - 17:00**	**OP32**	**102**

Friday, September 4th, 2015

Chair	Piotr Targowski			
Investigation of unique group of painted silk banners from Polish collection	Anna Klisińska-Kopacz	**9:00 - 9:20**	**OP33**	**106**
Degradation of Cu-pigments of medival wall paintings in the chapel of Vipperow	Martin A. Ziemann	**9:20 - 9:40**	**OP34**	**108**
Raman Spectroscopy Analysis of Terra Sigillata: the Yellow Pigment of Marbled Sigillata	Tian Wang	**9:40 - 10:00**	**OP35**	**109**
Identification of pigments mixtures by imaging data obtained by LA-ICP-MS supported by Raman spectroscopy	Olga Syta	**10:00 - 10:20**	**OP36**	**111**
Raman analysis of color minerals from the Stone-Age sites at Gubs gorge (North-West Caucasus)	Alexander Pakhunov	**10:20 - 10:40**	**OP37**	**112**
Round Table				
Chair	Sandrine Pagès-Camagna			
The integrating activity project IPERION_CH: a further step toward a European research infrastructure in heritage science	Bruno Brunetti	**11:10 - 12:40**	**PL3**	**114**
Prospective European research infrastructure E-RIHS and its Polish partner E-RIHS PL	Piotr Targowski	**11:10 - 12:40**	**TS8**	**116**

Poster Session

Chairs Claudia Conti, Pietro Baraldi

Appendix

Tuesday, **September 1st**

PL1

Mobile Raman Spectroscopy in Art and Archaeology: Challenges and Opportunities

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In archaeometry, the aim of all research should be to try to maximise the amount of information that is obtained during a study, while minimising the (risk on) damage to the artefact. Several strategies can be developed, to approach this aim. One can think on using several complementary non-destructive approaches, to maximise the information that is obtained. On the other hand, by using sensitive analytical techniques, the sample size can be reduced. Finally, using mobile instrumentation for in situ investigations is a straightforward approach to reduce the damage to the artefact.

Raman spectroscopy is well-known as an excellent approach for the study of art objects and antiquities[1]. Typically, several favourable features are cited, such as the ability to obtain a molecular spectrum from micrometer-sized particles (compatible with the dimensions of a pigment grain), the speed of analysis and the relatively straightforward interpretation (at least as far as comparison with reference spectra is possible). Raman spectroscopy can also often provide information on the inorganic as well as on the organic fraction. Moreover, the technique is non-destructive and thus the microsamples remain available for future investigations. Finally, By using fibre-optics, the approach can perfectly be deployed for in situ studies.

However, despite the advantageous features of the approach, Raman spectroscopy, and especially mobile Raman spectroscopy, can suffer from some drawbacks, that compose serious challenges to the investigator. Fluorescence and interferences from ambient light are typical issues, that need to be tackled. Practical challenges are inherently connected to fieldwork. Stability issues hamper the micro-analysis, time constraints force the analysis to decide between moving to the next point or performing long investigations, varnish layers may interfere, electrical power can be an issue, etc. Finally, spectral interpretation is not always as straightforward, compared to in vitro-analysis, as the environmental conditions are less under control. However, many of these issues can be overcome, by decent planning and performing direct in situ investigations form often a great opportunity in archaeometry.

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TS1

From past to future possibilities on the Application of Raman spectroscopy in Art and Archaeology

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Keywords: Raman spectroscopy; trendsetting; Art; Archaeology

The field of Cultural Heritage Science is vast and complex, encompassing analytical and physical chemistry, biology, engineering, materials science, etc. Thus, scientists are the professionals who can study the materials and the way that these materials age in a given environment. Nowadays, Analytical Chemistry, one of the Science involved in such studies, is given answers about the conservation state of the Cultural Heritage assets that are under observation or rehabilitation.

At the beginning, the scientific analyses were focused on the characterization of the nature and composition of original materials (pigments, binders, porous materials, etc.), using different Analytical Techniques: spectroscopy (FT-IR, Raman spectroscopy, molecular fluorescence, UV-VIS, NIR, etc.), X-ray based techniques (X-Ray Diffraction, X-Ray Fluorescence, Synchrotron-XRD/XRF, etc.), microscopy (e.g. electron microscopy, scanning-probe microscopy) and chromatographic techniques (liquid, gas and ion chromatography). Among them, Raman spectroscopy gained a relevant role being nowadays the most used one for characterisation purposes. But, what is coming in the near future?.

Raman spectroscopy will continue playing a key role in the characterization phase of future studies, due to (a) the advances in the quality of the commercially available portable spectrometers for field analysis, that will include dual systems, most sensitive detectors, several laser configurations for sample excitation at different wavenumbers, etc., (b) the introduction of commercially available pulsed lasers at small scale, that will promote the development of stand-off Raman portable devices, (c) the decrease in the cost of the Raman imaging systems, that will spread their availability for most of the laboratories, (d) the improvement in the mathematical (chemometrics, statistics, etc.) treatment of complex spectra, that will solve situations where several compounds promote the current band overlapping problem, (e) the integration of the Raman information with information from other techniques on the same working scale, that will give us a more unequivocal identification of all the compounds present in the samples.

Today the characterization ends in the identification of all of the compounds present in the different parts of the CH assets, i.e. a classical qualitative analysis of the objects. But in the near future, this will be extended to the quantification of each compound. Three strategies could be envisaged from the last contributions published the last year, all of them making use of the knowledge about the nature of the compounds present in the sample under analysis: (a) the use of external calibration procedures if the selected wavenumber for each compound is not interfered by Raman signals of the other compounds (absence of matrix effects), (b) the use of multianalytical calibration (standards having several of the compounds present in the sample) when the Raman signals overlap, using chemometric methods like PLS1 (First type of Partial Least Squares procedure), (c) the decomposition of the whole spectrum in the individual part of each compound and then referring that individualized information to the corresponding calibrant for the given compounds, (d) the construction of sophisticated algorithms to implement the previous strategies to analyse each pixel in the Raman images leading the possibility to perform quantitative maps of the objects.

The study of the degradation process, and the identification of the sources that cause the impacts, will be a fundamental step in modern knowledge based remediation actions, to limit further damages and preserve artworks belonging to the cultural heritage. This will be done by merging the characterisation of original and deteriorate compounds (the so-called spectroscopic speciation) with the ascertaining of the chemical reactions responsible of the decaying pathways (the so-called thermodynamic speciation), because most of these deteriorations are due to the reactivity between original compounds and chemicals present in the environment surrounding the CH asset. This reactivity happens not only in CH assets impacted by urban atmospheres due to pollution but also in Museums (volatiles from objects, CO_2 from visitors, microorganisms colonisation), in open air but non-polluted environments (efflorescence in cold and low humidity conditions, formation of biofilms, etc.), in caves and underway locations and in all places that are not free from the influence of CO_2, an important acid in high humidity conditions (H_2CO_3 aerosol), and the influence of NH_4NO_3 and other organic acids coming from natural plant decomposition processes and bird dropping.

The application of these new remediation treatments/procedures, based on the scientific knowledge of the problems to be solved, will be advantageous because we will have a prediction capability of the expected behavior (we will know the surface to be treated and how the different compounds will act when the treatment is carried out). Here Raman spectroscopy will play an important role because it will validate the effectiveness of the procedure during the application steps and after finishing the remediation works, evaluating the influence with time.

This strategy has been applied to follow the laser cleaning works measuring the Raman spectra of the "cleaned" surface to guarantee the absence of damage due to the laser power used. In the future, the use of stand-off Raman systems will improve those works performed on big surfaces like facades of historical buildings because its applicability does not require the use of scaffoldings (the most expensive part in the building restoration budget). In the short term, stand-off systems coupling Raman and LIBS measurements (combining molecular and elemental information) will be available for field analysis works.

Acknowledgements

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OP1

An Insight into the spectroscopic properties and metal coordination of artistic logwood inks

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Keywords: logwood inks, works of art, Raman, FTIR, metal coordination,

At the end of the 19th and beginning of the 20th century, logwood inks were prepared by boiling heartwood chips from the tree *Haematoxylum campechianum*, mixing the decoction with a variety of inorganic salts, such as $AlK(SO_4)_2.12H_2O$ or other alum salts, $FeSO_4.7H_2O$, $Fe(NO_3)_2$,$CuSO_4.5H_2O$, or K_2CrO_4, and adding a solution of dextrine or gum as binding medium. The main colorant in the logwood extract is hematein that forms when hematoxylin present in the heartwood of the tree is oxidized during the extraction. Various amounts of other colorants, such as a derivative of brazilein, large amounts of tannins and other still unidentified colorants have been reported to be present in logwood [1]. Inks with different hues could be obtained when these different inorganic salts, or mixtures, were added, andthe hues could be modifiedby changing the proportions of the ingredients or by adding acetic acid, oxalic acid, or sodium carbonate [2,3]. In a Raman and XRF study of a group of drawings by Van Gogh it was discovered that he did not use a 'traditional' iron gall ink as initially suspected based in the visual appearance but a rather relatively new logwood ink formulation, that now appears to have faded considerably (Fig. 1)[4].The properties of the complexes formed between a dye and a mordant determine in part the colorants' lightfastness [5]and, therefore, structural and chemical information on these compounds are relevant for the conservation and preservation of works of art where the media are present.

An alum logwood ink was synthetized following a 19th century recipe andit was characterized by Raman spectroscopy and ^{27}Al NMR. The Raman spectra obtained constitute suitable references for the unambiguous identification of the ink in works of art and NMR revealed that the predominant coordinationsof the Al (III) species in the crystallized material and in the ink applied on paper are different[6].Fe- and Fe/Cu- based logwood inks were also synthesized following different recipes in 19th and early 20th century manuals and were characterizedby Raman spectroscopy, FTIR, EPR,and ESI-MS.The FTIR spectra recorded were found to be dominated by features due to sulfates and the binding media in the ink formulations The Raman analysis showed that the characteristic features of the different inks studied depend on the historic recipe used, attesting to the challenges that their identification in works of art present.

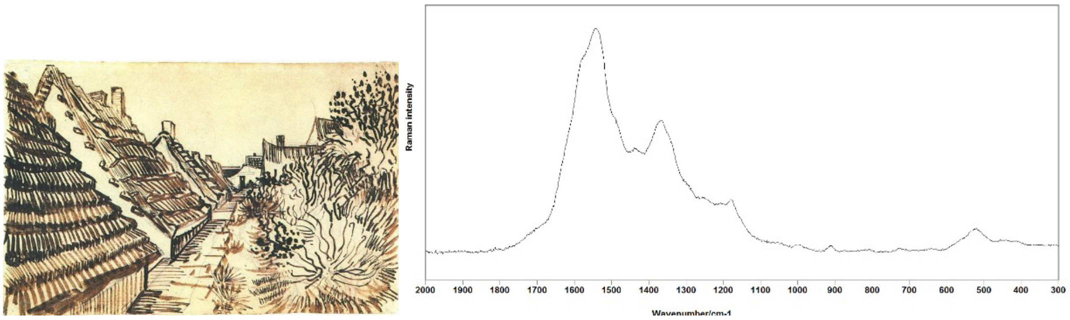

Figure 1. *Street in Saintes-Maries-de-la-Mer*, Vincent van Gogh (MMA# 48.190.1), left, and Raman spectrum showing that van Gogh used a Cr-logwood ink in this drawing, right.

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OP2

Application of Raman Microscopy to Analysis of Paper in Documents and Works of Art

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Keywords: paper analysis, dating of paper, authentication

Usually, paper is a cheap mass product. However, as a support for historic or important documents and works of art, paper can be of high value. Hence, paper objects are more and more subject to art forgeries and fraud [1]. In most cases, the detection of forgeries can not only be done on the basis of scientific art expertise.Therefore, chemical analytical methods also have to be employed.

The complex composition of papers still today presents a great challenge to chemical analysis, especially when the used methods have to be non-destructive and paper components are only present in low concentrations. Raman microscopy offers new opportunities to chemical paper analysis. Raman measurements have a high chemical specifity and the use of an excitation laser and an optical microscope provides for a very high spatial resolution of up to 1 µm. In addition, Raman spectroscopy is particularly suited to paper analysis because of the weak Raman activity for OH groups. As numerous OH groups are present in cellulose these vibrations are not dominating in the Raman spectra of paper, like they do in the infrared spectra. Instead, characteristic Raman bandsof other paper components can be easier identified [2].

Despite the great potentials of Raman microscopy for paper analysis, so far, only few Raman studies have been reported on paper which is used as a support of documents and works of art [3]. There are many publications dealing with the analysis of color pigments and printing or writing inks on paper but not with the paper itself [4].

The presentation will give results of Raman spectroscopic studies on different old papers. By using the Raman imaging technique, the chemical structure, that means the presence and distribution of different paper components on the surface or along the cross-section, are visualized. This includes different fibers, filler pigments, sizing compounds and others. Beside the intentionally added components to the paper, also other substances that came as trace particles with the main components in the paper or were formed during the production process can be detectedand identified.The working hypothesis behind our studies is that the presence and the distributionof different paper compounds including the trace particles contain information about the potential production year and production place of the paper and its treatments. Eventually, the Raman images could be used as “finger prints” of different papers and can give objective indications of the authenticity of works of art or documents on paper.

Figure 1 gives two examples of Raman images of paper surfaces. Figure 1A shows the starch distribution on the surface of a modern paper. Figure 1B demonstrates the detection of traces of $CaSO_4$ in three different stages of hydration on a paper document from the year 1938. It is assumed that the $CaSO_4$ was not intentionally added to the paper. It was formed during the production process as gypsum by the combination of the sulphate from the sizing aid alum and the calcium ions in the process water. The dehydration of the gypsum took place in the drying section of the paper machine at temperatures over 120 °C.

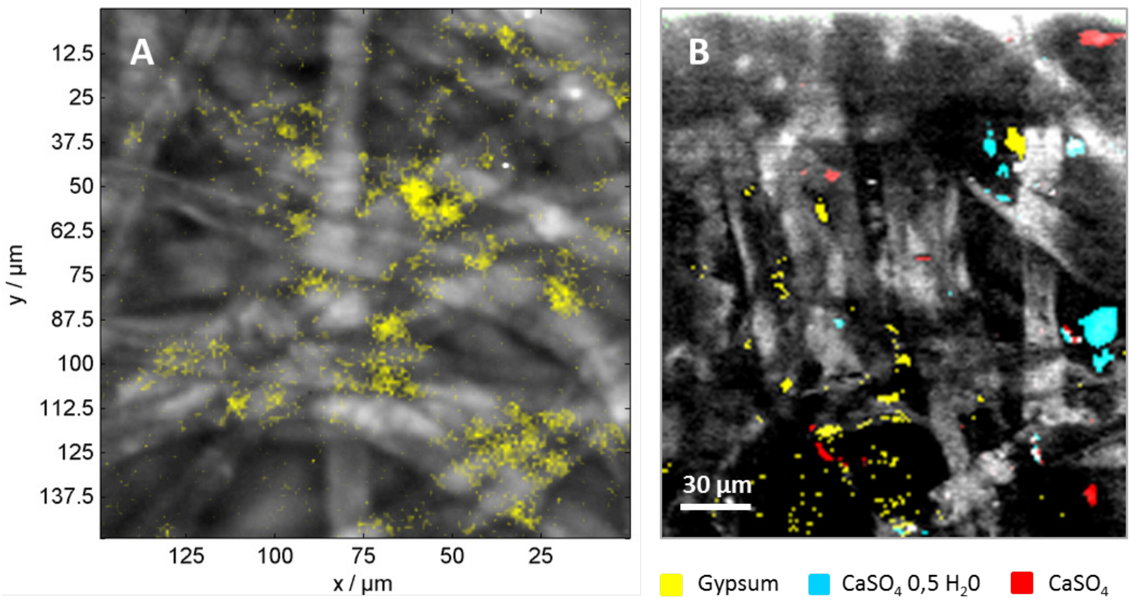

Figure 1 A) Raman image of the surface of a starch sized modern paper. Areas with starch are yellow. B) Raman image of the surface of an old paper (1938) with particles of $CaSO_4$in different stages of hydration.

The Raman measurements which will be presented were done with two different Raman microscopes. The first one was a dispersive Raman spectrometer system from Kaiser Optical Systems. The HoloLab Series 5000 Raman system consisted of a 785 nm diode laser for excitation, a Raman microscope Leica DMLP, a HoloSpec spectrograph f/1.8 and a liquid nitrogen cooled CCD detector. The second system was a Raman Microscope WITec alpha 300M+ with a 532 nm laser.

The results of this study demonstrate the great potential and the new possibilities of Raman microscopy to analyse chemical components and additives in paper. This spectroscopic method makes high-resolution and high specific paper analysis possible in a way that was not feasible before. This allows new insight in the chemical composition and structure of old papers and could considerably support the combat against forgery and fraud of documents and works of art on paper. The obtained results encourage further studies in this direction.

Acknowledgements

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OP3

A Comprehensive Investigation of Paul Gauguin's Graphic Works on Paper

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Keywords: Inking and printing techniques, material and media characterization

Never formally trained as an artist, Paul Gauguin (1848-1903) led a tumultuous and peripatetic life. As a young man he spent several years at sea before becoming a stockbroker in Paris. When the stock market crashed in 1882, he took various odd jobs and began to make art in earnest. In the 1880s he travelled to Brittany, South America and Martinique. In 1891 he made his first voyage to Tahiti where he intended to escape European civilization and locate a "primitive" idyll. The landscape, people, flora and fauna he found on the island would remain a constant subject in his prints, drawings, watercolors and transfer drawings.

Gauguin's works on paper are his most personal[1]. Yet, despite their enormous significance for the artist, to this day these works have received very little technical study. The Art Institute of Chicago has the largest and most comprehensive collection of Gauguin's graphic works outside of Paris. A centerpiece of this collection is 31 impressions from Gauguin's famed *Noa Noa* (Fragrant Scent) series (figure 1). In *Noa Noa*, Gauguin described his Tahitian experience[2] through text and imagery. For this ambitious undertaking he concurrently carved 10 woodblocksfor the illustrations that opened each chapter. He experimentedwith different ways of inking and printing the blocks and numerous impressions fromeach block exist.

Figure 1. Two impressions from *Noa Noa*. On the left, an example with thick dimensional media: *Maruru*(*Offering of Gratitude*), 1893-94, The Art Institute of Chicago, 2002.249. On the right, an example with delicate watercolor washes: *L'univers est créé* (*Creation of the Universe*), 1893-94, The Art Institute of Chicago, 1948.260.

Some of the prints in the Chicago collection represent the earliest monochromatic states,printed on poor quality paper (sometimes pink), while others that represent later states are much more elaborate with additional printed or hand-applied colors. Among the 31*Noa Noa* prints in the collection, there are two distinct groups of particular interestfor in-depth analysis based on their morphology (Figure 1). In one group the artist used thick, dimensional yellow, green, and orange media under and over the black ink used to print the block itself. In the other group Gauguin hand-applied delicate watercolor washes of colorover impressions printed in deep black printing ink.

These prints may be characterized by Gauguin's very complex and experimental processes, often involving applications of various organic media mixed with pigments before the final inking of the block[3]. Here, for the first time a multi-analytical approach using Raman, FT-Raman, Reflectance FTIR, Micro-XRF spectroscopy and close microscopic observation was used to scientifically unravel the printing processes and uncover the palette and organic materials used by the artist (Figure 2). The opportunities and challenges posed by the various analytical approaches will be discussed and for the first time comprehensive identification of both pigments and media in Paul Gauguin's *Noa Noa* series of woodblock prints will be presented.

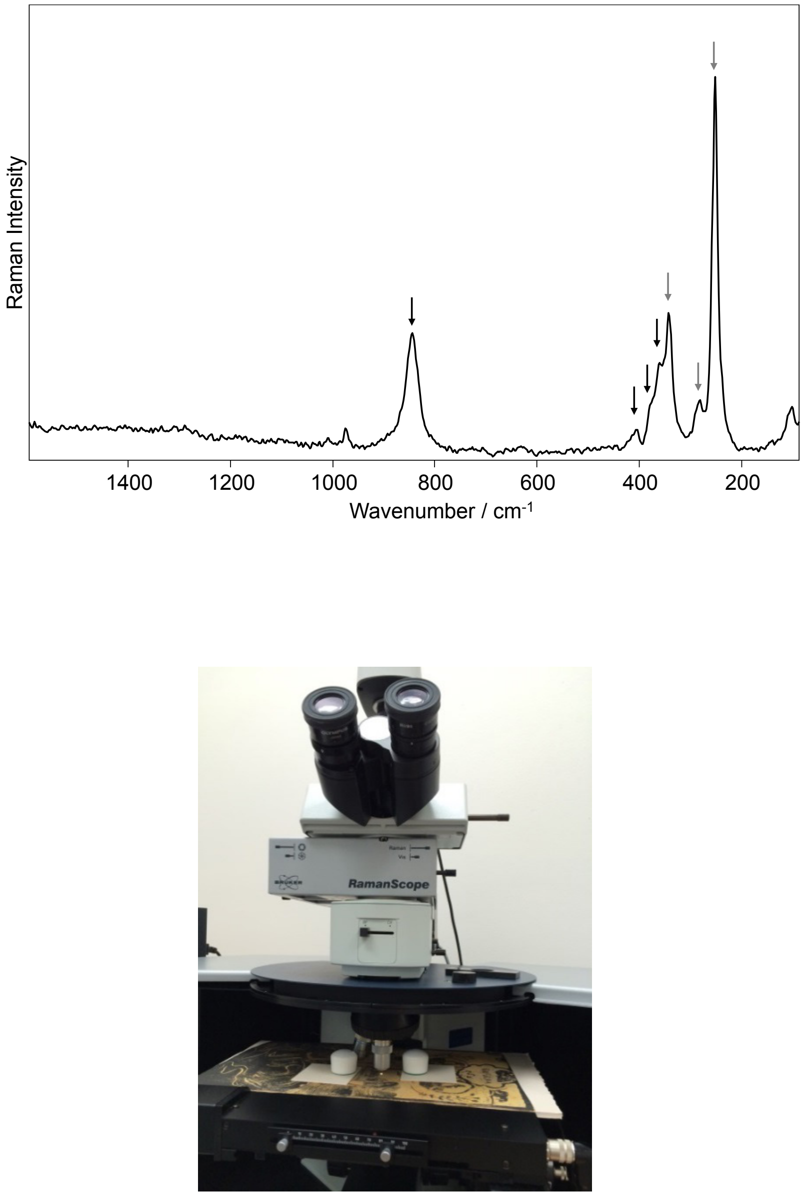

Figure 2. Up: In-situ FT-Raman analysis of *Noa Noa* (1948.255, The Art Institute of Chicago). Down: FT-Raman spectrum of the thick yellow in the background that shows bands related to vermilion (grey arrows) and chrome yellow (black arrows).

Acknowledgements

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TS2

Back to basics: from materials science to conservation.

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The fortune of Raman spectroscopy in the field of art and archaeology is due to its ability to get information, in completely non-destructive way, on a very wide range of different materials: organics and inorganics, fluids or solids, crystalline and amorphous, in bulk, thin film or nanostructure form.

In addition to the results obtained with the standard micro-Raman setup, the technique development made possible to collect information on objects and materials previously considered very hard to study. First of all, mobile, portable and handheld systems allowed the analysis of unmovable artifacts, making Raman spectroscopy a frequent presence during the study campaigns in museums, churches, archaeological sites. The new InGaAs detector arrays allow to study highly fluorescent materials using the Nd:YAG 1064 nm as excitation, without the disadvantages of the FT-Raman setup (heating, measurement time). The very fast, recently introduced, high electron mobility CCD detectors, reducing the acquisition time of some orders of magnitude, give us the possibility to realize Raman micro-mappings with very large space definition, even in 3D and moreover resolved in time.

Not only the instruments, but also the technique itself was improved. As a couple of examples, very fluorescent and low-concentration dyes are analyzed thanks to the enhancement of SERS effect, while SORS technique is starting to allow the study of deep, unexposed layers of materials.

In all the recent literature related to archaeometry and conservation science, it is evident the increase in importance of the multi-analytical approach required by the complexity of the field. Some “standard” setup usually include a “molecular plus elemental” combination; a classical case is Raman plus XRF or Raman and SEM-EDXS. Other typical combinations are “full vibrational” (Raman + FTIR) plus an organic-aimed technique (e.g. GC/MS) for paintings or plus a “structural” technique (XRD or ND) for ceramics. Sometimes Raman spectroscopy is coupled with a different technique in the same instrument like in Raman/SEM-EDXS, Raman/ATR (in particular to obtain tip enhancement effects - TERS), FT-Raman /FT-IR, even if the trend to couple instruments is not so significant as expected some years ago.

All this factors cause a huge data-flow that we need to manage, correlate and interpret in the correct way. The conservation scientists are usually submerged by data, spectra and tables. Luckily, even the data analysis process evolved. Chemometrics (multivariate analysis, PCA, cluster analysis, correlation graphs)is becoming increasingly common in Raman publications, even in the field of art and archaeology. In addition, most of the Raman patterns could be easily and quickly identified by searchable electronic databases, gaining the precious time necessary to put all the data together.
This means that usually we have insufficient time to deepen the knowledge of the materials we are studying. The risk to stay on the surface and loose details is great, especially in the case of the literature related to conservation and cultural heritage. Most of the materials we are studying and characterizing (or simply that we encounter during our diagnostic measurements) have been investigated for long time and well characterized in different scientific fields. For many of them it exists a huge literature, even related to Raman spectroscopy, that we often ignore because it’s outside our usual environment.

It is the case, as an example, of semiconductors. Many pigments are semiconductors sensu strictu (cadmium yellow, orpiment, cinnabar, etc.) or wide-gap semiconductors (e.g. titania) and they received a lot of attention starting from 30 years ago with many publications in the field of solid state physics. Of course, not all may be of interest for archaeometry, but a lot of information could be taken without starting again from the beginning (… from a blank sheet….).. This is the case of finite-size effects (phonon confinement, strain), very important for the interpretation of nano-crystalline titania, often present in both natural and synthetic forms in the materials we analyze and that could be important to have correct compositional information from cadmium yellow and red (CdS-CdSe solid solutions).

Countless Raman papers are present on iron oxides, from chemistry to solid state physics, from magnetism to mineralogy: this is a huge amount of information useful to understand phase transformations, disorder, size and heating effects, necessary to correctly interpret the Raman spectra and to understand the history of the artifacts we analyze.
Many examples could be found in the study of pottery: here it is very easy to get different results when using different techniques. The ternary feldspars usually present in the ceramic bodies are often classified as plagioclase when using diffraction techniques, while they look like potassium feldspars by Raman spectroscopy (especially when using automated databases). The interpretation of this complex behavior is not easy, but many elements useful for an answer are found in the mineralogical-petrographical literature, starting from some decades ago. We must draw in the same branch of knowledge to find the elements for the study of gems and stone artifacts.

The deep, detailed, atomic-scale knowledge of the materials is the key to go further in the understanding of their vibrational behavior. This is necessary to start fruitfully to couple the experiments with the simulations, an important trend for the future. The ab-initio calculations of Raman spectra (wavenumbers, intensity, polarization) are now a reality, disclosing new possibilities for Raman spectroscopy, even in the art and archaeology field, where complex materials require a complex approach.

OP4

Micro-Raman Spectroscopy for the Archaeology of the Iberians

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Keywords: Iberians, Iron Age, Archaeometry, MRS, EDXRF, TXRF, pigments, raw materials

The knowledge and dissemination of the culture of Iberians (VI-I ct. b.C.) have experienced great progress within the last two decades, becoming one of the most important fields in the study of the Protohistory of the Iberian Peninsula. However, despite these advances, there are several topics which need further research in Iberian Archaeology, such as the processes of manufacturing and decoration of different kinds of artefacts, and the choice of raw materials, including pigments.

In this frame, the University Research Institute for Iberian Archaeology, the Department of Physical and Analytical Chemistry of the University of Jaén (Spain) and the Department of Archaeology of Ghent University (Belgium) are involved, since 2004, in a multidisciplinary research line focused on the study of the abovementioned processes of manufacturing and decoration using Micro Raman Spectroscopy over a wide range of Iberians archaeological materials [1, 2].

This research comprises a set of materials dated between the pre-Iberian phase (VII ct. b.C.) and the Late Iberian phase (I ct. b.C). The typology of these materials includes ceramics, plaster with and without decoration, decorated sculptural fragments, stone urns and glass paste (Figure 1). All coming from different contexts (domestic, funerary, military, ritual) located in twelve archaeological sites in the provinces of Jaén, Córdoba, Granada and Málaga [2, 3].

The set of samples analyzed by MRS reaches 300 (250 ceramics and 50 samples of other materials). In some cases, when the Raman spectrum was inconclusive, the results were precised and completed using energy dispersive X-ray fluorescence (EDXRF), total reflection X-ray fluorescence (XRF) and X-ray diffraction (XRD). EDXRF and TXRF were also applied to obtain an accurate value of the concentration of various minerals present in the pigments of the decorations.

The use of MRS together with EDXRF, XRF and XRD is allowing information on: manufacturing, mineral concentration in pigments, application of decorations on ceramics before or after firing, and the group of raw materials and pigments more characteristics among the Iberians.For decorations ceramics, physico-chemical analysis determined the presence of pigments made from hematite, goethite, cinnabar, magnetite, amorphous carbon andmanganese oxides. For the materials employed in plasters, benches, storage structures and pavements, the most common minerals are quartz, gypsum, calcite, dolomite and hematite. In the decoration of stone materials, hematite and amorphous carbon were used. The colours of the glass paste recovered in the Iberian contexts were obtained using Naples yellow, Egyptian blue and calcium pyro-antimonate.

Finally, all information obtained will be shared from a catalog and database on-line currently under development. This database will provide information on archaeological contexts, materials and pigments used by the Iberians, methodology and techniques of analysis applied and incorporate 3D models of materials under analysis.

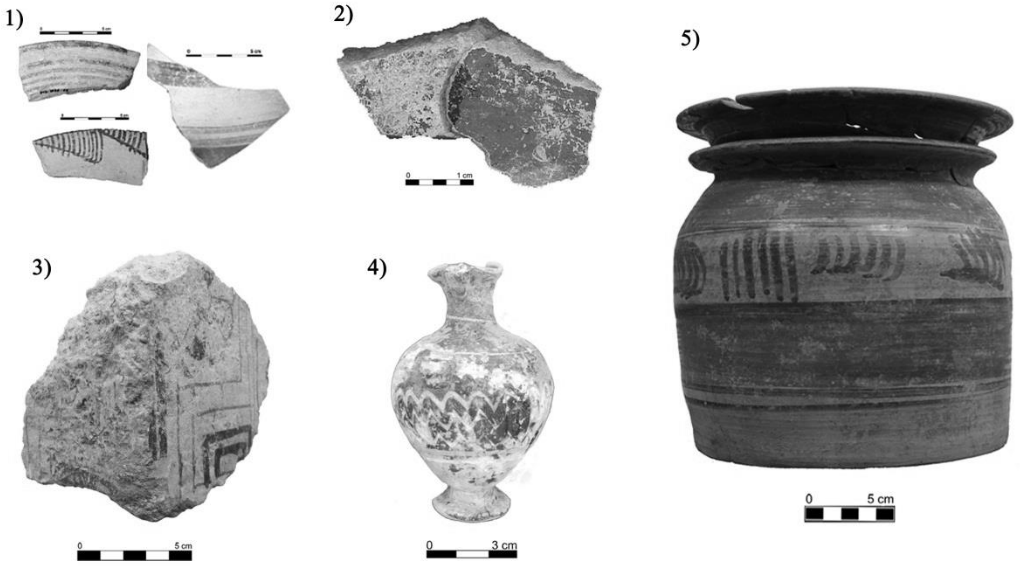

Figure 1. Iberian archaeological material analyzed by MRS**.** 1 Ceramic with red bands,2. Black and red plaster, 3. Funerary urn, 4. Oinochoe of glass paste, 5. Kalathos.

Acknowledgements

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OP5

Spectroscopic characterization of carbon based pigments used for decoration of prehistoric ceramic

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Keywords: carbon based pigments, Raman spectroscopy, SEM-EDS, GC-MS

Raman spectroscopy is widely used in the differentiation of various carbonaceous materials and identification of carbon based pigments used in the art and in the decoration of the prehistoric ceramic. In order to obtain a good quality spectrum which allows us to identify the analyzed pigments, specific excitation conditions are required[1, 2]. Moreover, the process of manufacturing of the ceramic may influence the quality of the reordered Raman spectrum and hinder or even make impossible the identification of the origin of the used materials[3]. Then complementary techniques are required in order to deliver data necessary in completing the study.

The investigations were conducted for archeological objects discovered in several excavation in the south-western region of Poland: the largest collection of Hallstatt, painted ceramic in Poland discovered in Domaslaw (Fig. 1a) and the collection of Early Iron Age pottery excavated in Wojkowice and Proszkowa (Poland) (Fig. 1b). In order to recreate the decorating and manufacturing processes of ceramics, the approach based on micro-Raman analysis, luminescence investigations, scanning electron microscopy with EDS and gas chromatography with mass spectroscopy (CG-MS) was established and then expanded in several cases by the application of widely used nondestructive techniques like petrographic analysis, X-ray diffraction (XRD) and thermogravimetric analysis (TGA). During the investigations in the collaboration with archeologists, ceramic vessels and reference samples were manufactured according to reconstructed conditions of the firing processes.

Figure 1 a) Hallstatt ceramic discovered in Domasław (Poland) b) Early Iron Age pottery discovered Wojkowice and Proszkowa (Poland).

Comprehensive investigations delivered information about decorating and manufacturing process of Hallstatt vessel collection discovered in Domasław. Although the Raman analysis was successful in the identifications of red ornaments visible on the surface of the ceramic (red ochre). Obtained results suggested the use of carbonaceous materials but it was not possible to precisely identify the origin of the material used in the black ornaments. Due to application of the GC-MS analysis it was established that the wood tar was used for manufacturing of the black painting material.

Early Iron Age pottery excavated in Wojkowice and Proszkowa was characterized by the black layer present on the surface. It was suggested by archeologists that the black surface might have originated from the presence of the black iron oxide, but the performed Raman analysis suggested the use of the carbonaceous material. The SEM-EDS analysis allowed us to list the possible origin of these materials. It revealed the presence of indicatory elements which suggested the application of the graphite materials originated from the deposits in the Lower Silesia.

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OP6

Characterization of natural, synthetic and imitation opals

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Keywords: Opals, Synthetics, Imitation, Raman, XRD, SEM

Opals are water-bearing micro- to non-crystalline materials,composed ofmicro-spheres of hydrated silica (SiO_2*n H_2O) with a high degree of structural disorder. Due to their optical properties, opalshave been largely used in jewelry and as decorative elements in art works. The characteristic optical phenomenon of the opal, called “play of color”, is due to the interaction of light with their pseudo-structure composed of regularly-spaced layers consisting ofmicroscopic (average diameter few hundreds of nm)silica spheres. According to the gemological classification, opals are classified depending on the presence or absence of this optical phenomenon. Due to their high economic value, rarity and preciousness, different kind of imitations and synthetic opals are available on the market possiblyreplacing original gems in artworks; for this reason, it is mandatory to distinguish the stonesof natural origin from those produced in the laboratory (that have the same chemical composition) and from the various imitations (that only have the same appearance).
Basedon the mineralogical composition, opals can be classified into three typologies, depending on the main constituent: opal-C (cristobalite-α, less disordered structure),opal-CT (cristobalite-α and tridymite-α, disordered structure), both typically of volcanic origin, and opal-A (amorphous opal, most disordered structure), generally of sedimentary origin.

Due to the structural disorder at long-range, hydrous silica is a rather complex material, and its study requires the combination of different analyticalmethods.

Raman spectroscopy is a suitable tool to investigate opals [1-4] andto identify theirdifferent geological provenance, because of its ability to detect the presence of nano-sized domains of silica polymorphs, as well as the presence of non-crystalline phases in the assemblage.The spectroscopic data can be implemented by XRD (long-range order information), SEM (morphological imaging) and FTIR (presence and distribution of H_2O/OH, CO_2 and other molecular arrangements)for a complete characterizationof the material [5-7].

This study is aimedatcharacterizing, by Raman and FTIR spectroscopies, in combination with XRD and SEM,a set of more than 20 naturalopals coming from the main known deposits all around the world: Australia, Madagascar, Slovakia, Mexico, Honduras and Ethiopia. The samples have been studied with the aim ofdefining a method to distinguishtheir geological occurrence;comparison with synthetic materials and imitations is also presented.

Raman measurements were performed using three different laser sources (532, 633 and 785 nm, respectively) to find the best experimental conditions and to minimize fluorescence background. As an example, we report a comparison between the spectra of asample from Ethiopia characterized by a broad band around 335 $cm^{-1}$and one from Australia (large band centered around 420 cm^{-1}).The different position of these large bands are symptomatic of different silicaticstructures.Indeed the band around 420 cm^{-1} evidences an amorphous structure, suggesting a likely sedimentary originof the Australian sample [1]. Instead, the band at 335 $cm^{-1,}$found in the sample from Ethiopia, can be ascribed to a large proportion of nanosizeddomains with tridymite-type atomic arrangements [4],thussuggesting a volcanic origin of this sample.

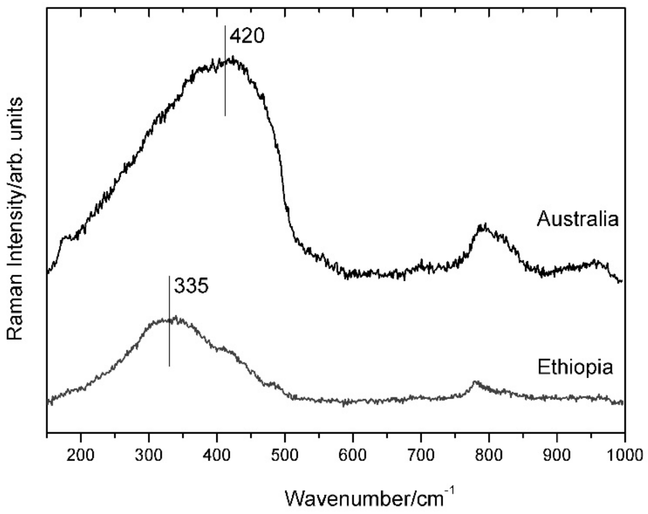

Figure1.Raman spectra of opals from Ethiopia and Australia. Spectra were arbitrary stacked for a better visualization.

Complementary FTIR spectra have shown the presence of carbon dioxide in some of the examined samples. This is anadditional piece of useful information for distinguishing opals from different deposits.

In this work we will show that, bycombining data from different techniques and in particular thanks to a detailed Raman investigation, it is possible to evidence fingerprints ofthe geological origin (volcanic vs sedimentary) and likely provenance of natural opals, and to distinguish synthetic/imitation vs natural opals.

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OP7

Discovery and characterization of challacolloite, an uncommon chloride on a fifteenth-century polychrome terracotta relief by Michele da Firenze

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Keywords: Challacolloite, potassium lead chloride, terracotta, polychromy, Michele da Firenze

In preparation for exhibition, the fifteenth-century gilt and polychromed terracotta relief, *Virgin and Child* by Michele da Firenze (Figure 1) in the collection of the Yale University Art Gallery, was recently conserved. The crystallization of water-soluble salts was suspected as the main reason behind its poor condition. Characterization using Raman spectroscopy, x-ray diffraction, and scanning electron microscopy / energy dispersive x-ray spectroscopy revealed the presence of KPb_2Cl_5.

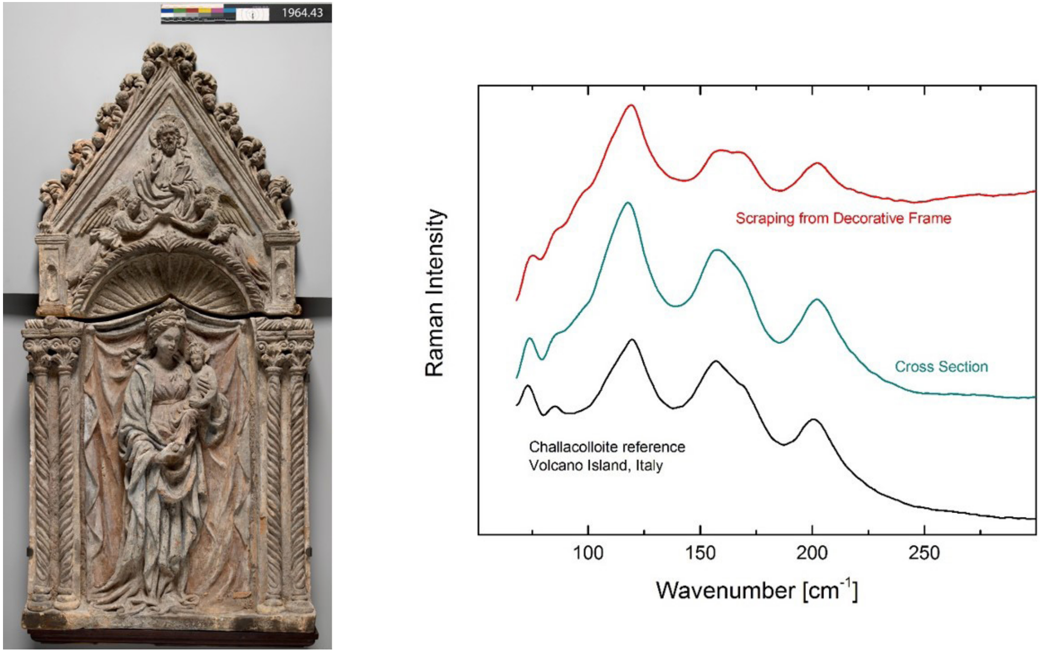

Figure 1. left: "Virgin and Child" by Michele da Firenze (Yale University Art Gallery, Maitland F. Griggs, B.A. 1896, Fund, 1964.43),ca. 1435, Terracotta, 137.2 x 65.4 cm (54 x 25 3/4 in.)**right:** Raman spectra of samples from the art work compared to a reference sample

Detection of this compound has not been previously reported in association with cultural heritage objects. In nature it occurs as challacolloite, a mineral first named after a finding at the Challacollo silver mine inIquique, Chile only in 2005. It forms at high temperatures in fumaroles of volcanos, including those in Italy and Japan [1].

The form and distribution of challacolloite crystals on the *Virgin and Child*has been investigated by scanning electron microscopy and Raman mapping of cross sections. At 785 nm excitation KPb_2Cl_5Raman spectra with a good signal to noise ratio can be acquired in less than a minute (Figure 1, right) and make the compound suitable for mapping. The resulting spatial distributionmaps of KPb_2Cl_5 show formation on the surface as well as inter and intra-layer growth. As a consequence, the paint layer structure looses its cohesion and this results in delamination and an exteremly friable surface.

While it is not known what caused the presence of the challocolloite, it can be speculated that the formation of KPb_2Cl_5resulted from the chemical reaction of lead white through harsh past treatments possibly involving the use of hyrdochloric acid and potassium containing cleaning solutions such as lye.

Acknowledgements

This research made use of the XRD facilities of the Chemical and Biophysical Instrumentation Center at Yale University with assistance by Brendon Mercado. Search of powder diffraction files and phase identification was carried out with assistance from Daniela Morales-Acosta (postdoctoral associate) at the Yale Center for Research on Interface Structures and Phenomena (CRISP). We thank Paola D'Agostino, Yale University Art Gallery; Challacolloite: Prof. Jochen Schlüter, Mineralogical Museum of the University of Hamburg, Germany and GianlucaOdicino, AssociazioneMicromineralogicaItaliana; Stefan Nicolescu, Yale Peabody Museum of Natural History

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OP8

Revealing the chemistry of ancient medicinal or cosmetic preparations containing heavy metals

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Keywords: ancient eye-medicines, mineral phase's characterization

Medicine was widely developed during the ancient times as the Ancient Egyptians, Greeks and then Romans prioritized public health. Some physicians, named oculists, were specialists in eye care. They used medicines called collyria, a Greek term related to their small bread-like shape. These medicines mainly contained heavy metals, plants and gums. This research aims to reveal the chemical composition, structure and manufacturing process of collyria.

This work can be described by three simultaneous parts. The first one concerns the study of ancient texts. A few ancient physicians and naturalists have written down their science and, fortunately, some collyria recipes were passed down. But these recipes have been translated, transcribed and sometimes even copied from one author to another. They used the terms of the time, rather unclear nowadays, which need to be associated with chemicals. This work may help to understand the exact chemistry behind the words and methods to reproduce it.

Due to the low availability of archaeological samples, the second part of this research focuses on replicating the likely chemical systems in collyria. Simplified systems are synthesized and analysed. We aim to reproduce the inorganic processes developed during collyria's synthesis. In order to study the chemistry and structural features of these prepared mixtures, we combine Raman spectroscopy, X-ray fluorescence (XRF) and X-ray diffraction (XRD). Our Raman device enables the observation of ultra low frequencies (ULF), the most sensible frequency range for the structural order of heavy metal. The low frequency range is not well referenced and we constituted our own spectra bank with the most common heavy metal derivates (oxides, carbonates, etc...). When the Raman spectra of those compounds are fully determined, the ancient recipes of collyria can be reconstituted and then their analysis can be compared to the archaeological ones.

Archaeological collyria are extremely rare, but some fragments are made available to be analysed. This constitutes the third and last part of our research. The collyria of the Musée gallo-romain de Lyon and the Bibliothèque Nationale de France were analysed and the results of their analysis were compared to the theoritical recipes. The analytical process developed to study model systems is adequate and efficient to ensure the study of archaeological collyria.

Among our corpus of archaeological artefacts, the collyrium called «stratioticum», the «soldier mixture», drawed our attention. It was found in Lyon and is one of the rare stampted collyria which can be attached to ancient recipes. It is constituted of only to mineral compounds, cerussite, $PbCO_3$ and hydrozincite, $Zn_5(CO_3)_2(OH)_6$, which correspond to *cerussa* and *cadmia* in the ancient recipes named stratioticum or stratioticon. This makes one step further in the comprehension of ancient terms and thus in the very principle of ancient medical processes.

Acknowledgements

We wish to thanks the Musée gallo-romain de Lyon, the Bibliothèque Nationale de France and the Musée d'Archéologie Nationale and the Institut National de Recherches Archéologiques Préventives (Inrap) which have allowed us to analyse their archaeological collyria.

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OP9

Studying the degradation of arsenic sulfide pigments by the use of tandem Raman spectroscopy-electrochemistry

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Keywords: Arsenic sulfides, Raman spectroscopy, electrochemistry, degradation

Since antiquity, semi-conductors such as vermilion (HgS), cadmium yellow and red (CdS and CdS,Se), titanium white (TiO_2) or arsenic sulfides (As_2S_3/As_4S_4) appear to have been widely used by artists as pigments. Even though they are all semi-conductors, they present different behaviors toward light, some being more stable than others. It has recently been established that (in)stability of the pigments can be rapidly characterized by measuring their thermodynamic oxidation and reduction potential [1, 2]. This method does not require lengthy exposure of the pigments to (chemical or physical) degrading agents. The arsenic sulfide pigments group (the yellow orpiment, As_2S_3 and red realgar, As_4S_4) appears to be part of the non-stable pigments, quickly degrading to arsenic oxide and arsenates upon light exposure [3, 4]. As arsenic sulfides are excellent Raman scatters, their photo-oxidation can easily be monitored with the aid of Raman spectroscopy. Additionally, changes in photo-activity can be recorded via electrochemistry, and such measurements may be indicative of changes in the pigment structure. The Raman spectral data may help to better identify the chemical (redox) transformations that give rise to the photo-current. The combination of an electrochemical setup and Raman spectroscopy appears then to be powerful combination to understand the rather complex photo-oxidation of arsenic sulfide pigments. Experiments conducted on natural commercially available pigments show that exposure to a green laser for a given period of time induces a decrease in the resulting photo-current, most likely due to the transformation of arsenic sulfide into its oxidized form, arsenic oxide. For the first time, the tandem of Raman spectroscopy and open clamp photo current measurement data will be presented for arsenic sulfide pigments.

Acknowledgements

This work has been financially supported by the Belgian Science Policy Office (BELSPO) through the research program Science for a Sustainable Development – SDD, “Long-term role and fate of metal-sulfides in painted works of art – S2ART” (SD/RI/04A).

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OP10

The green paints in the paradise wing of the triptych *The Last Judgement* by Hieronymus Bosch in the Paintings Gallery of the Academy of Fine Arts Vienna

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Keywords: Raman spectroscopy, green pigments, copper

Figure 1. *The Last Judgement* Triptychby Hieronymus Bosch, central panel and outer panels

The triptych *The Last Judgement* by Hieronymus Bosch, one of the most outstanding works of art in the collection of the Gemäldegalerie der BildendenKünste Wien paintings gallery of the Academy of Fine Arts Vienna, has been the subject of a collaborative research project between art historians, conservators and scientists. Investigations of art historical aspects as well as issues of painting technique were the main focus.

A complete documentation in the visible, infrared, UV and x-ray radiation range was carried out and a range of samples was taken for cross-sections, which were first analysedby optical microscopy and scanning electron microscopy in combination with energy dispersive x-ray microanalysis (SEM/EDX). By these means, it was possible toshow that the painting technique and palette are typical for the period, featuring traditional pigments such as lead white, carbon black, as well as azurite in the blues, vermillion, iron oxides and red lakes in the reds, lead tin yellow and ochre in the yellows [1].

Furthermore, the SEM/EDX analyses have revealed that mainly copper containing green pigments are present in the green paint layers of various parts of the altar piece. In order to differentiate the big variety of copper green materials such as malachite, verdigris, posnjakite, brochantite, atacamite as well as copper resinate, used as green glaze, it is necessary to perform compound specific analytical studies [2]. Raman spectroscopy was chosen as complementary technique, as it allows to distinguish between pigments of the same colour by studying their diverse structural properties. As a result, we clarified the chemical type of the pigments (mineral, natural organic or synthetic) and achieved a clear identification of the green materials that were employed in these panel paintings.

For the Raman analysis two instruments were available: Aramis of Jobin-Yvon, in the Institute of Science and Technology in Art, Academy of Fine Arts Vienna and the LabRam 800HR of Jobin-Yvon, in the Institute of Chemical Technologies and Analytics of the Vienna University of Technology. The Aramis Raman spectrometer is equipped with three lasers (633 nm, 532 nm, 785 nm) and Notch Rayleigh filters, whereas the LabRam 800HR has two lasers (633 nm HeNe and 532 nm frequency-doubled NdYAG DPSS) and two holographic super-Notch Rayleigh filters as well as an imaging system.

Green copper pigments identified by Raman spectroscopy in this altarpiece are malachite, a basic copper carbonate ($CuCO_3*Cu(OH)_2$), verdigris, which is the name of basic copper acetate $Cu(CH_3COO)_2\cdot[Cu(OH)_2]_3\cdot 2H_2O$, and copper resinate. The main components of this green copper glaze are copper salts of resin acid.

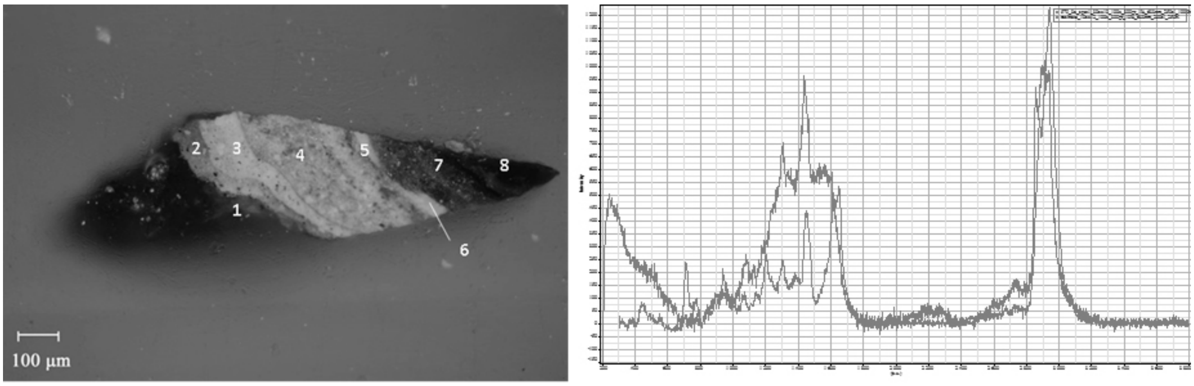

Figure 2. Layer structures of a cross-section in which Raman analyses was performed. In layer 7 copper resinate could be identified.

Acknowledgements

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OP11

Comparative Pallet Characterization in easel paintings of Two Well-Known 19th Century Colombian Artists by Confocal Raman Spectroscopy

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Keywords: Colombian art XIX century, easel painting, micro-Raman confocal spectroscopy, optical microscopy, oil on canvas

This work introduces the application of modern analytical techniques in the study of Colombian cultural heritage. Specifically, Raman spectroscopy has been used for first time in Colombia in this field, generating in this way a dynamic union between science and patrimonial science. This study aims towards the material characterization of the paint work of two well-known artists of the nineteenth century in Colombia to see the transition in the use of materials and the change of the oil on canvas technique in the country in the XIXth century.

The art in South America after the Spanish colonization was guided by the Catholic Church. Among these are easel painting and oil paint techniques; such works were limited to oral learning using pictorial supplies available in the region. During XIX century the country became open to global arts as well as techniques, styles and possibilities of representation apart from religious situations. This time coincided with the introduction of industrialization and the development of commercial and portable painting materials; resulting in the creation of a formal art academy in Colombia.

The cultural heritage studies conducted on similar artworks in Colombia before the present research could only use destructive and low-resolution methods. Naturally, this left open many analytical questions.

Raman spectroscopy has become one of the most important noninvasive analytical tools in studies related to art and cultural heritage, due to its resolution, fast performance, and accuracy among others. By this reason and for the first time, this analytical tool was chosen as a mandatory technology to generate the proper knowledge in studying Colombian heritage.
By using the techniques of confocal micro-Raman spectroscopy and observation under light microscopy, it was proposed to identify the color palette of paint work done with the technique of oil on canvas by Epifanio Garay (1849-1903) (21 works) and Jose Maria Espinosa (1796-1883) (14 works), two renowned artists from XIX century in the collections of the National Museum of Colombia.

For the present study micro cut samples were taken from damaged areas on the artworks, trying to cover all possible colors and tones present on them. A confocal Olympus BX41 fluorescence microscope coupled with a Raman spectrometer Horiba® XPLORA together with a set of laser emissions 785 nm, 638 nm and 532 nm, was used to acquire the spectral data, through which it then was possible to characterize the chemical composition of the samples. To this end, a novel method for handling and storing samples obtained by micro cut was developed, which allowed direct measurements in each micro sample from the surface, the back and the stratigraphic layers, thereby increasing the total area of analysis on each sample, and decreasing the preparation time of each sample. Similarly, an optical device for in situ measurements was developed to confirm the presence of the compounds detected in the micro-cuts in areas of impossible sampling.

The analysis of both Raman results and the observation under microscope resulted in the accurate identification of the pictorial palette of both artists, pigments as vermillion, black carbon, Prussian blue, lead white, among others was clearly identified. In the same way, their pictorial base preparation and their artistic technique used to produce the artwork was identified. As part of the historical discussion, the entry of pictorial supplies from industrial productions in this period of the nineteenth century was evident, as the homogeneous size grain in pigments as vermillion, red ochre, yellow ochre, etc.; and through this the change in the techniques of producing art in Colombia.

Consequently, for the first time in the country, a scientific basis for the identification and comparison of the works of these two artists was established. These results provide a comparative base to authenticate attributed works and a better guidance for future auditors in the processes of restoration, consolidation and conservation of the cultural heritage of Colombia.

Figure 1. Photography example of one paint work studied for each artist a) Batalladel Río Palo Ca. 1850. José María Espinosa Prieto. Paint (oil on canvas). 81 x 121 cm. Reg. 3423. Colection National Museum of Colombia picture: ©Museo Nacional de Colombia/Juan Camilo Segura b) La mujerdellevita de los montes de Efraím, 1899. Epifanio Julián Garay Caicedo. Paint (oil on canvas). 139 x 198,5 cm. Reg. 2103. Colection National Museum of Colombia Picture: ©Museo Nacional de Colombia/Juan Camilo Segura

Acknowledgements

This work was made possible thanks to the collaboration of the National Museum of Colombia, their Chief restorer Maria Catalina Plazas and by financial means from the Faculty of Science - Department of Chemistry of the University of Los Andes Colombia.

OP12

Raman microspectroscopy and laser ablation of old paper samples with foxings

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Keywords: paper composition, Raman microspectroscopy, laser ablation, sampling

For identification, dating and correct restoration of historical paper sample it is expedient to know exact composition of the sample due to complexity and inhomogeneity of paper.

The main component (about 90%) of paper is cellulose which is a polysaccharide with a degree of polymerization of about several thousands. The type of cellulose depends on a production material (wood, cotton, flax, etc.), but any cellulose molecule undergoes oxidation which results in paper degradation. Cellulose oxidation is chemically and physically inhomogeneous and complicated process which yields the crucial changes in paper composition and the corresponding changes in its optical properties (paper becomes yellowish due to the shift of absorption spectrum into the low frequency range). Note, that degradation rate depends on the type of cellulose.

In addition to homogeneous discoloration, paper often exhibits foxings (dark-brown spots) with average size of several millimeters. In the foxed area the paper is much more fragile and oxidized. The first possible reason of foxings formation is additional oxidation provided by vital activity of fungi. The second one is an oxidation catalyzed by metal atoms.

Fillers and sizing agents are also included in paper composition. They provide durability, whiteness and brightness of paper.

Raman and IR spectroscopy can be used for determination of the cellulose type. For example, the spectral peaks at 1600 and 1660 cm^{-1} are assigned to lignin that is characteristic of the wood pulp. Atthesametime, directapplicationofvibrationalspectroscopyforidentificationofadditionalcomponentsinthepaperis ineffective due to the background scattering or absorption in cellulose.Note the lack of literature data on Raman spectroscopy of foxings.

At present, paper components with low concentrations are normally identified with the help of chemical methods. However, chemical substances may destructively affect cellulose fibers.

In this work, we propose to use laser ablation for extracting paper components and to employ Raman microspectroscopy for non destructive identification of a blated particles.

The ablation experiments are performed using the second-harmonic radiation of the Nd:YAG laser with a pulse duration of 10 ns, repetition rate of 10 Hz, and pulse energy of up to 180 mJ. The diameter of the laser spot on the sample is 6 mm, the corresponding pulse intensity is about 60 MW/cm2, and the fluence 0.64 J/cm2. The sample is shifted along the horizontal direction at 0.3 mm/s to avoid thermal damage. Ablated partials are collected on the BaF_2 plate.

For the Raman measurements, we use a DXR Raman microscope (Thermo Electron Corporation) with excitation at 780 nm. In the experiments, we use a 50x objective and a confocal pinhole with a diameter of 50 μm, so that the diameter of the focal spot is 0.7 μm and the axial resolution (10 μm) is comparable to the diameter of a cellulose fiber. Thus, we perform the measurements on the single fibers. The laser power on the sample is 24 mW, and the accumulation time is 600 s per spectrum. The identification of the components is based on the Raman spectra of reference substances and Raman databases.

We study five paper samples with foxings that differ by composition and production dates. After ablation procedure, different substances such as cellulose, protein, and minerals are identified.

The laser ablation allows the extraction of particles containing filling and sizing compounds that can be studied using spectroscopic methods, in particular, Raman (micro)spectroscopy with excitation in the near-IR spectral range in the absence of strong background signals of cellulose fibers. The absence of the large cellulose fibers among the ablation products and earlier results on the structure of laser-irradiated papers indicate the absence of noticeable damage of paper materials.

Acknowledgements

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Wednesday, **September 2nd**

TS3

Raman spectroscopy for Art and Archaeology: 30 years of pushing the envelope in cultural heritage studies

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More than three decades after the first pioneering papers ushering the advent of Raman microscopy on the analytical scene for the investigation of works of art the technique has become a staple in the investigation of the myriad materials that make up our cultural, anthropological, archaeological and artistic patrimony. Its characteristic of non-invasiveness, high spatial resolution, molecular specificity, tunability of excitation to overcome fluorescence problems, and, lately , portability and coupling with other analytical techniques have made it a formidable ally of cultural heritage scientist.

This presentation will highlight the milestones reached, notable examples in the investigation of artistic and archaeological materials and their deterioration products, as well as recent new developments in applications, instrumentation, and methodologies, including the significant upsurge of Surface Enhanced Raman Scattering (SERS). In the past ten years SERS has literally exploded in the field, allowing the detection of naturally occurring and synthetic colorants in ultra-small samples with unprecedented sensitivity. The broad spectrum of SERS analytical methodologies and approaches will be reviewed in the context of notable examples of works of art and archaeological artifacts.

This talk will provide a review for those relatively new to the field as well as highlight challenges and opportunities for further developments and applications in the future .

OP13

FT-Raman analyses of dyes and lac pigments in folk arts and crafts in the interiors of Decorative Farmhouses of Hälsingland, Sweden, UNESCO World Heritage

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Keywords: dyes, dyestuff, colouring matters, lac pigments, FT-Raman, computational methods

This pilot study is about method development using FT-Raman supplemented with computational methods for analyzing dyes and lac pigments used in folk art and craft from Hälsingland, Sweden, during the 18th and 19th century. The study is part of an interdisciplinary four years long project funded by the Swedish Research Council (Vetenskapsrådet). Conservation scientists, chemists, physicists, conservators, art historians and ethnologists from different Swedish universities are collaborating to make a holistic approach and material characterization of wall paintings, painted wall-hangings, decorated wooden furniture and patterned textiles in Decorated Farmhouses of Hälsingland, UNESCO World Heritage since 2012. Spectroscopic methods combined with historic sources are used to understand the materials and the context and time when these artefacts were made. The interdisciplinary collaboration is essential and in this way, new and deeper knowledge of the paint, coatings, painting techniques and dyeing methods in the 18th and 19th century Swedish folk art and handicrafts can be obtained. The relevant research questions span over a wide range, for example about the existence and time frame of woad and turkish red dye. Suitable materials for characterization are for example clothing, which are often possible to date historically due embroidered monograms. Therefore, the material characterization of clothing dyes may shed light on the usage and distribution of various folk art techniques.

In the pilot study we present different historic dyestuff such as safflower, cochineals, madder, turkish red, brazilwood, fustic, birch leaves, weld, turmeric, woad, indigo and indigo carmine - all common in Sweden during this period. The dye references were made according to old Swedish recipes. Different textile fibres - cotton, wool and linen/flax - were dyed. In addition various colouring matters - for example purpurin, alizarin, atranorin, orcein, myricetin, luteolin, quercetin, rhamnetin, emodin, crocin, curcummin, kaempferol, indigotin and indirubin - were tested to identify specific fingerprint regions for each dye. In order to assist the interpretation of the vibrational spectra of the samples, computational methods were performed.

A typical case study is presented below: threads from an authentic textile, a blue skirt from early 19th century Delsbo parish, were analyzed using FT-Raman spectroscopy. The spectra were then compared with reference spectra. The Raman spectrum of a blue colored linen warp thread is shown together with the spectrum of pure indigotin as a reference (Figure 1). Preliminary results indicate that we are able to identify the main peaks as originating from indigotin in addition background from the linen fibre, suggesting indigo as the dye. Woad was also a common dye during the 18th and 19th century in Sweden [1]. Different from indigo, woad may also contain kaempferol. The comparison with reference spectra however did not yield a match in the fingerprint regions of kaempferol at f.ex. 1188 cm-1 and 1606 cm-1 [2, 3]. Therefore we may exclude woad as an ingredient in the colouring dye of this specific piece of clothing. Historic sources from 18th century usually mention woad as an additional ingredient in the indigo vat to catalyze and help the bacterial fermentation process [4, 5]. During 19th century though, woad is more seldom mentioned as an ingredient and perhaps this is an example of a more modern indigo vat.

Other preliminary results shows that almost all pure colouring matters and some of the dyed textile fibres are easy to analyze with FT-Raman. However, it is difficult to analyse red dyes with this method. Furthermore, wool sometimes complicates the analyses. Therefore, we will continue using FT-Raman analyses and the computational models, supplemented with other analytical methods such as SERS and field-free APCI-TOF MS.

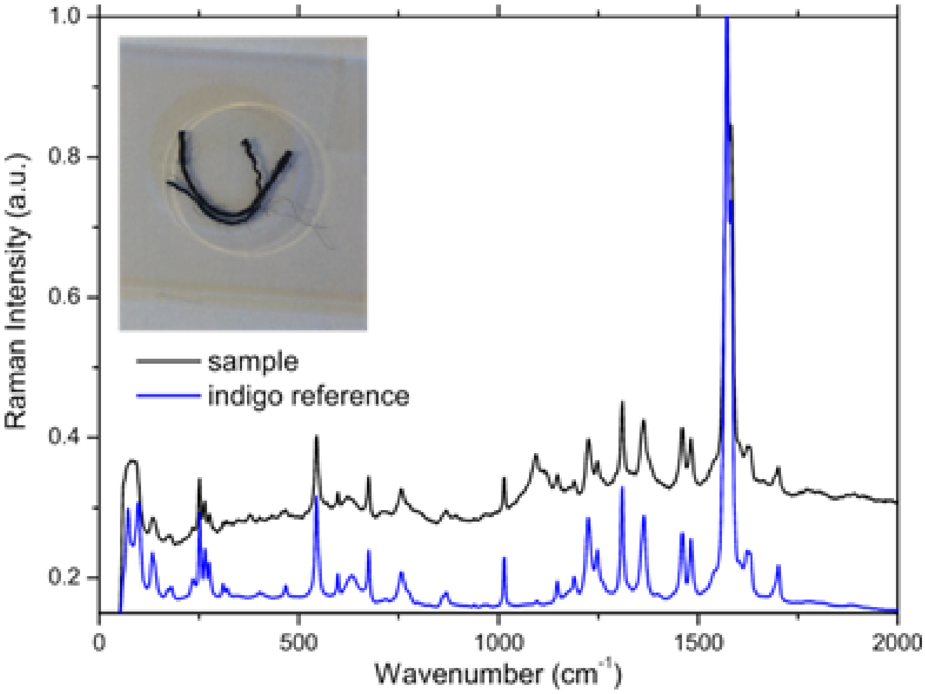

Figure 1. FT-Raman spectra of a blue colored linen warp (upper line) and pure indigo as a powder (line below). The inset shows a photograph of the threads.

Acknowledgment

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OP14

New frontiers of Raman spectroscopy in conservation science

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Keywords: non-destructive micro-Raman spectroscopy; optical fiber, conservation science,
painting analysis

Raman spectroscopy is a technique that has frequently been applied for the investigation of art and heritage objects. The analysis of the materials is essential to gain knowledge about the techniques employed by the artists, as well as, to understand their conservation, condition and degradation processes. Advantages like its ability to identify materials at a micrometer-scale and its Nondestructive character of this technique as well as ability to identify materials at a micrometer-scale and sub-micrometer scale are greatly appreciated in conservation science.

In this work we would like to introduce new features of Renishaw Wire 4 software like 3D imaging, particles stat analysis and remote measurements which could be use in artworks.

We will demonstrate example of Raman diagnosis for the conservation of masterpieces at Raphael cartoon "Scuola di Atene". The Renishaw Raman microscope, equipped with a Renishaw video compact fiber optic probe, installed on a flat trolley was used for this studies and cartoon was mounted on a flipping table to allow measurements both vertical and horizontal positions. We identified the chemical nature of the materials used to generate the sketch, as well as conservation conditions.

Acknowledgements

Special thanks to Armida Sodo, Alfonso Pio Russo and Annalaura Casanova Municchia (Università Roma Tre, Department of Science – Rome, Italy) for performing measurements and providing data..

TS4

Raman spectroscopy: from Museum to archaeological excavations

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Keywords: Chile, Egypt, Cyprus, pigments, alteration, smalt

Analyses on museum objects, such painted sculptures, easel paintings, drawings, glasses, glazes, are generally multiscale and complementary, because the studied subject is composite.
Generally, non invasive analysis is performed, and the Raman spectroscopy is a reliable tool to obtain data concerning the structure of the components. Combined with other results (XRF, PIXE, FORS, multispectral images, microsampling), one can propose characterization of dye, mineral, alteration compound or state of polymerization inside an amorphous phase.

Normally performed inside laboratory, the portable device permits to obtain the same data directly on field: inside museum, storage or excavation, during restoration or for research.

Restoration of the winged Victory

Examples of results obtained on objects from Mediterranean area (Cyprus, Egypt) or from European collections permit to explain the importance of Raman for the Cultural Heritage.

OP15

Multi-analytical approach to the study of archaeological iron corrosion products

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Keywords: corrosion, iron artefacts, Raman spectroscopy, conservation of iron artefact

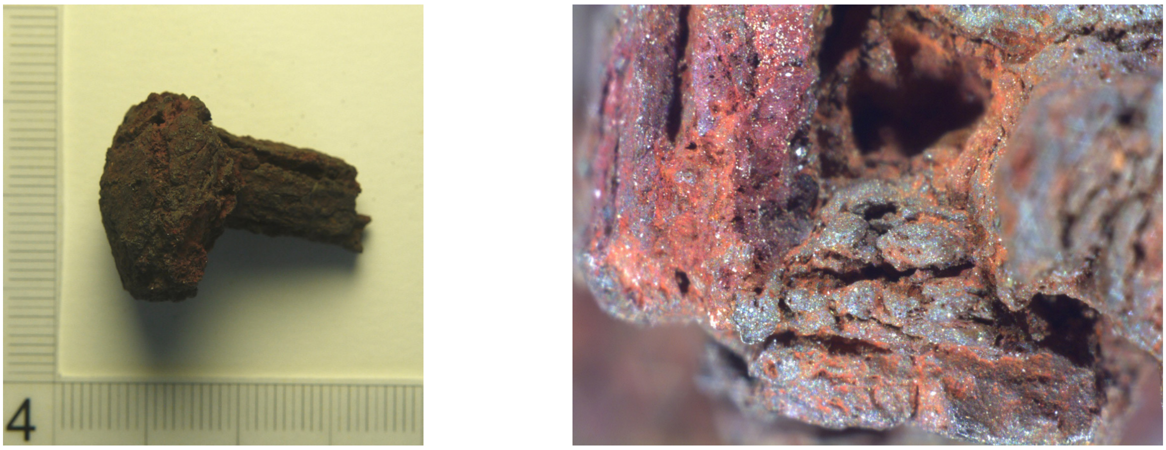
Preservation of iron artefacts is one of the main problems encountered by scientists involved in the protection of the metallic cultural heritage. As a matter of facts, the corrosion of archaeological iron artefacts results in a mineralization of the surface, which little by little becomes completely coated by a corrosion product layer. Subsequently, the metal core continues to corrode and the degradation phenomenon provokes flaking of the mineral crust, until the metal core is completely oxidized. Finally, in some cases the archaeological iron artefacts lose entirely their shape and become unsuitable for exhibition or further studies.

In order to establish proper conservation procedures, a complete understanding of the corrosion mechanisms of archaeological iron artefacts is needed, taking into account both the modifications that occur while the artefact is buried in soil and how these changes affect the degradation mechanism and the artefact stability after excavation [1].

This study deals with the characterisation of the corrosion products of iron artefacts, four nails and one axe, coming from the archaeological site of Tharros, in Sardinia (Italy). The city of Tharros has its origins in the 2nd millennium BC, when it was inhabited by the nuragic people, until the Phoenicians began to occupy the area in 8th century BC, followed by Punic and Roman people; finally it was abandoned around 1070 AD.

The multi-analytical approach utilized consists in the microstructural and micro-morphological study of the artefacts; both the bulk alloy and corrosion product layers were characterised by means of OM, SEM-EDS, XRD and Raman techniques. Scanning electron images and EDS spectra were obtained using a FEI scanning electron microscope equipped with an EDAX GENESIS spectrometer. The XRD spectra were collected by means of a Philips X'PERT conventional diffractometer, with Cu anode. The Raman spectra were obtained using a micro/macro Jobin Yvon Mod. LabRam HRVIS, equipped with a motorized x-y stage and an Olympus microscope. The backscattered Raman signal was collected with 50x objective and the Raman spectra were obtained for a non-oriented crystal. The 632.8 nm line of a He-Ne laser was used as excitation; the laser power was controlled by means of a series of density filters. The minimum lateral and depth resolution was set to few micrometers. The system was calibrated using the 520.6 cm^{-1} Raman band of silicon, before each experimental session. The spectra were collected with multiple acquisitions (2 to 3) with single counting times ranging between 20 and 30 seconds. The spectra were recorded using the LabSpec 5 program from100 to 4000 cm^{-1}.

Dealing with the iron nails (one is shown in Fig. 1a), from the micro-morphological point of view, different typologies of corrosion products were detected in the different areas of the surface. In particular, the XRD and Raman analyses put in evidence the presence of goethite (FeOOH) and lepidocrocite (FeOOH) in correspondence of the yellow-red areas; on the contrary, poorly crystallised maghemite (Fe_2O_3) and magnetite (Fe_3O_4) are mainly present in the internal zones of the artefacts (as it is possible to observe in the OM image of Fig.1b), characterised by dark grey-black colours.



(a) (b)

Figure 1. Iron nail coming from the excavation site of Tharros (a); OM image showing the nail cross-section, where areas of different colours can be easily observed (b).

The presence of magnetite, one of most stable iron oxide, in correspondence to the artefact core, justifies the good conservation condition of the nails.

Different findings were observed on the axe, which during the ten years after the removal from soil, was subjected to a severe degradation process. The Raman and SEM analyses shown, in particular, the presence of akaganeite (α-FeOOH) needle-like crystals, which grown rarely in nature and mainly in chlorides ions rich environments [2]. The presence of chlorides ions in the corrosion product layer and the volume increase due to the formation of iron hydroxides, induced the flacking of the surface, thus compromising dramatically the integrity of the artefact.

Acknowledgements

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OP16

A new insight into polyurethane foams degradation – the use of Raman spectroscopy for the evaluation of long-term storage conditions

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Keywords: conservation, polyurethane foam, long-term storage conditions, infrared and Raman spectroscopy

This research aims at bringing new contributions for the evaluation of storage conditions for ether- and ester-based polyurethane foams (PUR) based on Raman spectroscopy. By showing a life-expectancy of 20 to 50 years, many polyurethane objects show severe degradation signs (yellowing, crumbling and brittleness) which, so far, cannot be prevented [1-4].

Aiming to establish a preservation strategy, a natural ageing experiment (during 12 months at 45-55% relative humidity in the dark) is being carried out for the study of four different storage conditions: in open air at room temperature (T), enclosed at room T, enclosed at low T (11-13ºC) and enclosed at room T without oxygen. For the anoxic conditions, oxygen absorbers were used and the enclosed systems consist on barrier film bags. The selected PUR reference samples are composed of 2,6- and 2,4-toluenediisocyanates (TDI), poly[di(ethylene glycol) adipate] (for the ester-based) and poly(propylene glycol) (for the ether-based), with 50 Kg/m^3 density. For the assessment of chemical and physical molecular degradation, PUR samples are analysed every 3 months by infrared (transmission mode) and Raman (633 nm laser) micro-spectroscopies. To examine surface morphology and PUR fluorescence, optical microscopy (under UV and visible light) has been applied. Colour changes have been followed by colorimetric measurements.

Although some conservation studies have been focusing on the deterioration of PUR [1-4], neither has used Raman spectroscopy to study the polymer molecular degradation. According to this research, the promising results obtained show it as a powerful tool in the detection of early stages of PUR molecular degradation, in particular in the region 1600-1750 cm^{-1}. Raman spectroscopy is showing spectral variations (Fig.1) which may correspond to the formation of new C=C bonds (causing yellowing) on the main molecular structure (broadening of 1620 cm^{-1} peak and increase of 1640 cm^{-1} peak relative intensity) and, to the formation of new hydrogen-bonds in its secondary structure (increase of relative intensities at 1665 cm^{-1} and 1700 cm^{-1}) [5, 6]. Furthermore, peak area and peak width at half maximum for the benzene ring stretching vibration at 1620 cm^{-1} are calculated, by fitting with a Lorentzian function, as well as peak ratios with respect to C-H$_2$ bending at 1455 (for the ether-based) and 1447 cm^{-1} (ester-based). The function fitting and peak ratios enable the detection of unclear spectral variations. This has proven Raman spectroscopy as an advantageous technique in contrast with infrared spectroscopy where no molecular changes are detected.

The anoxic enclosure is showing the best results for the stability of polyurethane foams (ether-based) while the open system is the most harmful (for ether- and ester-based PUR). Concerning the yellowing of polyurethane, the enclosed systems (regardless the presence of oxygen and temperature) are proving to minimise colour changes ($\Delta E<2$). This shows a new insight into the importance of oxygen and its long-term availability in the yellowing of polyurethane foams (in the dark).

In general, this experiment has enabled new contributions for the lowering of PUR high degradation rate.

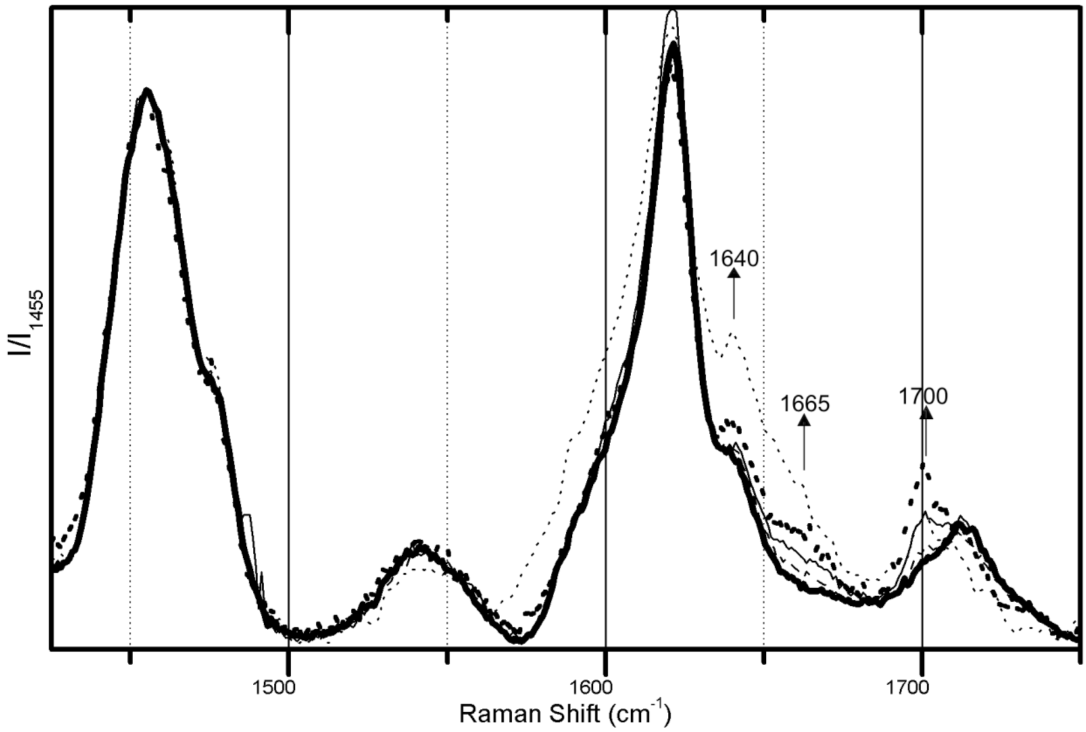

Figure 1 Raman spectra of ether-based polyurethane foams before and after six months of natural ageing in different storage conditions: unaged (bold line), enclosed/anoxic (dash line), enclosed/low T (thin line), enclosed (bold dots), open (thin dots).

Acknowledgements

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OP17

Multidisciplinary approach to characterize an unusual blackish patina on the Neang Khmau temple- Archaeological Khmer area (Cambodia)

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Keywords: Patina, Stone deterioration, Archaeological site, Manganese oxides, Laterite

In the archaeological Khmer complex (Cambodia), an unusual blackish patina on the external walls of the Neang Khmau temple has been observed during a recent archeological survey. It is distributed over all the four facades, covering a relevant part of the vertical surfaces protected from rainfall (Fig.1). The temple, dated X century, is located on the top of a hill in a cleared area, subject to high ventilation, high solar radiation and relevant rainfall. It was built by using laterite bricks, a natural material rich in aluminium, iron, manganese, titanium and silica, formed in hot and wet tropical areas [1, 2]. The temple looks heavily colonized from lichens and cyanobacteria respectively in the lower and upper parts. In general, blackish alterations can be due to cyanobacteria colonization, which is heavily recurrent in tropical countries [3, 4], to a chemical modification of the material, or to an accumulation of pollutants (*black crusts*). Distinguishing among these alteration patterns is mandatory for a correct conservation or restoration treatment, although this is often not easy and requires a multidisciplinary approach. A preliminary investigation on the collected samples excluded a biological colonization as origin of the blackish alteration of the temple laterite bricks. An intuition that was corroborated by the observation that the blackish patinas are visible in areas protected from water percolation.

In this work we have investigated the physico-chemical origin of this unusual patina by identifying its mineralogical and chemical composition. Raman and FTIR spectroscopies, SEM-EDS and X-Ray diffraction have been applied to characterize the alteration products [5]. Analyses have been performed both on single fragments and on polished rock sections of samples collected from all the four temple sides in order to check for any variation due to different exposition. Petrographic and SEM examination of the polished sections showed the black patina (Fig.1) to consist of alternating reddish and blackish mineral layers, few tenths of microns thick. Combination of SEM-EDS and powder diffraction revealed that the black layers, in particular, are mainly composed of poorly crystalline Mn minerals, which could be better characterized on the basis of the Raman and FTIR spectra.

This peculiar alteration pattern is interpreted as due to the tropical climatic conditions of Cambodia. Indeed the alternation of wet and dry seasons may favor the migration of ions and their successive immobilization in regions not directly subject to leaching. During the dry season the evaporation process gives rise to an active mobilization of iron and manganese from the inner areas of the stones towards the surface. The process ceases when humidity restores an equilibrium.

We cannot exclude, however, a past role of bacteria, which could have contributed to dissolution of cations from the stone, and eventual production of such patina [7, 8]. Indeed it is well known in the literature that both autotrophic and heterotrophic microorganisms can oxidize some iron and manganese minerals [9, 10], although we have not found any signature of organic products.

Figure 1. a) Neang Khmoa Temple (South exposition); b) detail of the stone surface; c) stereomicroscope sample observation

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TS5

Extension of Spatially Offset Raman Spectroscopy to the Microscale for Conservation Science

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Keywords: micro-SORS, painted layers, non-destructive

Here we present a recently developed variant of Spatially Offset Raman Spectroscopy (SORS [1]) for the non-invasive analysis of thin painted layers, micro-SORS.
The knowledge of the composition of artworks subsurface is critically important. Direct information on the stratigraphy of painted surfaces is essential for conservation as well as deeper understanding of artist's technique. It is also important to monitor the presence of decay products under the surface or the distribution of conservation treatments inside the substrate. In general, Raman spectroscopy can probe subsurface composition only with (semi-)transparent samples. With paintings the layers are however often highly diffusely scattering. As such one has to resort frequently to cross sectional analysis by Raman spectroscopy. However this approach is destructive and cannot always be applied to precious artworks.

The direct application of SORS to paintings has not been possible so far. Due to the magnitude of excitation laser beam and Raman collection area diameters (as well as spatial offsets) conventional SORS is restricted to relatively thick layers, namely on the order of mm's or more while the position of the concealed substances in artworks is by a magnitude or two thinner. The method we propose [2] is not as effective as full SORS but it is easily deployable on microscale using conventional confocal Raman microscope. The measurements are performed in different sample positions (Figure 1), (i) first, with the sample surface in the correct image plane (the 'zero' position) and (ii) with the sample displaced away from the microscope objective along the microscope objective axis by a 'defocusing distance Dz' to induce defocusing of the laser illumination and Raman collection zones on sample surface. The former measurement (the zero position) yields a spectrum dominated by the surface layer and corresponds conceptually to a zero-spatially offset measurement in conventional SORS analysis. The displaced measurements (defocused positions) yield Raman spectra which have a higher relative content of the sublayers.

There are several advantages in using the defocused modality of micro-SORS. Firstly, it does not require any particular set-up or reconfiguration to a conventional confocal Raman microscope. Secondly, moving the sample surface away from the Raman microscope objective the measurement is not restricted by microscope working distance.

The concept is demonstrated by its application to the non-destructive interrogation of painted layers in real objects of art [3], where conventional Raman microscopy would not be applicable. The most representative measurements were acquired on painted sculptures originating from the Sacred Mounts, prestigious devotional places constructed during the late fifteenth and seventeenth centuries in North Italy. Other application examples outside cultural heritage will also be presented.

The technique extends the depth applicability of Raman spectroscopy and with its inherently high chemical specificity expands the portfolio of existing non-destructive analytical tools in cultural heritage. The method has a potential for being developed into a portable totally non-invasive analytical tool.

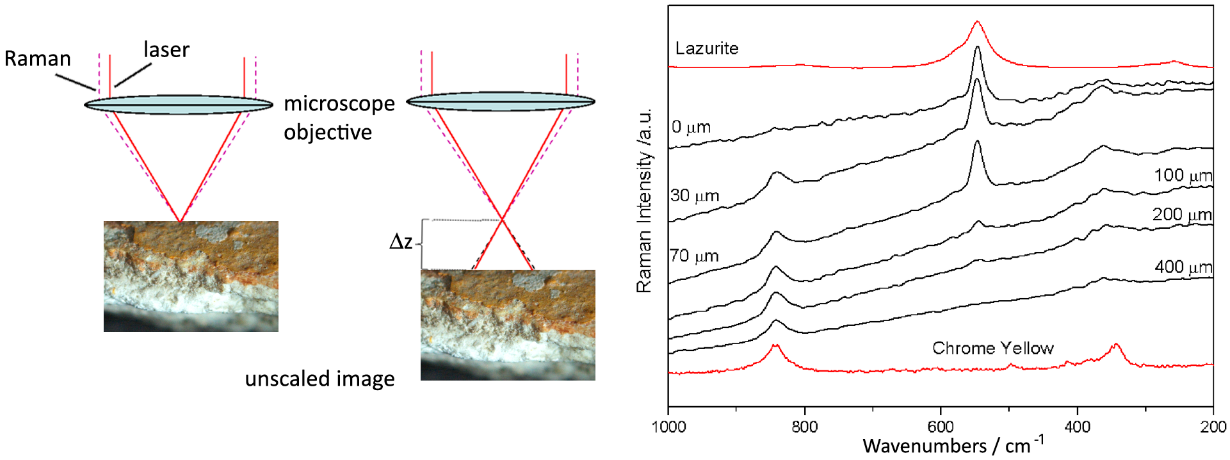

Figure 1 Schematic diagrame of defocusing micro-SORS measurements (left) and defocused Raman spectra (right) shown for different distances from the imaged plane indicated next to each spectrum (0 = 'imaged' position).

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OP18

Combined spectroscopic analysis of beads from the tombs of Kindoki, MbanzaNsundi, Lower Congo

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Keywords: glass beads, Congo, Raman spectroscopy, handheld XRF, chemometrics

The materials studied here come from a Western African context and are likely to be of European origin. Excavations have been carried out in Lower Congo province of the DRC since 2012 in the framework of the KongoKing project [1], [2]. The project is devoted to the study of the origin and early history of the kingdom (before AD 1500) through an interdisciplinary approach (archaeological and historical linguistic).

The beads excavated in the burial site of Kindoki (metal beads and bells, shells and glass beads) have been analysed by means of handheld X-ray fluorescence and micro Raman spectroscopy, in order to characterize the glass matrix as well as the pigments and opacifiers.This information can help to clarify the manufacture techniqueandserve as an indicator of the origin of the beads. Moreover, the application of chemometrics on the data obtained from the handheld X-ray fluorescence can highlight similarities in the glass composition.

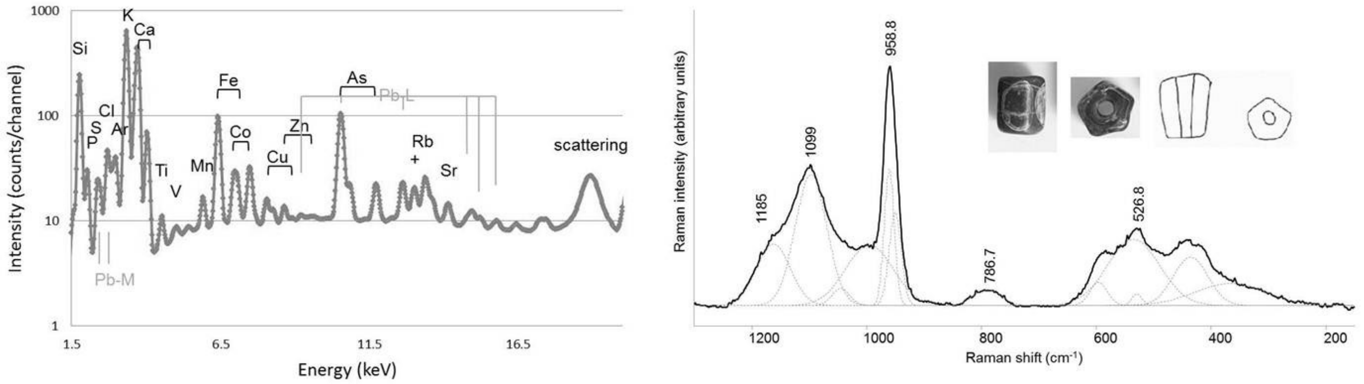

Figure 1. Left: hXRF spectrum of the blue beads, showing the presence of Co. **Right:**Ramanspectrum of the same beads (532nm laser). In addition to the silicate bending and stretching envelopes, the most intense band of hydroxyapatite due to bone white (ca. 960 cm^{-1}) is clearly visible.

The combination of Raman spectroscopy with elemental techniques for the study of glass materials is well established, yet it was not often applied to the study of glass trade beads[3].

The qualitative information provided by hXRF can be successfully improved by the observation of the Raman signature of the glass (Figure 1): the bending and stretching modes of the silicate network are affected by the type and amount of stabilizers, flux and network formers (Ca, Mg; Na, K; Pb), so that different types of glass can be recognized on the basis of their spectrum[4].

Acknowledgements

The authors thank Ghent University for its financial support through the concerted research actions (GOA) program, the KongoKing project Starting Grant No. 284126 of the European Research Council awarded to Koen Bostoen and the Special Research Fund of Ghent University.

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OP19

Combined spectroscopic and paleobiologic approach to the provenance investigation of painting materials

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Keywords: provenance investigations, painting analysis, fossil organisms

Recently, during the restoration work in the parish church in Niedźwiedzice (Poland) a portrait of a nobleman Wolff von Buswoy was discovered painted on the wooden panel. The painting dated to 1550 was missing for years and currently it is recognized by art historians as the oldest preserved painting created in Silesia. Its historical value for cultural heritage of this region is uncontested. Although the biography and achievements of the noble man depicted in the painting were widely known to the historians, there was no information about the mysterious painter.

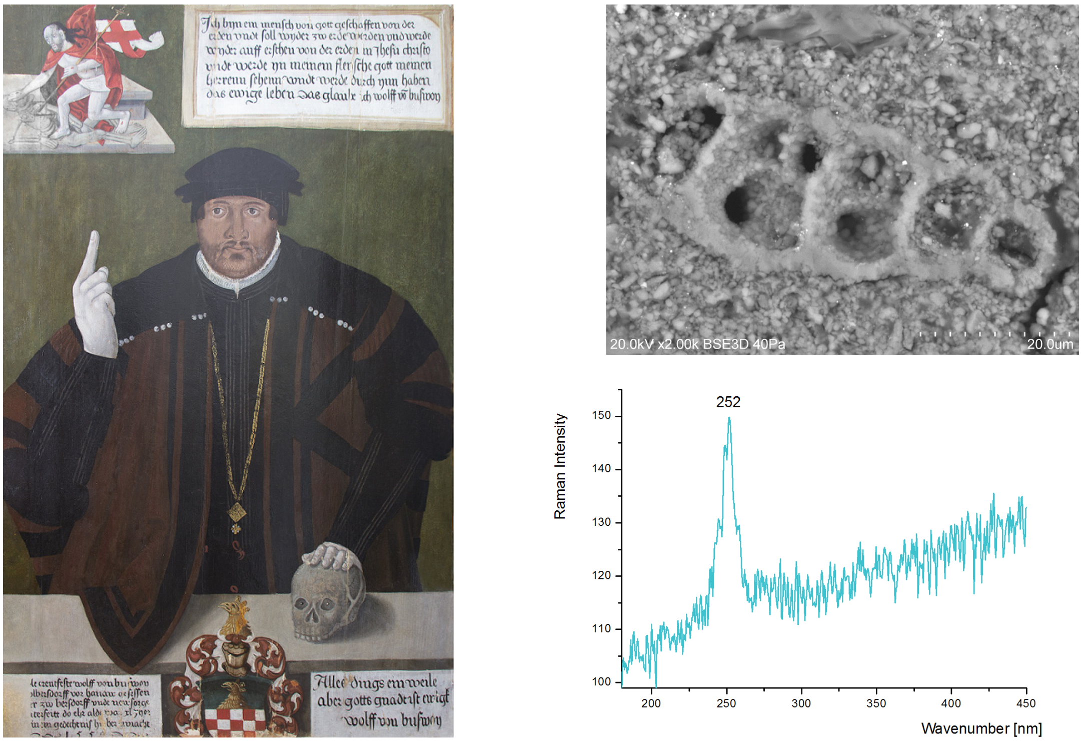

Figure 1. On the left, *Wolff von Buswoy, 1550*, Niedzwiedzice. On the right, SEM picture of foraminifera(top) andRaman spectrumof vermilion (bottom).

A priceless artistic value of the painting suggests that the artist originated rather from the Western Europe than from the Silesian region. In the attempt to establish the place of creation of the discovered painting and probably the provenance of the painter, the multispectral investigations focused on the painting techniques and the origin of the painting materials were carried out.

Based on results of the preliminary noninvasive investigation which included VIS and IR photography and X-ray imaging the most suitable places for sampling were selected. Thecross-sections prepared from the collected samples were subjected to spectroscopic investigation in order to determine pigments, binding media and the painter techniques. The characteristic features of the painting techniques were revealed due to the application of the optical microscopy and the analysis of the stratigraphy. The SEM-EDS, Raman spectroscopy and microXRD analysis allowed us to identify the palette of the pigments: azurite, malachite, red lead and carbon based pigment. Raman spectroscopy investigation confirmed also presence of HgS and micro XRD study proved it is a cinnabar.

The preliminary SEM studies revealed lead presence, Raman spectra although obscured by fluorescence suggested white lead pigment and micro XRD confirmed it as hydrocerussite. Raman and micro XRD investigations revealed also that the $CaCO_3$ used in the ground layer originated from natural calcite. The artist applied both types of the binding media: oil and tempera which was confirmed by the GC-MS analysis.

Interesting results that indicate the origin of the raw material used as the ground layer were delivered by SEM-EDS investigations. The presence of foraminifera[1] and coccoliths[2] was detected in all cross-sections in the ground layer. Foraminifera are a single-celled organisms with a long-lasting geological record that spans the entire Earth's Phanerozoic history. They may be planktic or benthic, and they usually produce a test (or shell) which is constituted from several chambers. The shell is made of aragonite and usually contains grains of some minerals or other particles glued together. The diameter of shells is usually smaller than 0.5 mm. Coccoliths were deposited in Cretaceous times. They create a calcite platelets that interlock around the single cell of the coccolitophorids. Depending on the species, these discs have a diameter ranging from 5 to 15 μm or more and are composed of 20 to 60 individual, submicrometer calcite crystals. Due to the further paleobiology investigations we might be able to determine more precisely the region of Europe from which originate the foraminifera and cocoliths revealed in the investigated samples. We expect that this information would allow us to confirm the provenance of materials used by the artist in the analyzed painting.

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OP20

Micro-Raman analysis of prehistoric rock art in Patagonia (Argentina)

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Keywords: rock art, Patagonia, Raman Spectroscopy, haematite, pigments identification, degradation products

Research on prehistoric Patagonian rock art can reveal information about the origin of the pigments (minerals or clay like materials) used for painting pictograms in an abstract style called "*Grecas*". Moreover, it can help protecting this valuable world heritage by tracking the environmental interference through the identification of (bio)degradation products. These artefacts are extremely vulnerable due to precipitation patterns, temperature and vegetation (bioclimatic variables) and lithological and structural characteristics of the rock support. These factors, introduce many variables for the preservation of these works and for understanding the chemical degradation processes that take place.

Raman Spectroscopy was mainly used for the identification of the components that compose the mixtures in each layer found in the rock art (Patagonia steppe, Piedra Parada valley, middle Chubut river). Painting layers vary in colour from dark red to orange and green, some containing black granules. Stratigraphic analysis and optical microscopy revealed an intermediate white layer between the rock support and the painting layer. The nature of this patina-layer is examined with micro-Raman spectroscopy, and it is thought that specific areas were selected where this white layer is present to perform the rock art. As the number of cross-sections in this study is limited, further research is needed to fully confirm this hypothesis.

Furthermore, Raman analysis revealed the presence of an organic material probably used as a binding media inside the painting mixtures. Human activity sets a question on the identification of the carbon-based materials found in the pigmented layers. Degradation products found from the chemical analysis in combination with the macroscopic observation of flaking underline the interference of the environmental conditions.

Figure 1: Left: Protected shelter found in the Piedra Parada valley, middle Chubut river, Patagonia, Argentina. **Right:** Red, orange and white abstract pictograms found on basaltic rock. In some cases a layer of patina was found on the rock.

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OP21

Famous Historic Chrysoprase Deposit in Szklary, Poland: Raman Characterisation of Ni-bearing Minerals

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Keywords: chrysoprase, gemology, Ni-bearing clay minerals

Chrysoprase is an apple green variety of chalcedony coloured by inclusions of Ni-bearing minerals. It is one of the rarest types of microcrystalline quartz, and up to now, its mining sites are rather scarce, with the most important ones located in Australia, Kazakhstan, Tanzania and Poland.[1-3]From the historical point of view, the most significant locality of chrysoprase is the polish Szklary deposit in Lower Silesia. Since mediaeval times,it has been a source of high-quality material for European nobility, which is documented e.g. by its occurrence in the wall decorations of the Chapel of St. Wenceslaus in the Cathedral of St. Vitus in Prague created during the reign of the emperor Charles IV. in 1372.[4]The Szklary massif is a serpentinite body of early Palaeozoic age, which is – in the upper part – severely weathered to laterite of the "New Caledonia" type.[5]

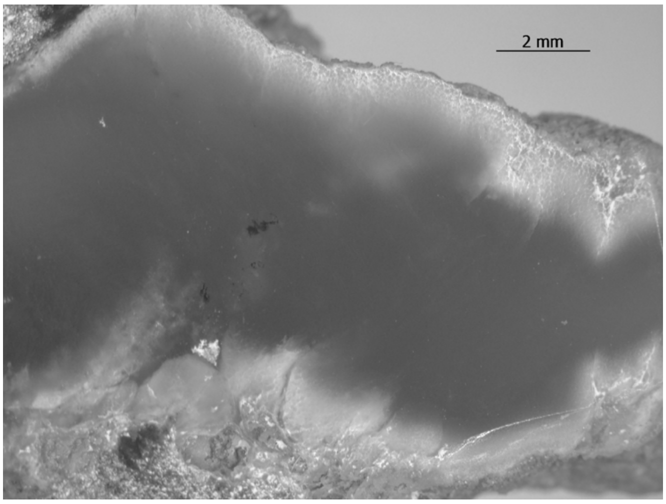

Figure 1. Vein of chrysoprase from Szklary, Lower Silesia, Poland.

A field trip has been carried out by the authors and several types of green Ni-bearing minerals were collected. Furthermore, chrysoprase from the Szklary locality has been obtained from reputable mineral dealers (Fig. 1).

Some of the chrysoprasesamples were cut in the form of cabochon and were described from the gemmological point of view with an emphasis on their colour, translucency, UV luminescence, refraction index and specific gravity. These measurements were complemented by Raman micro-spectroscopy.Interestingly, we have encountered other green minerals on the market from Szklary deposit erroneously identified as chrysoprase. That is also why we have analysed the collected green Szklary minerals by electron probe micro-analysis, Raman micro-spectroscopy and powder X-ray diffraction (XRD).

The identified minerals belonged to the vaguely defined group of "garnierites", which is not an officially recognised mineral species, but is used for the description of Ni-bearing talc- and serpentine-like minerals with 1:1 and 2:1 clay structure.[6,7] Their specific Raman spectra led to a clear and unambiguous differentiation from chrysoprase and may be comfortably used for their detection in unknown samples, evenon site using portable Raman spectrometers. The results of Raman micro-spectroscopy were in agreement with the results of X-ray diffraction; while the XRD provided quantitative ratios of the phases present in the samples, Raman measurements enabled the analysis of small heterogeneities as well as tiny veins in cross-section. Raman micro-spectroscopy proved to be an efficient method for identification of chrysoprase, which may beaccompanied by other Ni-bearing minerals, in the form of mineralogical samples, but also in the form of polished slabs and gems adorning pieces of art.

Acknowledgements

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Thursday, **September 3rd**

PL2

Exploiting Raman abilities: from spectra recording to advanced data treatment. Focuses on natural organic substances involved in cultural heritage studies

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Keywords: advanced analytical parameters, spectra treatment,

Raman spectroscopy could be performed through a high variety of devices, each having advantages, but none being the "perfect" universal one. Because of their complex chemistry and sometimes some implementation constraints, cultural heritage samples offer many challenges. First, obtaining a spectrum requires adapted analytical conditions by playing with many parameters (from various parts of the spectrometers to sample preparation or signal enhancement). Beyond, the extraction of meaningful information from the spectrum requests an important knowledge of cultural heritage material specificities and spectroscopy, but also data treatment skills. Through various examples, this presentation will illustrate how by playing with instruments or spectra the obtained information can enlighten the past.

Examples will be largely taken from the study of natural organic substances. These are widely used in History and constitute a precious testimony of human exploitation strategies, exchange networks and techniques for their implementation in numerous ancient objects. These materials have been for a long time neglected because of their poor conservation and challenging characterisation. With the re-evaluation of vibrational spectroscopies potentialities through spectral treatment procedures; alternatives or complements to the current analytical strategies based on separation methods can be proposed.

Other examples related to minerals, pigments or iron corrosion products will be discussed to illustrate the use of imaging, resonant analysis, on-site measurements, or measurements coupled to thermal treatments to seek the evolution of material properties.

The presented results will give an overview of the contribution of Raman spectroscopy for various cultural heritage matters: from material identification to objects conservation but also to the enhancement of the history of technology knowledge.

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OP22

Automatic Classification System of Raman Spectra Applied to Pigments Analysis

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Keywords: Raman spectroscopy, pigment classification, principal component analysis, multiple discriminant analysis

Raman spectroscopy has proved to be a powerful technique for the non-destructive characterization of constituent pigmentation in art works[1]. This task is important for the cataloguing, conservation and restoration of paintings. It is well known that Raman spectroscopy, being a spectroscopic method for molecular analysis, is able to discriminate between different molecular species based on the acquired Raman spectra. This discrimination is generally performed through visual comparison between Raman spectra measured on analyzed art works with an appropriate set of reference Raman spectra. In general, these reference spectra are measured from pigment powders under certain measurement conditions. However, pigments in works of art are usually mixed with other materials (such as binding agents, varnishes, other pigments, …) so that a Raman spectrum measured directly on an analyzed art work can lose specific information due to different reasons. Indeed, these external agents may hamper the acquisition of the Raman spectra of the pigments and may hinder their interpretation. Moreover, measurement conditions may produce changes in the spectrum of a specific pigment which may lead to an erroneous identification[2]. Furthermore, certain pigments can be found in natural and synthetic forms as the ultramarine blue[3] or in different polymorphs as the PB15[4]. There is little difference between the Raman spectra of these pigments and therefore their automated analysis is a challenge. The discrimination between them, this is, between the natural and synthetic forms or between different polymorphs, is an important topic in preservation of art works because the pigments differ not only in their chemical and physical characteristics (such as stability, solubility and hue) but also appeared at different times on the paint market and thus they may be used as markers for dating and authenticating art works.

In the present work, several chemometric techniques were explored to develop an analytical method to automatically discriminate between Raman spectra that are very similar between them. Hence, a fully automatic classification system of Raman spectra of pigments is presented. The system is aimed to be a fully automatic tool to help the analyst in the complex process of pigments classification. Concretely, it is based on the chemometric techniques of principal component analysis (PCA) and multiple discriminant analysis (MDA), and a decision algorithm specifically developed to select the corresponding reference class with no user input. PCA deals with the whole set of input data without paying specific attention to any underlying class structure, whereas MDA deals directly with the discrimination between classes. In this work, PCA is used as a dimensionality reduction procedure which projects the input spectra onto an uncorrelated space, equivalent in information content, where the spectral differences are highlighted and redundancies are removed. The spectral expression obtained through the PCA projection is then used to obtain a discriminant space by means of MDA. This discriminant space minimizes the differences between spectra belonging to a same class while maximizing the inter-class differences. The combination of both chemometric techniques allows to obtain well-defined classes, providing a powerful way to achieve class separability so that it is possible to discriminate between very similar spectra in an automatic way (see *Figure 1*).

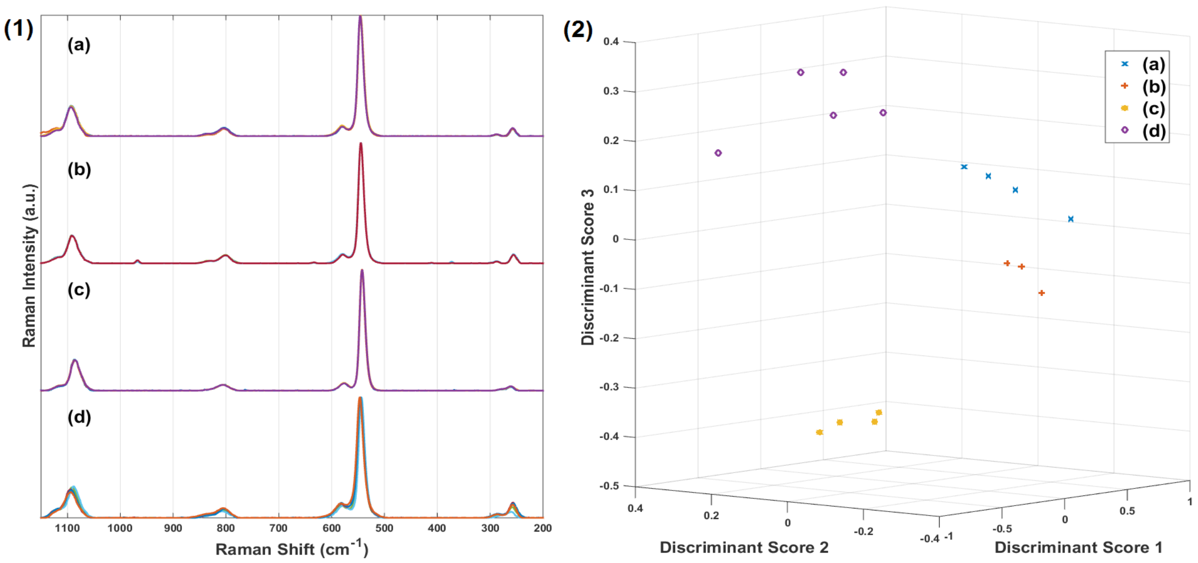

Figure 1. Example of differentiation between natural ultramarine blue from Afghanistan (a), Chile (b), and Siberia (c), and synthetic ultramarine blue (d): Raman spectra are shown in (1) and the discriminant projection obtained through the proposed methodology is shown in (2).

In order to diagnose the performance of the proposed methodology it was studied in a simulation stage simulating different practical problems commonly found in the spectral classification. The method was applied to the classification of artistic pigments in experimental cases, verifying the correct behavior of the implemented system. The reliable and consistent results that were obtained make the methodology a helpful tool suitable for the classification of pigments. Finally, although the proposed system has mainly been applied in pigment analysis, it could also be used in other fields to discriminate spectra that have very little differences.

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OP23

Suitability of DFT Modelling for Raman spectral Interpretation of Copper Complexes

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Keywords: Copper complexes, Degradation, Vibrational Spectral Interpretation, DFT

In the past few years, several works have appeared in literature dealing with the characterization of copper complexes and their degradation processes in object of artistic relevance. Green copper-based pigments represent a wide category of compounds provided by different chemical and physical properties. In particular, copper(II) carboxylates form a variety of structures together with monodentate ligands, such as for instance ammonia.

In this work, we present the valuable use of Density Functional Theory (DTF) calculations for the vibrational spectral interpretation of the experimental Raman and IRmeasurements of a simple copper acetate complex, that may be concieved as being among the simplest representative of a copper soap – diacetatodiamminecopper(II). Moreover, this particular copper complex emerges as a byproduct in the synthesis of the well known green pigment verdigris. Computational chemistry is a very valuable tool for the prediction and the rationalization of the nature of the vibrational features of transition metal complexes , since it provides wortwhile pieces of information comprising chemical structure, properties and reactivity of these chemical species.

With our approach we demonstrate the strategy for building relevant molecular models of the above mentioned chemical species. We also demonstrate the ability of this approach to describe structural features that are not directly observable by use of X-ray based methods.

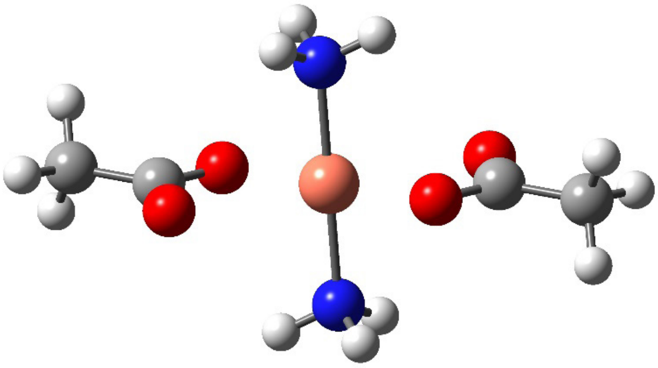

Figure 1. Molecular structure of diacetatodiamminecopper(II).

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OP24

Going beyond single colorant identification with surface-enhanced Raman spectroscopy (SERS): a systematic study of natural red dyes in mixtures

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Keywords: SERS, dye mixtures

Over the past 10 years, surface-enhanced Raman spectroscopy (SERS) has found increased applicability in the field of cultural heritage research for the detection and identification of colorants in works of art and historical textiles[1-5].

One of the main drawbacks of the technique is related to its inability to resolve mixtures of dyes, which may result in the preferential detection of the component with the highest SERS cross section or the one with the highest affinity for the metal substrate employed for analysis[6]. This poses a real challenge, as it is well known that, throughout history, colorants were often used in combination to produce particular shades[7]. Thus far, the actual capabilities of SERS for the simultaneous detection of dyes in mixtures have been explored in very few studies, which reported spectra of binary mixtures of reference alizarin, purpurin and lac dye[8,9] or described preliminary experiments combining thin layer chromatography (TLC) with SERS to leverage a simple and accessible separation technique with enhanced detection capabilities[10,11,12].

In the present work, a broad systematic study was conducted to determine the detection limits of SERS for a wide number of natural red dyes in mixtures, including alizarin, purpurin, carminic acid, laccaid acid and brazilein, analyzed as reference solutions and in mock-up red lake oil paints. As a first step, SERS spectra of binary mixtures of the dyes in various relative proportions were recorded on two different SERS substrates, i.e. Lee-Meisel citrate-reduced silver colloids and silver film over nanospheres (AgFONs). This aimed to qualitatively establish relative detection limits for each dye when present in solution alongside another colorant, and to gain a deeper understanding of how different metal substrates and analytical methodologies may affect dye identification. Secondly, the same binary mixtures of dyes were analyzed with SERS in red lake oil paint reconstructions prepared according to 19th-century historical recipes. For this set of samples, SERS analysis was performed after hydrolysis with HF[3] and only used Lee-Meisel silver colloids as SERS active substrate.

The experiments highlighted significant differences between results on silver colloids and FONs both for what concerns the contribution of each individual dye in the mixture to the SERS spectrum and, sometimes, also in terms of position and relative intensities of bands. Ultimately, this work demonstrates that, in some cases, the spectral contribution of the second dye in the mixture is not detected unless it is present in significant concentrations. These new results underscore the need for more experimentation in the area of combined separation (e.g. via TLC or microfluidics) and SERS detection of colorants in artworks.

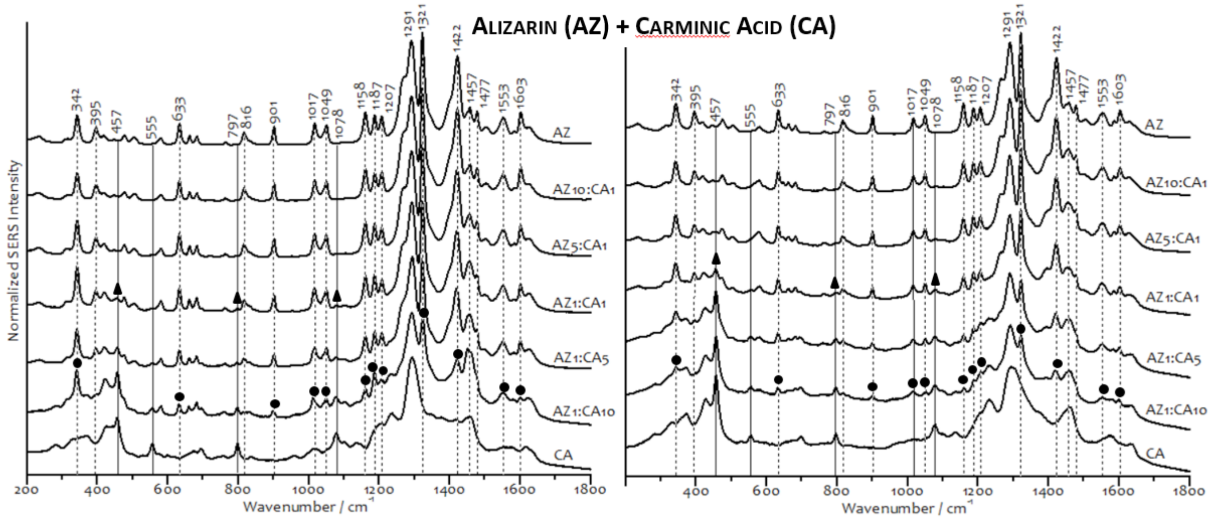

Figure 1. SERS spectra of mixtures of alizarin (AZ) and carminic acid (CA) in different relative ratios taken on Ag colloids (left) and FONs (right). Qualitative limits of detection (LOD) were determined as follows: LOD (AZ) = AZ1:CA10 and LOD (CA) = AZ1:CA1, on both metal substrates.

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OP25

Multi-analytical approach combining conventional Raman and SERS with fluorescence lifetime spectroscopy and HPLC for the study of twenty historical lake pigments

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Keywords: Raman, SERS, lakes

Twenty red lakes from the Lefranc& Bourgeois Archive (France) and dating from 1890 to 1921 have been investigated using a combination of molecular spectroscopic and chromatographic techniques (Figure 1). In this historical period it is given that many variants or formulations were used to improve the quality of artists' pigments. This study, in particular has been conducted exploiting spectroscopies such as non-destructive conventional Raman, SERS, UV-Vis absorption and time-resolved fluorescence spectroscopy, and HPLC with DAD or MS detection for the characterization of organic pigment formulations.
As a preliminary step, X-Ray fluorescence and FT-IR analysis were performed in order to characterize the historical samples and to identify the inorganic substrates present.

Conventional Raman measurements were carried out to directly investigate the molecular composition of the unknown materials discriminating the formulations based on mordent-based lake pigments and dyestuffs. When fluorescence hindered measurements, colloidal SERS permitted the identification of main and some minor colorants. In the absence of luminescence, SERS and Raman provided complementary information regarding the dyestuff composition.

Simultaneously, fluorescence lifetime spectroscopy provided information regarding the multiple radiative pathways in the lake samples, and highlighted appreciable differences based on the presence of different mordants. HPLC analyses, using both DAD and ESI-Q-ToF detectors, permitted the identification of several minor components distinguishing amongst natural and synthetic formulations as well as highlighting between different recipes for the extraction of dyes from the raw materials.

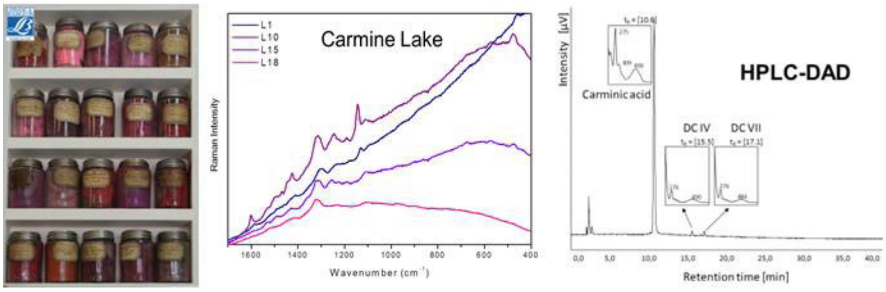

Figure 1.(a) Image of the twenty historical samples (b) Raman spectra of Carmine lake based samples and (c) chromatogram of a carminic acid based sample

This research of historical samples provides key data for the interpretation of in situ analysis on early 20th C. paintings. The final aim of the project, in fact, is to apply non invasive techniques, like fluorescence lifetime [1], Raman and SERS [2] spectroscopy as well as NIR, reflected UV and UV fluorescence imaging, directly in-situ on futurists' paintings.

Acknowledgements

This research was funded by MIUR (FIRB 2012), FUTURAHMA- *"Futurism Research Art History and Material Analysis/ oppure From Futurism to Classicism (1910-1922). The role of technique, the study of variation and problems of conservation (1910-1922)"*, RBFR12PHL4_002.

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OP26

Portable SERS analysis assisted with additional techniques to characterize the ancient recipe used to prepare Pompeian pink and purple pigments

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Keywords: portable SERS, Pompeian pink and purple pigments, organic dyes, madder lake

In the literature, different works can be found about the characterization of Pompeian pink and purple pigments. In most of them, chromatographic techniques [1] have been applied to identify the nature of the organic dyes, but also multianalytical methodologies [2] to approach the ancient recipes used to prepare those pigments. The Naples National Archaeological Museum (MANN) possesses a wide collection of bowls containing raw pigments used for the creation of Pompeian wall paintings. In the work of Aliatis et al. [3], due to a strong fluorescence effect, Raman spectroscopy was not useful to perform a complete characterization of the organic dyes, responsible of pink colours in Pompeian pink pigments from MANN. As an alternative, Surface-Enhanced Raman Spectroscopy (SERS) can be applied. Therefore, in this work, portable SERS was evaluated as a powerful technique to determine the nature of the main organic dye used in two Pompeian pink (117323 and 117342) and purple (117365) pigments preserved in bowls as raw pigments in the MANN. In this sense, two portable Raman spectrometers (innoRam, $B_{\&}WTEK_{INC.}$, Newark, USA) implementing 785 and 532 nm excitation lasers respectively, and coupled to a video microsampling system (BAC151B, $B_{\&}WTEK_{INC.}$) with dual laser wavelength port were used. The quality of these SERS spectra was compared with those acquired with a confocal Raman microscope (inVia, Renishaw, Gloucestershire, UK). UV-Visible-NIR and chromatographic techniques were also used to compare and contrast the SERS results.

To develop the portable SERS methodology, Ag nanoparticles (Ag-NPs) were synthesized following different methods (e.g. Lee-Meisel and Creighton). UV-Visible, TEM and Raman spectroscopy were used to test the efficacy of synthesized Ag-NPs. For the SERS analysis, direct measurements of the raw pigments without sample pre-treatment were conducted. However, best quality SERS spectra were obtained performing a previous acid extraction of raw pigments few milligrams followed by a liquid-liquid extraction with hexane. The organic phase and active colloid were deposited on a quartz microscopic slide and evaporated to perform direct SERS measurements. In order to improve the quality of SERS spectra, the hexane extracts were evaporated to dryness and the residue was reconstituted in methanol. Thanks to this last methodology, it was possible to identify the presence of madder lake in the three analyzed pigments even using 0.4 mg of each raw pigment. These results evidence that the portable SERS methodology developed can be useful to extract reliable information without using very expensive Raman microscopes, and it can be also applied *in situ* (e.g. in museums, storage rooms, etc.), without the necessity of transporting the raw material and only using few milligrams of the pigment.

Regarding the Pompeian purple pigment, it is made up of a mixture of pink and blue pigment grains. In the blue pigment grains, Egyptian blue was identified (see Figure 1).

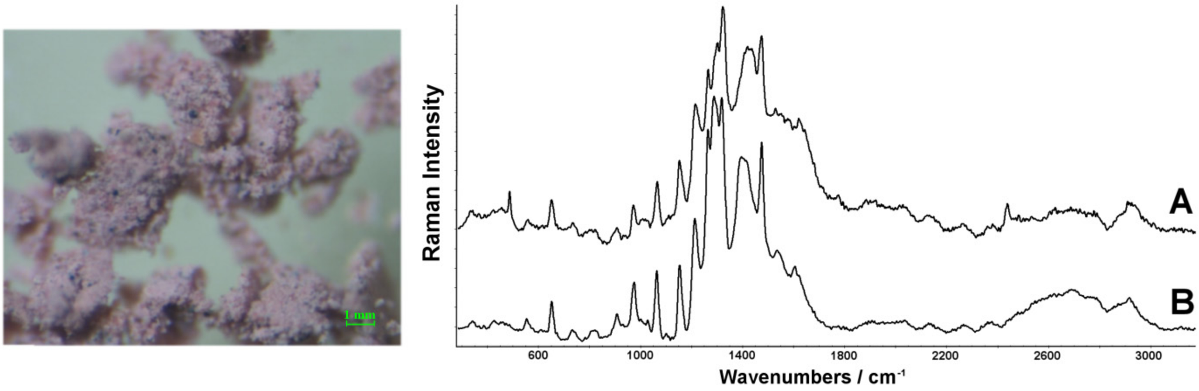

Figure 1. Microphotograph of pink pigment 1173242 and representative SERS spectra of madder lake reference material (A) and pink pigment 1173242 (B) organic phase showing madder bands.

To get more information about the ancient recipe of each pigment, the inorganic mordants were also characterized. Using SEM-EDS, a similar elemental composition was identified for each one (Al, Si and O as major elements, C, K, Ca and Cu as minor elements and F, Na, Mg, P, S, K and Fe as minor-trace elements). Heavier elements (Zn, As, Pb and Sr) were also detected using ED-XRF. XRD results suggest the use of an amorphous material with some crystalline kaolinite phases in some of the pigments. Infrared spectra from pigments are quite similar (3360, 1633, 1576, 1427 and 998 cm^{-1}), suggesting a possible use of allophone as mordant, which could be dyed with madder lake to obtain the pink pigments. This amorphous clay mineral can be found in the surroundings of the Vesuvius and it was also identified in Pompeian white pigments.

Acknowledgements

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OP27

SERS identification of orchil and *folium* mixtures on purple codices: a methodological approach on model samples

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Keywords: dyes identification, parchment, manuscripts, SERS, planar chromatography

Purple codices are very precious manuscripts produced from the Late Antiquity to the Middle Ages. They were written in silver and golden inks on purple-coloured parchments and produced to be owned by Kings and Emperors. About a hundred of these artworks still survive, mainly conserved in libraries and archives.

Even though the parchment was said to be coloured with Tyrian purple, recent scientific evidences deny the use of this prized pigment. In particular, the results obtained on some manuscripts by different research groups with non-invasive and micro-invasive techniques (e.g. portable fluorescence, lifetime measurements, fibre optics reflectance spectroscopy, subtracted-shifted Raman spectroscopy, LC-qTOF-MS) would mainly point to the use of orchil, a dye obtained from different species of lichens [1-3]. In addition, in a few manuscripts non-invasive spectroscopic investigations point to the possible use of both orchil and *folium* (a dye obtained from the plant *Chrozophora tinctoria* A. Juss.) [3].

A recent work underlined that both dyes are easily recognizable by means of SERS [4] but no experimental data are currently available about the possibility of identifying them when they are mixed or superimposed on parchment.

This work presents the first methodological approach on model samples of dyed parchments to set up a procedure for the contextual identification of these dyes in purple codices. For this purpose, parchment dyed only with orchil, only with *folium*, with orchil and *folium* superimposed or in mixture were prepared in the laboratory according to the scarce information available in ancient treatises. These samples were subjected to SERS analyses after different pre-treatments in order to assess the most suitable procedure to obtain signals from both the dyes.

As a first approach, the measurements were carried out by directly coating the parchments with silver colloidal pastes [5-6]. The tests highlighted that the morphology of the parchment strongly conditions the likelihood of obtaining SER signals from the dyes. In addition, SER spectra recorded on parchments dyed with both dyes showed only the signals of orchil.

A second set of measurements was carried out by SERS on water solutions containing different ratio of both orchil and *folium*, in order to check whether the signals of these two dyes can be recorded contextually. It emerged that SER signals of *folium* are obscured by signals of orchil when both the dyes are present, even if the concentration of *folium* is much higher than those of orchil (up to 18:1 *folium*:orchil; Figure 1).

Moreover, extracts from minute fragments (less than 1x1 mm) of parchment dyed only with *folium* or orchil were obtained with different extraction solutions and investigated by SERS in order to identify an extraction procedure suitable for both orchil and *folium*. The optimal procedure was found to be an extraction with formic acid.

Further work was then devoted to the separation of orchil and *folium* by means of planar chromatography, in order to remove the effect of orchil on the SER signals of *folium*. We succeeded in separating these two dyes starting from water solutions or with the dyes dissolved in formic acid. SER spectra of orchil and *folium* were then obtained by directly coating with the silver colloidal paste the coloured spots on the plate.

This work highlighted that the SER signals of orchil and *folium* cannot be detected simultaneously when the two dyes are present. Furthermore, a micro-extraction of the dyes from the parchment is needed in order to overcome the issues raised by the parchment matrix and to perform the separation of orchil and *folium* prior to SERS analysis. The feasibility of this approach is demonstrated by the results obtained by coupling planar chromatography and SERS on mixed solutions of orchil and *folium*, while the separation of the extracts obtained from parchment samples is still underway.

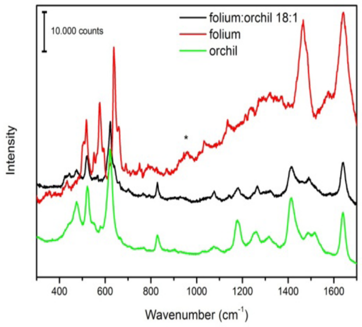

Figure 1. SER spectra of water solutions of *folium* (red line), orchil (green line) and *folium*:orchil 18:1 (black line). All the signals recorded on the mixture can be attributed to orchil.

Acknowledgements

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TS6

Raman forbronze characterization: case studies and treatments

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Keywords: bronze, patina, secondary corrosion products, corrosion inhibition, Raman investigation

Copper and its alloys tend to react with oxygen and humidity in air, when exposed to different environments. Copper and bronze first react to form the red cuprous oxide-cuprite, which in clean atmosphere slowly oxidizes to cupric oxide of a black colour, tenorite. The process is called natural patination.

When bronze surfaces are exposed outdoors, the aggressive pollutants in atmosphere usuallyform acid rain, and secondary corrosion products might form,containing sulphates, nitrates, chlorides etc. This results in the change of the appearance of a bronze surface and/or the change of the structure of the exposed alloys due to leaching action of acid rain [1].

On the other hand, artists frequently deliberately patinate bronze for visual effects to achieve different colours of the surface, the process being called artificial patination. On artists' patinated bronze the patinas composed of Cu_2S, cuprite, atacamite, gerhardite and rouaite can be found [2]. Afterthe artificial patinationthe surface is usually protected by applying different protection systems. These are inhibitors of corrosion, waxes and other chemical compounds like lacquers on the basis of metaacrylates with or without inhibitors.For many years benzotriazole (BTA) was used for protection of copper alloys but due to its toxicity it has to be replaced by some less toxic compounds. The inhibitor action of traditionally used BTAwas compared to other, environmentally friendly azole type inhibitors,such as 2-mercaptobenzimidazole (MBI) and tolyl methyl imidazole (TMI), andtheiraction with different patinas was studied.Raman analysis showed chemical bonding of BTA to Cu through triazole ring, while in the case of MBI, the inhibitor interaction through S substituted in the imidazolering for both, pure copper and bronze was identified[3]. The TMI- tolyl methyl imidazole already found its efficient behaviour in protection of historical patinas and was already electrochemically evaluated [4]. Thereby, its mechanism of inhibition was tested in practice and verified through accelerated ageing in acid rain and inpolluted humid air environment.A special attention was given to its behaviour in indoor storage conditions where volatile organic pollutants may cause further damage. These data are of extreme importance to properly plan conservation treatments ofbronze objects, as well as for establishing the appropriate environmental conditions for their storage and display.

The inhibitors' action in different environments was first tested on prepared model samples of bronze and patinas (brown sulphide, green chloride and green nitrate patina).Their behaviour was monitored by Raman spectroscopy after the exposure to simulated urban acid rain, for a period of 35 days, as well as after the exposure to indoor pollutants. As case studies different archaeological bronze objects (see Figure 1) were selected and analysed. The Roman bronze objects, all showing signs of corrosion, were excavated in 2011 at the old military barracks archaeological site in Ptuj, Slovenia. A wide pallet of corrosion products, such as cuprite, chalcocite, malachite and other carbonate based minerals,etc. was found by Raman analysis. Furthermore, some compounds, like hematite, amorphous carbon, quartz, originating from the surrounding burial environment, were also identified. The TMI inhibition action was then tested also on these objects and evaluated after the exposure to outdoor (bronze) and indoor pollutants (archaeological bronze).

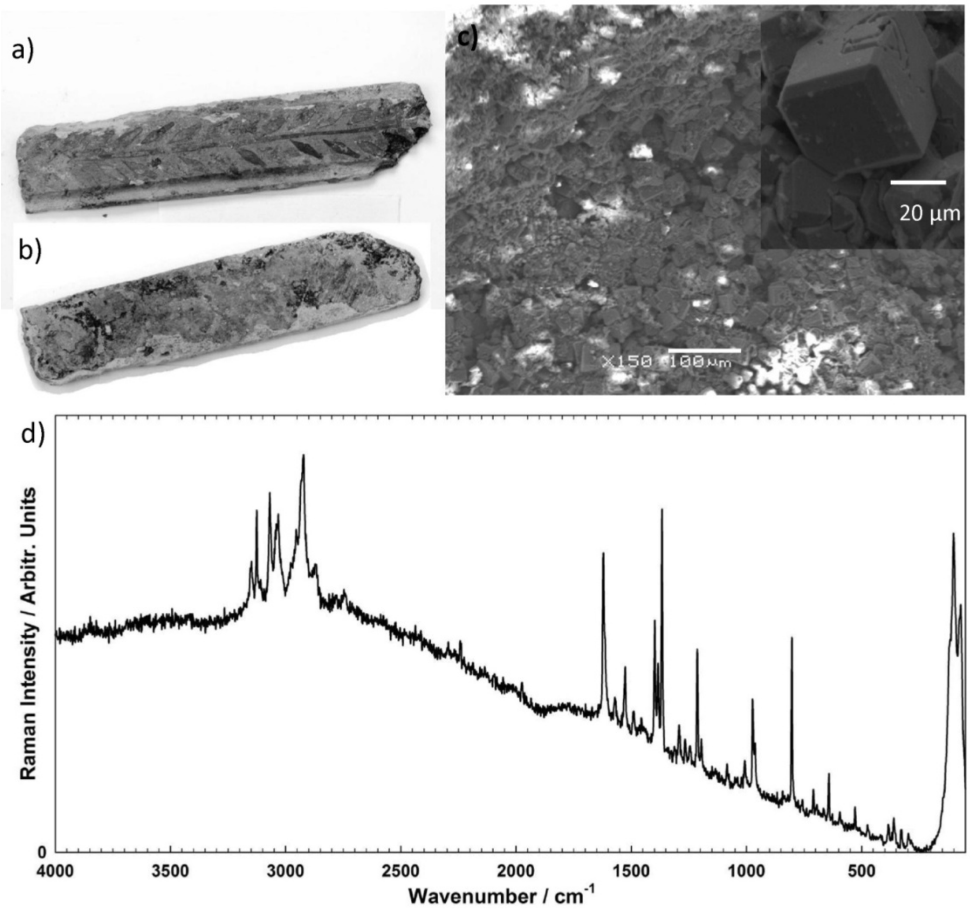

Figure 1. Examination before applying inhibitor tolyl methyl imidazole (TMI) on ancient Roman bronze plate: front side a), back side b) SEM investigation of patina's morphology c) and Raman spectrum of TMI applied on the surface of a bronze model d).

Acknowledgements

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OP28

Raman investigation of surface layers on copper cargo from XV c. ship wreck excavated in the Gdańsk Bay - contribution to study of the trade routing in medieval Europe

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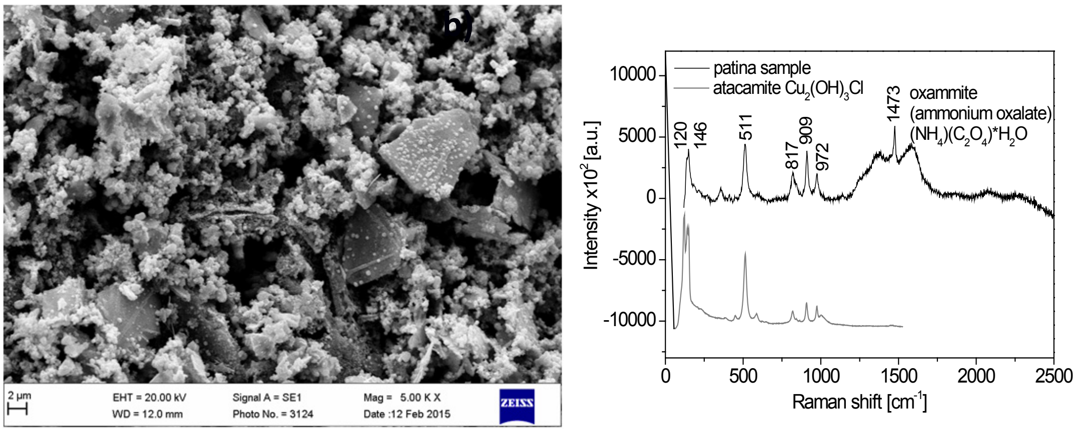
Keywords: medieval copper, patina, corrosion products, sea water corrosion, organic compounds

We report results of the surface layer study performed by means of the Raman and complementary spectroscopic techniques for a collection of medieval copper objects. These remained submerged in sea water at a depth of 16 m as cargo part of the ship which sunk in 1408. The ship wreck and remnants of the cargo were excavated in Gdańsk Bay. The investigated collection consists of ca 230 ingots of copper. Dimensions of the oval specimens are in the range of 14-61 cm and mass up to 18 kg (total 2 tonns)

[1]. However, the surface porosity and encrustation coverage of the excavated ingots indicates that the original dimensions and masses were larger and decreased due to long term exposure to corrosive and biologically active saline environment. In the Raman spectra of superficial layers the presence of bands corresponding to atacamite



a) b)

Figure 1. The SEM image of the surface morphology of corrosion layer from copper plate with visible organic compounds (a), and Raman spectra: of the patina sample (black line) with presence of organic compound - oxammite and reference spectrum (grey line) of atacamite (b).

($Cu_2(OH)_3Cl$, chalcopyrite $CuFeS_2$ and cuprite Cu_2O has been observed for ingots numbered as P549, 551, and 552, respectively [2,3]. The structured band centred at 1473 cm^{-1} was ascribed to organic oxammite $[(NH_4)_2(C_2O_4)*H_2O]$ in agreement with FTIR data and the microstructure of the layer observed in SEM images - see Fig. 1. The XRF spectra of the ingot P547 revealed except of Cu the presence of Fe, Pb, Ag, Sn, (admixtures) and traces of, Cd, In, Mn, Ni, Sb and Zn. Bands of Ca were ascribed to surface contaminants and were confirmed by the LIBS measurements which showed also lines of Na and Ba. This was also in agreement with the EDS spectrum (P547) averaged over surface area of 900 x 1200 mm. Bands of sulphur and carbon observed in this spectrum were ascribed to organic reaction products with sea water and tar covering partially the ingots and also with potash ($KMnO_4$, K_2CO_3, K_2SO_4) found in the excavated cargo. Based on previous studies of raw material composition of the copper ingots their origin - the region of Banska Bystrica has been suggested. It coincides with known historical data about late medieval Hungarian copper which was one of the most important export and trade goods, and was the source of wealth and prestige of merchants from Kraków and Toruń [4]. In summary, results of this work in progress confirm the authenticity and origin of the objects and represent an important contribution to understanding of the trade routes along the south-north axis in medieval Europe.

Acknowledgements

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OP29

Deterioration of Iron Nails from Historical Structures Exposed to Coastal Town Atmosphere: Investigation of Corrosion Layers by Micro-Raman Spectroscopy

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Keywords: Iron corrosion products, historic iron nails, coastal town atmosphere, micro-raman spectroscopy, SEM-EDX, XRD, FTIR

Characterization of corrosion layers and iron oxide phases on iron artifacts is important for long term prediction of complex iron corrosion mechanisms in different atmospheric condition and for improvements in corrosion resistance, maintenance and conservation treatments of iron artifacts.

In Ottoman architecture, wrought iron nails were widely used as reinforcing and jointing elements in stone and brick masonry. In this study, corrosion layers of some structural iron nails from a 16th century brick masonry dome of Kiliç Ali Pasha Bath in Istanbul and from a 19th century stone masonry dwellings in Phocaea, Izmir were studied. Those nails were embedded in the structures and partly exposed to coastal town atmospheric conditions. 16th century nails were partly embedded in pozzolanic lime mortar of the brick masonry while the 19th century nails were embedded in building stone, tuff.

Corrosion layers of those iron nails being low carbon steel were examined with a Senterra Bruker micro-Raman spectrometer at 532 nm laser beam, 0.2 mW power and 200 seconds integration time. In addition, SEM-EDX analyses of corrosion layers were done. Powdered samples scraped from the corrosion layers were studied by using XRD and FTIR. The presence of two main corrosion layers at the surface next to the metal body: namely "inner corrosion layer" (ICL) and "transformed medium" (TM) that included the depositions from the surrounding media were observed for 16th century nails (Figure 1), whereas those layers were not so distinctly separated in 19th century nails (Figure 2) (3,4). Starting from the metal-corrosion interface (MI) towards TM layer, Raman spectroscopic analysis of 16th century nails showed the presence of magnetite, magnetite/maghemite, hematite, lepidocrocite, goethite and ferric sulfate rich locations[1,3,4,5]. 19th century nails revealed the presence of maghemite/lepidocrocite next to the metal, followed by a thick layer of goethite, maghemite, lepidocrocite and akaganeite phases[1,3,4,5] (Figure 2).

Survival of those iron artifacts with rather low thickness of corrosion layers in coastal atmospheric conditions indicated success of iron metallurgy in 16th and 19th centuries[2]. Relative proportions of iron oxide phases observed in Raman spectrometry were estimated by XRD and FTIR analyses of powdered samples collected from corrosion layers as well as qualitative phase distribution maps of corrosion layers by Raman spectrometry and considering efficiency of Raman signals for individual phases of iron oxides[5]. The results were compared with the literature and discussed for long-term corrosion mechanisms of iron nails in atmospheric conditions.

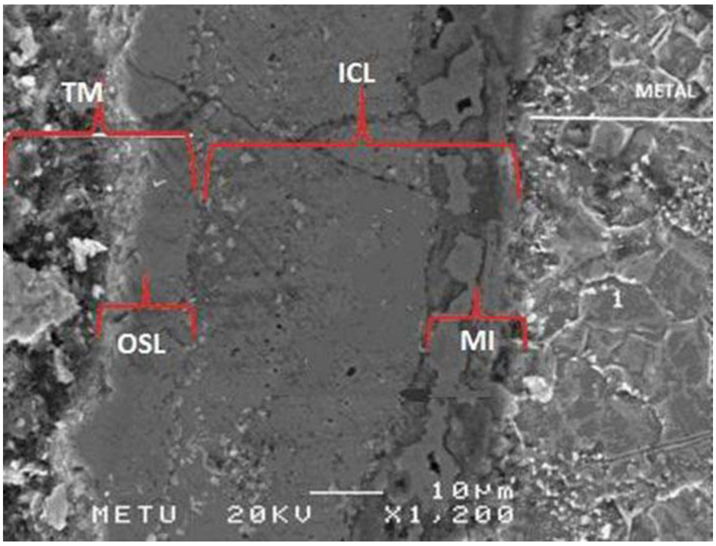

Figure 1. SEM view of a 16th century iron nail from the brick masonry dome in Istanbul : **MI:** Metal -ICL interface; **ICL:** Inner Corrosion Layer; (Thickness of ICL: 50mm - 100mm); **OSL:** Original surface limit; **TM:** Transformed Media (ICL-TM Interface includes OSL).

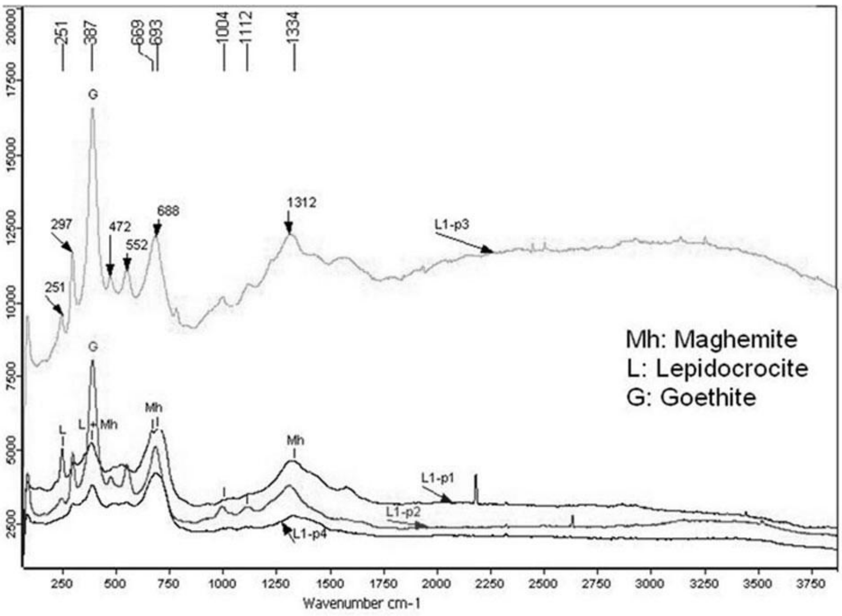

Figure 2. Raman microscopic view (20X) of a 19th century nail from a stone masonry dwelling in Phocaea and corresponding raman spectra: i) spectrum L1–P1 at MI identified as Maghemite/lepidocrocite and ii) spectra next to **MI** in **ICL** towards **TM**, L1-p2, L1-p3, L1-p4 respectively showing goethite rich regions. Spectra taken at 532 nm, 0.2 mW, 200 seconds.

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OP30

Identification of salts from deteriorated stone of historical monuments using micro-Raman spectroscopy, X-ray diffraction and SEM-EDS

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Keywords: stone, deterioration, salt

Crystallization of salts is an important deterioration factor of stone monuments. However, very small size of salt crystals, often their complex composition, and a low concentration compared with the main minerals of the stone (chiefly in case of polymineral sandstones) make their identification difficult. As a result, the use of a single analytical method is often not sufficient to identify positively the deterioration products[1, 2]. On the other hand, protection limits in sampling stone monuments prevent usually a comprehensive application of analytical methods, which makes clarity of results problematic. In this work, micro-Raman spectroscopy, scanning electron microscopy and, in some cases, X-ray diffractometry have been used.

Samples were taken from the limestone figure of St. Clare and the sandstone arch of the plastered niche around the sculpture (XVIIIth century), located in the gate leading to the monastery of the Poor Clares in Kraków.The samples represent a weathered crust (black crust) on the limestone and efflorescences on the sandstone surface.

The phase composition of the deterioration products was determined using mainly micro-Raman spectroscopy. The spectra were recorded with a Thermo Scientific DXR Raman Microscope with a 900 grooves/mm grating and a CCD detector. A 532 nm laser was used as an excitation source. Wherever possible (depending on the sample size), the phase composition was additionally established using X-ray diffractometry (XRD) with a RigakuMiniFlex 600 instrument. The measurement conditions were as follows: $Cu_{K\alpha}$ anode generator settings 40 kV and 15 mA, recording range3-70°2α, step size 0.05°,counting time 1 sec/step. A FEI 200 Quanta FEG microscope with an EDS/EDAX spectrometer was used for detailed studies of the microstructure and elemental analysis of the weathered crusts and efflorescences. The maximum excitation voltage was 20 kV and the pressure 60 Pa (low vacuum); the samples were not coated.

In most of the Raman spectra more than one phase have been identified. The black crust on the limestone sculpture is composed chiefly of amorphous carbon (broad Raman bands at ~1600 and ~1300 cm^{-1}), gypsum $CaSO_4{\cdot}2H_2O$ (main Raman band at 1008 cm^{-1}) and calcite $CaCO_3$ (bands at 1085 and 712 cm^{-1}), the latter being the major component of the sculpture stone. The composition of the efflorescences on the sandstone arch is more complex. The salt minerals include thenardite Na_2SO_4 (main band 995 cm^{-1}), syngenite $K_2Ca(SO_4)_2{\cdot}H_2O$ (main bands 1006 and 982 cm^{-1}), gypsum ($CaSO_4{\cdot}2H_2O$), nitreKNO_3(main band 1051 cm^{-1}), calcite ($CaCO_3$)and, probably, nitratine$NaNO_3$ (main band 1065cm^{-1}). Additionally, a presence of mirabilite $Na_2SO_4{\cdot}10H_2O$ (bands at 992 cm^{-1} and characteristic sets of bands 645, 632, 620 cm^{-1} and 466, 458, 452 cm^{-1}) mayalsobe possible. With an increase of the temperature and a decrease of the humidity, mirabilite loses its water and grades into thenardite. In case of the band around 1065 cm^{-1} attributed to nitratine, its presence maybe due to witherite $BaCO_3$ (main band 1060 cm^{-1}) and/or alstonite$BaCa(CO_3)_2$ (main band 1064 cm^{-1}).The origin of the band at 143cm^{-1} is not clear: it may indicative of anatase TiO_2, but this mineral occurs occasionally in sandstones.

Based on a microstructure and elemental analyses, the salt phases mentioned have been detected during SEM-EDS investigations. Except the natural components of the stones, XRD analyses confirm the presence of gypsum in the crust on the limestone sculpture and of thenardite accompanied by traces of syngenite and gypsum in the efflorescences on the sandstone arch. Lower number of the phases detected results first of all from the multiphase composition of the samples: it is due totheconcentrationof some mineralsbelow their detection limits.

The presence of the sulphate and nitrate anions of the salts precipitating on the surfaces of the stones should be explained by air pollution, whereas the main source of their cations (Ca, K, Na and, possibly, Ba) must rather be contributed to weathering of mineral rock components. There is another possible source of barium, the cation of witherite and/or alstonite found in some samples. Barium in the form of $Ba(OH)_2$ can originate from previous restoration processes, in which it could be used to remove dangerous sulphates from the stone[3].

In this study the combined methods of micro-Raman spectroscopy and scanning electron microscopy proved to be necessary for identifying the complex stone deterioration products. Additionally, wherever possible because of a sample size, the results have been confirmed by XRD analysis. The significance of the micro-Raman and SEM-EDS methods should be particularly stressed in two cases: when sufficient samples cannot be taken and/or when the amounts of salts are too low to be detected with XRD techniques. A sound knowledge on the type of salts present in the stone can be helpful in making appropriate decisions with regard to the methods of stone desalination and conservation.

Acknowledgements

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TS7

Uncomon pigments and dyes identified through Raman microscopy

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OP31

Smalt characterization with Raman spectroscopy

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Keywords: Raman spectroscopy, FT-IR, SEM-EDS-WDS, smalt identification

In 2011, Polish conservators-restorers discovered wall paintings in Zhovka Castle (now Western Ukraine) founded at the end of 16th century by a Polish military commander Stanislaw Zolkiewski. Interdisciplinary research on painted decoration was undertaken, including in-depth material studies. In two different rooms of the palace two different kinds of smalt (potassium silicate glass colored by a small amount of cobalt) were identified. Historically, it is known that different hues of smalt available on the market were achieved by varying cobalt oxide to sand/quartz ratio [1]. The price of the final product depended on the cobalt content.

First, the two kinds of smalt were studied with optical microscopy (observation of cross sections with reflective light, observation of microscopic slides in transmitted and polarized light). Afterwards energy-dispersive and additionally wavelength-dispersive X-ray spectroscopy was applied in order to estimate the average content of cobalt in the smalt grains and the differences in elemental composition. Qualitative and quantitative analysis were performed. While in decorative painted frieze an expensive, containing more cobalt (*ca.* 5%), pigment was used, in a monochrome decoration of the adjacent room the painter(s) had recourse to a cheaper pigment, with lower cobalt content (*ca.* 1,5%). Furthermore, EDS and WDS spectra showed the presence of important quantities of nickel and bismuth in the dark blue smalt. To confirm the pigment identification two complementary molecular vibrational techniques were employed, such as FT-IR and Raman spectroscopy.

The FT-IR ATR study of the two pigments allowed to detect in the case of dark blue smalt characteristic bands at 1637, 1021 and 770 cm^{-1}, while in the case of light blue smalt only non-specific bands were observed. Hence, the pigment identification was possible solely on the basis of elemental composition.

Eventually, a comparative study of dark blue and light blue smalt with Raman spectroscopy was undertaken. Fragments of paint layers containing smalt were pre-treated with hydrochloric acid in order to eliminate the influence of calcium carbonate. Measurements were performed on pure pigment utilizing the green laser excitation wavelength (514.5 nm). Five measurements (each one from a different pigment grain) were recorded for each type of smalt. The obtained results were in good agreement with IR spectra. While in the case of the dark blue smalt the characteristic band at 465 cm^{-1} was present [2], and peaks at 207, 287, 506, 513, 881 cm^{-1} were recorded, in the case of light blue smalt it was difficult to register any characteristic peak at all.

Raman and IR spectroscopy could be used as quantitative techniques, as band areas are proportional to concentration of characteristic compounds. The experiment clearly showed that in the case of high quality smalt with high concentration of cobalt it was possible to identify the pigment on the basis of the obtained spectra (IR and Raman). However, both vibrational techniques provided insufficient information in the case of light blue smalt, where lower cobalt concentration was measured. In the last case elemental composition combined with optical microscopy proved to be more reliable for pigment identification. The question arises what is the correlation between the detection limit of Raman spectroscopy and the cobalt content in smalt.

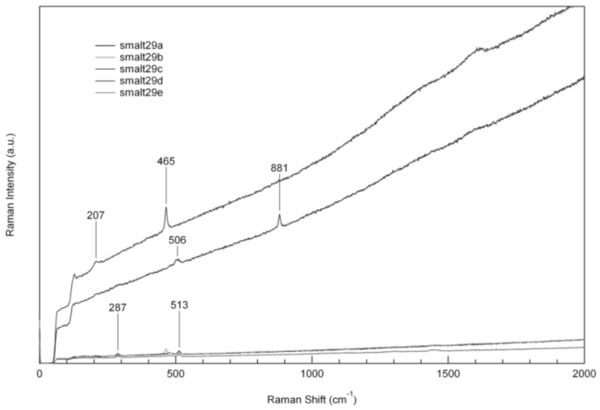

Figure 1. Raman spectra of 5 different grains of dark blue smalt.

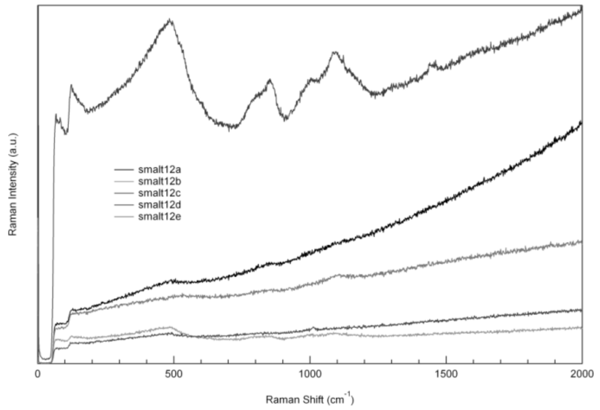

Figure 2. Raman spectra of 5 different grains of light blue smalt.

Acknowledgements

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OP32

Raman and infrared spectroscopy of megafauna and human ancient bones recovered from submerged caves in Yucatan, Mexico

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Keywords:bones, Raman spectroscopy, infrared spectroscopy, SERS

Quintana Roo, located at the northeastern part of Yucatan peninsula houses one of the largest submerged interconected cave systems in the world, with a presumed extension of 7000 km of which about 700 km have been explored so far. The aspect of this region was very different thousands of years ago, since these caves were dry. Sea level was 100 m below the actual level, but at the end of the Pleistocene and beginning of Holocene, between 13,000 and 7000 years before present, the sea-level started to rise [1].

From these complex systems of caves skeletal remains have been recovered since 2005 by experienced divers, both from human and extinct animals, such as horses, tapirs, elephants, peccaries, etc. Frequently the skeletal remains, human and animal, have been found fully articulated and in anatomicallly preserved positions, suggesting that the individuals were deposited or laid there and were not transported bywater. Thus, most of the remains experienced a decay in situ. Due to the permanent exposure to fresh water, the organic portion of bones has decayed, making radiocarbon dating challenging. The purpose of this work was to obtain Raman and infrared data from this collection of animal and human bones, considering the time they have been deposited in fresh or saline water and the fact that the animal bones pertained to animals extinct long ago. Also, SERS (Surface Enhanced Raman Spectroscopy) was tested as a means to obtain otherwise not observable human bone spectra.

Eight bone remains were analyzed: Two from humans and six from extint fauna: *Pecari, Equus,Notroterio, Hemiauquenia, Agoutidaey Xenarthro*.Samples were analyzed as fragments or as powders.Otherwise fluorescent samples were treated as powderswith silver colloids, obtained as in ref. [2], and through SERS (Surface Enhanced Raman Spectroscopy) it was possible to observe Raman spectra. Measured bandwidths were consistent with those from ancient bones, ranging from 12 to 8 cm^{-1}, as reported in [3]. Fig. 1 shows two spectra from bone and tooth from extinct animals, displaying the mineral portion of bone and also calcite.Infrared spectra were taken usingan ATR accesory with a diamond crystal. Radiocarbon dating is reported when possible. Raman and infrared data are discussed.

We can conclude that it was possible to obtain good Raman spectra for ancient bone remains even though they have been immersed in water for more than ten thousand years.As expected, best Raman spectra were obtained from animal teeth, as teeth are lesssubject to post-mortem alteration than bone[3].Also the SERS effect was usefulfor obtainingRaman spectra from decayed and ancient bones.

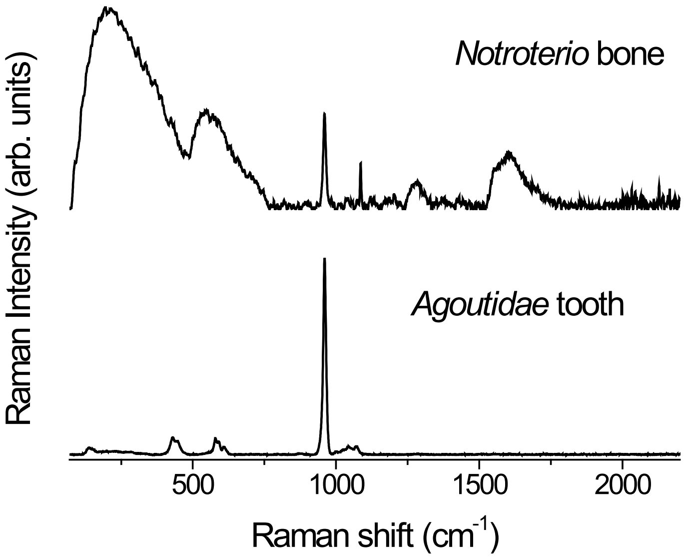

Fig. 1 Raman spectra of two extinct animals showing calcite (upper spectrum) and hydroxiapatite.

Acknowledgements

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Friday, **September 4th**

OP33

Investigation of unique group of painted silk banners from Polish collection

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Keywords: silk banner, pigments, mobile Raman spectroscopy, XRF, FTIR

In conservation science, analytical techniques which are non-destructive or micro-destructive are particularly important. During the last decade, Raman spectroscopy has become an established analytical technique for the study of art and antiquities [1 - 4]. Raman spectroscopy is sensitive and can deliver highly specific spectral signatures of the investigated materials. Using this technique it is possible to characterise nearly all of the inorganic pigments and materials present in the art objects. Another analytical technique commonly used for the study of historical objects is X-ray fluorescence spectroscopy (XRF). This method provides information about the elemental composition of the objects under analysis and can be used as a perfect complementary technique to molecular techniques such as Raman spectroscopy.

Historic textiles represent a very important part of material culture. The subject of the research was a unique group of banners painted on silk. Three 16th century banners from the Wawel Castle museum were studied. The first one, court banner is the oldest existing banner with an insignia function. It was created at the wedding and coronation of Sigismund II Augustus and his third wife, Catherine of Austria, which took place in 1553 in Krakow (Fig.1). The second, funeral banner was probably hung over tomb during or not long after the funeral of Stanisław Barzi (1530-1571), who was a royal courtier and a secretary to Sigismund II Augustus. The last one, battle banner was won in 1588 at the Battle of Byczyna, which was fought between the armies of Maximilian III Habsburg, pretender to the Polish throne, and Chancellor Jan Zamoyski, on the side of Sigismund III Vasa.

This work presents results which are extremely important owing to the significance of studied banners for Polish cultural heritage.

Figure 1. The court banner created at the royal wedding in 1553.

Analytical science can play an important role in characterising fibre behaviour, identifying used materials, assessing their deterioration and the conditions for preserving them. The research covered the series of analytical pictures in different ranges of electromagnetic radiation: near-infrared, visible light and ultraviolet. Thanks to the infrared analysis it was possible to see deep layers, not visible with the naked eye. Photos in the ultraviolet light have revealed places with binders.

According to oxidation and hydrolysis estimators of silk structure the state of silk degradation can be calculated [5]. Such defined estimators allow for simple risk assessment of historic textiles. The estimation of the degree of fibre damage in silk using a scanning electron microscopy and Fourier infrared spectroscopy was performed. Based on non-destructive ATR-FTIR analysis the condition of the battle banner, which is the most destroy object from the group of studied banners was described.

The portable equipment allowed performing analysis directly in the museum storage areas. Avoidance of any transfer of these fragile banners had obvious advantages for the integrity of the objects. By using mobile Raman and XRF instrumentation it was possible to investigate the artworks without the need for sampling.

XRF analysis and Raman spectroscopy were carried out at the same spots, on 20 points of each banner. For the pigments, gilding layers, and ground under the gildings, first the screening of elements using XRF was performed. Afterwards, the studied layers were analyzed by the non-invasive Raman system in order to ascertain their molecular compositions. When XRF was the only research technique used for pigment identification, definite identifications could be achieved only for some pigments, such as vermilion, thanks to the presence of specific key elements. Unfortunately, XRF could not determine which lead pigments were present. Therefore Raman spectroscopy was necessary to identify the type of compound. The identification of the type of the metals used in the gold and silver layer was possible only by use of XRF.

One of the most important features of the present work was to increase the knowledge of state of the preservation, the pigments and materials used in 16th century, the oldest Polish banners. The condition of the banners was described. The use of Raman and XRF performed by using mobile systems allowed to obtain as much information as possible in a non-invasive and a non-destructive way. Obtained data provided art historians with precise information about the techniques used in the creation of the work itself, and gave conservators and restorers guidelines about the materials necessary for conservation.

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OP34

Degradation of Cu-pigments of medival wall paintings in the chapel of Vipperow

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Keywords: wall paintings, pigment analysis, degradation processes, Cu-pigments

Medival mural paintings in the chapel of Vipperow (Northern Germany) are strongly affected by degradation effects with colour changings and extensive losses of the painting layer. During ongoing work of preservation and restoration of the paintings our mobile Raman spectrometer system MoRaS was used on-site to identify pigments and present degradation substances.

Results of on-site measurements gave reason for detailed studies of Tenorite and green Cu-pigment Atacamite in samples taken from the paintings. Many Raman spectra are superimposed by intens bands of spectra of whewellite or weddellite, calcite and/or gypsum (cf. spectrum in the figure) and/or an artifical binder. The interpretation of the spectra is based on high-resolution spectral data of minerals of the Atacamite group. The Raman based results give hints to decipher the original pigments and colours of the wall paintings.

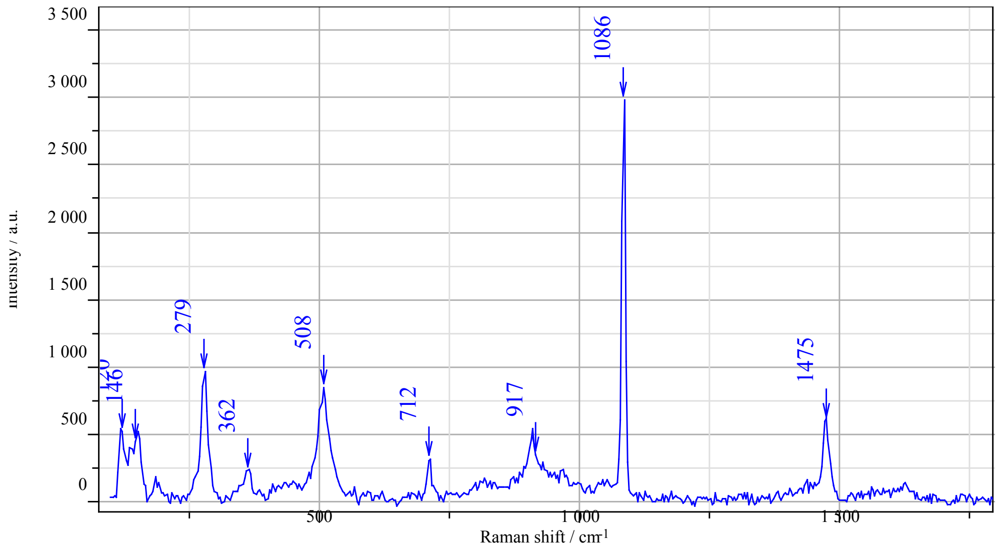

Fig: Raman spectrum of the painting layer with bands of atacamite (120, 146, 508, 911 cm^{-1}), calcite (279, 712, 1086 cm^{-1}) and weddelite (911, 1475 cm^{-1}).

Furthermore, a quite uncommon pigment alteration from azurite or malachite to tenorite was studied on samples of baroque mural paintings. During this alteration a biuret-complex is formed, which gives the painting a violet color. The detection of this change of color gives the proof for the presence of protein in the painting layer and indicates the application of the binder casein .

OP35

Raman Spectroscopy Analysis of Terra Sigillata: the Yellow Pigment of Marbled Sigillata

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Keywords: Terra sigillata, Raman spectroscopy, Pseudobrookite (Fe_2TiO_5), Mg substitution

Terra sigillata, as the most famous fine ware of the Roman period, represents a milestone of the manufacture of potteries with high gloss coating and relief decoration [1]. In addition to the terra sigillata production with red coating, the largest Gallic workshop (La Graufesenque) made a special type of terra sigillata, called “marbled” by the archeologists and characterized by a singular yellow high-gloss coating with red veins [2]. Electron microscope and X-ray diffraction studies showed that the yellow component of marbled sigillata was obtained from a titanium-rich clay preparation. The color is due to the formation of PS (pseudobrookite, Fe_2TiO_5) phase during firing [3]. In this work, Raman spectroscopy measurements were carried out to precisely characterize PS particles of the yellow pigment of marbled sigillata with the aim to further investigate its chromogenic mechanisms.

By means of an XploRA spectrometer (Horiba), Micro-Raman measurements were performed with the Raman excitation provided by a 532nm solid state laser. A 1-αm-diameter laser spot was provided with a 100× microscope objective used to focus laser beam and collect scattered light. The laser power of 0.725 mW was employed to optimize the signal/background ratio while avoid any influence on PS spectrum. Forty-three samples of marbled terra sigillata were selected. Twenty-three ones of them labeled as CS- and the others labeled as TSGM- were excavated in the old city of Narbonne and La Graufesenque workshop, respectively. The synthesized PS powder labeled as P47 was provided by M. Dondi, who has theoretically and experimentally manifested that colors achievable with PS pigments can be varied from deep brown shades to light brown depending on the composition of ceramic matrices [4].

The cardinal results displayed that PS crystals in the yellow pigment are distinct from the ones in the synthesized PS powder (see Figure 1). Raman spectra of PS crystals in yellow components showed the observed line broadening and red shift effects. The former feature is generically related to a wider distribution of energy levels. The latter feature is attributed to the insertion in the lattice of the lighter and smaller Mg species lead to a lowering of the average reduced mass and an induced strain due to the formation of shorter Mg–O bonds with respect to Fe–O bonds is expected.

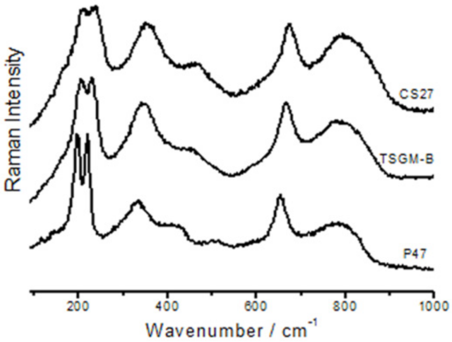

Figure 1. Raman spectra of PS in the synthesized powder (P47), an marbled sigillata slip of La Graufescenque (TSGM-B), an marbled sigillata slip of Narbonne (CS27).

Mg substation in the PS structure usually plays a dual role. On one hand, the partially disordered Mg distributions can stabilize the PS structure through involving a partial cationic disorder. In other words, PS is thermodynamically unstable since its enthalpy of formation is positive but stabilised by the configurational entropy of formation due to the cation disorder [5]. On the other hand, the Mg-Fe substitution has an influence on the color [6] and the fluctuation of Mg/Fe ratio could be at the origin of variation of the yellow color. Therefore, based on small PS crystals in charge of the yellow color with certainty, ancient potters have the competence to obtain countless different shades of the yellow components through altering the ratio of the concentrations of iron and magnesium in the raw clay. Results confirmed that the beautiful yellow color of marbled sigillata is related to the formation of a PS phase in which Fe was substituted by magnesium.

Acknowledgements

This work has been financially supported by the China Scholarship Council.

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OP36

Identification of pigments mixtures by imaging data obtained by LA-ICP-MS supported by Raman spectroscopy

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Keywords: pigment identification, painting analysis

Identification of pigments micro-samples gently taken from the XIXth century paintings was obtained by imaging data from LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry) and supported by Raman spectroscopy. Laser ablation can be executed during direct sampling from the surface of the analyzed objects or during investigation of micro-samples. The process of ablation offers possibility to obtain not only quantitative information about trace, minor or major elements but their distribution over the selected area at the surface or reconstruction of depth profiles. The advantage of using micro-samples is connected with possibility to analyze sampled material by several consecutive instrumental methods allowing reliable final interpretation of the results.

The advantages of using LA-ICP-MS (ELAN 9000, Perkin Elmer) over SEM-EDS (Zeiss Merlin) will be shown for the selected examples of multi-elemental analysis of heterogeneous particles taken from the XIXth century paintings. Mapping of elemental distribution was supported by Raman Spectroscopy which was used subsequently to confirm the identification of the mixtures of pigments [1]: White lead/$2PbCO_3.Pb(OH)_2$; Naples yellow/Pb_2Sb_2O7; Ochre/$Fe_2O_3{\cdot}H2O$; Cinnabar/HgS; White zinc/ZnO; Ultramarine/$Na_{8-10}Al_6Si_6O_{24}S_{2-4}$; Emerald green/$Cu[C_2H_3O_2]{\cdot}3Cu[AsO_2]_2$; smalt/$SiO_2+K_2O+Al_2O_3+CoO$; Cadmium yellow/CdS; Cobalt blue/$CoO{\cdot}Al2O_3$; Malachite/$2CuCO_3{\cdot}Cu(OH)_2$; Cerulean blue/CoO $nSnO_2$ and Carbon black/C.

The development of the multi-instrumental analytical strategy for identification of historic pigments will be presented with special attention to Laser Ablation ICP MS measurements and their role in the whole analytical protocol.

Acknowledgements

This work has been financially supported by the National Science Centre (NCN) of Poland: project No 2011/01/B/ST4/00478

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OP37

Raman analysis of color minerals from the Stone-Age sites at Gubs gorge (North-West Caucasus)

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Keywords: Upper Palaeolithic, North-West Caucasus, mineral pigments, rock art, micro Raman, SEM-EDX, PLM

The preliminary results on the study of color minerals from excavations multilayer Stone Age site Dvoinaya Cave and the analysis of rock-art pigments' samples in Gubs gorge are presented.

Gubs gorge is located in the foothills of the Northern slope of the Western Caucasus (Skalisty ridge). Two pairs of hand prints (positive picture) and several spots of red pigment were discovered on the open calcareous rock (the left bank of the river Gubs) at the elevation about 100 m above the level of the river Gubs (840 m above the sea level) by P.U. Autlev in 1950's. (Formozov, 1964). There are no any cultural remains on the foot of the rock. The small rocky ledge has a negative slope. Several Middle and Upper Paleolithic sites are located near the rock art but 20-30 m below. The age of the rock paintings is unknown. The motif of hand is a very popular in art in the world from Upper Paleolithic to the morden time. E. Leonova sampled pigment from handprint in 2014 (Fig. 1).

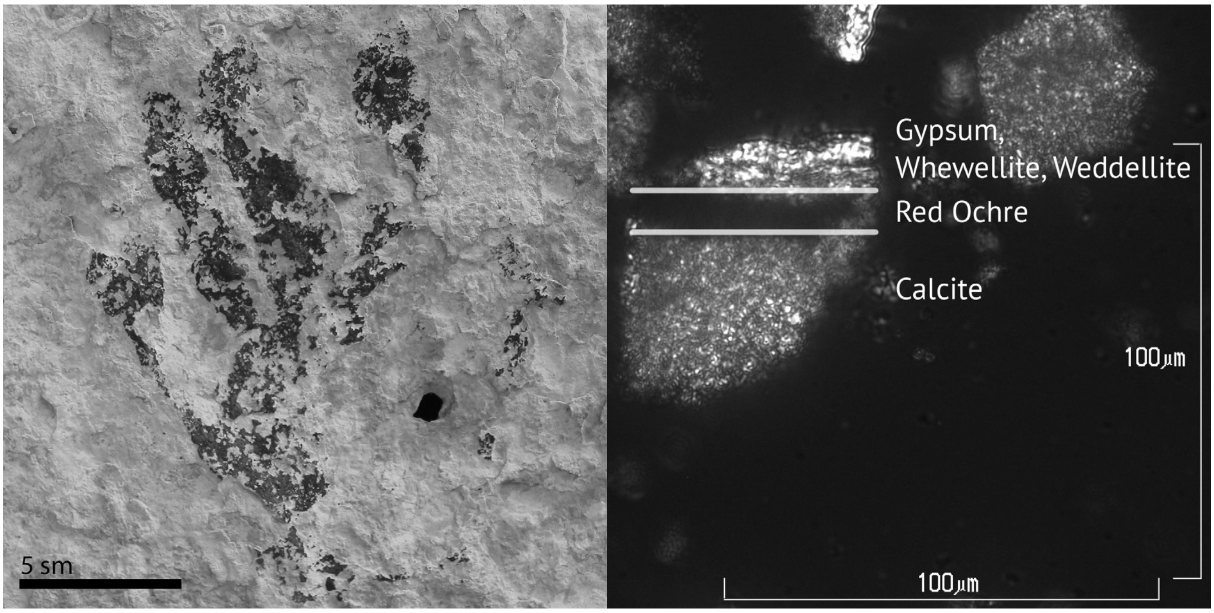

Figure 1. Handprint, Gub1-1 (photo by E. Leonova), PLM photo of cross-section of the sample Gub1-1.

To determine the composition of minerals we employ Thermo Scientific DXR Raman microscope with an excitation wavelength of 780 nm. SEM-EDX and polarized light microscopy were used to prove the results of Raman spectroscopy.

Red pigments of the wall paintings were identified as hematite (Raman data) and more accurately as red ochre (SEM-EDX data on Si and Al characteristic bands).

Complicated composition of white crystal-containing material on the surface of the paint layer was revealed. Gypsum is the dominant component but the material also contains whewellite and weddellite, which serve as indicators of biological activity on the wall surface (Edward et al., 2000). Such minerals are typical of sites with rock-wall painting.

Several mineral samples were found in the Upper Palaeolithic layer of Dvoinaya Cave. The Dvoinaya Cave is located in 2,5 km upstream from the rock art site. There are three cultural layers: Upper Palaeolithic (about 13000 BP), Early and Late Mesolithic (Leonova, 2014). One of the sample represents a concretion of yellow crystals with a size of 3-5 mm, that were identified as jarosite with the aid of Raman spectroscopy. Jarosite is a rare material in cultural layers, since it is easily involved in hydrolysis reactions. At temperatures of higher than 600°C, jarosite is transformed into hematite and mixed iron-potassium sulfate (Frost et al., 2005). Such a property could be used to obtain the red pigment.

The red mineral from the cultural layer is almost pure hematite with minor quartz impurity.

Trace amounts of red pigment were also found on the stone artifacts. In particular, a red mineral on the edge of end-scraper was identified as red ochre using the SEM-EDX results. Relatively small sizes of particles and presence of organic substances impede Raman measurements.

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PL3

The integrating activity project IPERION_CH: a further step toward a European research infrastructure in heritage science

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Keywords: European research, heritage science, research infrastructure.

Following and continuing the experience of the preceding projects LabS-TECH, Eu-ARTECH and CHARISMA, the integrating activity project IPERION-CH (*Integrated Platform for the European Research Infrastructure on Cultural Heritage*) groups together more than 24 European institutions that develop and promote advanced research in heritage science (http://www.iperionch.eu/). The consortium combines research laboratories with leading technology institutes on cultural heritage, to facilitate profitable interactions among scientists, conservator-restorers, archaeologists, and curators, working together towards the common objective of building up a unique distributed European Research Infrastructure in Heritage Science (ERIHS).

Within IPERION_CH, three different types of activities are jointly carried out by the partners, as: networking, research, and transnational access.
Within *networking*, coordinated initiatives will help to promote interoperability among European facilities in order to avoid duplications of efforts and resources. The vast program includes training and integration of young researchers from Europe and associated countries to reinforce links between the partners and the multidisciplinary communities external to the consortium.
Research activities are focused on advancing diagnostics for improving services and tools to be offered to researchers and professionals in heritage science. New portable instruments are developed and optimised; methods for organic analyses on historical and archaeological samples are developed, and digital tools and protocols for storing, re-using and sharing multi-format data are unified.
Through *transnational access*, facilities of the consortium are open to European scientists, conservator/restorers and curators, in order to enable researchers to conduct exemplary scientific studies on cultural heritage materials with no charge. Transnational access opportunities include complementary non-invasive techniques to minimise sampling (MOLAB), followed by more in-depth characterisation (FIXLAB), combined with consultation of comparative data stored in archives and collections from earlier heritage studies (ARCHLAB).

The mobile facility MOLAB offers European researchers a unique set of portable instrumentations for non invasive in-situ measurements, to develop diagnostics or monitor materials or test conservation procedures. The integrated MOLAB analytical techniques include Raman, FT-IR, XRF, UV-Vis absorption and emission, XRD, and NMR profilometry, together with imaging methods based on XRF, Vis-NIR, T-Hz, OCT, and Holografic Speckle Pattern Interferometry. Services are offered by the Italian CNR-ISTM and INO, University of Perugia, and Laboratorio Diagnostica di Spoleto; and by labs of CNRS, Paris, FR,; Nicolaus Copernicus University, Torun, PL, FORTH, Heraklion, GR, and RWTH, Aachen, DE.
The FIXLAB medium and large scale facilities are composed by two platforms: the first is based on the Accelerator New-AGLAE located in the *Palais du Louvre* and the Synchrptron SOLEIL, Paris, FR; the second is Hungarian and composed by the Accelerator ATOMKI of Debrecen and by the Budapest Neutron Centre, BNC. Access to the numerous beamlines and techniques of these installations will allow researchers to carry out sophisticated spectroscopic and imaging analyses on small objects or on macro and micro-samples.

Finally, the ARCHLAB consultation of the archives of 10 prestigious labs and museums will offer researchers new opportunity of access to data (spectra and images, mostly umpublished) produced in decades of activity by the laboratories of The National Gallery and The British Museum in London, UK; the Opificio Pietre Dure in Firenze, IT; the C2RMF in Paris, FR; the Museo del Prado in Madrid, ES; the RCE Agency in Amsterdam, NL; the Istitute Royale du Patrimoine Artistique in Brussels, BE: the Rathgen Forschungslabor Staatliche Museen zu Berlin, DE; the Instituto del Patrimonio Cultural de Espana, IPCE, Madrid, ES; the Centre for Art Technological Studies and Conservation, Copenhagen, DK.

Examples will be given of applications which demonstrate how it is possible, through the exploitation of the access program, to achieve excellent characterization of execution techniques, to identify material alterations, to test innovative restoration methods, or even to find new cases of scientific interest to be put under the focus of laboratory research.

Useful links: http://www.iperionch.eu/

TS8

Prospective European research infrastructure E-RIHS and its Polish partner E-RIHS PL

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Keywords: research infrastructure

E-RIHS is a proposed **E**uropean **R**esearch **I**nfrastructure for **H**eritage **S**cience submitted to the 2016 ESFRI (European Strategy Forum on Research Infrastructures) Roadmap. The decision is expected by end of 2015.
The proposed distributed research infrastructure will comprise:

- E-RIHS Headquarters and National Hubs;
- fixed and mobile national infrastructures of recognised excellence;
- physically accessible collections/archives;
- virtuallyaccessible heritage data.

E-RIHS will providestate-of-the-art tools and services to cross-disciplinary researchcommunities advancing understanding and preservation of global heritage.It will support:

- collaborative research,
- access to a wide rangeof cutting-edge scientific infrastructures, methodologies, data andtools,
- training in the use of these tools,
- public engagement,
- repositories for standardised data storage, analysis andinterpretation enabling full exploitation.

Representing more than thesum of its parts, E-RIHS will enable the access to advance heritagescience and to the distributed infrastructures in acoordinated and streamlined way, which has so far not been possible.E-RIHS is a common goal of national communities that recognise the valueof a fully strategic integrated approach with shared priorities,avoiding duplicated effort while increasing global competitiveness ofEuropean Heritage Science.

E-RIHSpursues a unique and cohesive entity of European world-class facilitiesand fosters an integrated platform in the global community of HeritageScience.E-RIHS will integrate research on four access platforms:

- MOLAB: access to advanced mobile analytical instrumentationfor non-invasive or minimally invasive measurements on valuable, fragileor immovable objects, archaeological sites and historical monuments. TheMObileLABoratories will allow its users to carry out complexmulti-technique diagnostic projects, allowing effective in situinvestigation.
- FIXLAB: access to large-scale and specific facilities withunique expertise in Heritage Science, for sophisticated scientificinvestigation on samples or whole objects, revealing micro-structuresand chemical composition, giving essential and invaluable insights intohistorical technologies, materials and species, their context,chronologies, alteration and degradation phenomena.
- ARCHLAB: physical access to archives and collections ofprestigious European museums, galleries, research institutions anduniversities containing non-digital samples and specimens and organizedscientific information.
- DIGILAB: virtual access to organized knowledge andscientific information in heritage data hubs – includingmultidimensional images, analytical data and documentation – from largeacademic as well as research and heritage institutions.

Research supported by E-RIHS will span several areas, including:

- Materials. Research will concentrate on understanding the properties and behaviour of materials constituting the CH objects covering questions about deterioration with time, origin of the artefact, its authenticity and others. Infrastructure will support the development of novel sensors, devices and techniques suitablefor application to a wide range of characterisation and measurementproblems related to CH objects.
- Environments. Research will focus on environmental impact on CH object, especially on changes of conditions during excavation, transfer to a museum or between museums, or as a result of soil erosion, changing air quality and/or climate change.
- Digital. The research areas include handling spatial, temporal and geometric data; knowledge representation, language engineering, pattern recognition and big-data analytics; image processing, computer graphics and interactive techniques for cultural heritage.

E-RIHS access and networking will be accompanied by high-level actionsfor training, dissemination, communication and knowledge/technologytransfer aimed at the global heritage community, with special attentionpaid to SMEs competitiveness and growth, and to social and culturalinnovation.

IPERION-CH will be the central nucleus of the new organisation and is providing the possibilities to launch the process.

The prospective Polish partner of E-RIHS is E-RIHS_PL. This virtual infrastructure is under construction. The starting point are letters of interest of 12 Polish institutions who declare the participation in the E-RIHS. Nevertheless, the initiative of open to all, interesting in providing service to preservation of cultural heritage in Poland. Major goal of this consortium is a preparation of participation of Poland in E-RIHS but also:

- fostering of nationwide and international scientific cooperation in development of physical/chemical techniques of examination of CH objects
- development of common research projects
- development of integrated system of technical support for institutions active on CH area by access to up-to-date research techniques (MOLAB_PL, FIXLAB_PL, ARCHLAB-PL)
- exchange of knowledge and experience via conferences and symposia („Analiza Chemiczna w Ochronie Zabytków”)
- cooperation with other projects, networks and infrastructures (e.g. DARIAH PL)

During the presentation information on E-RIHS and E-RIHS_PL will be given.

Useful links:

http://www.iperionch.eu/

http://uslugi.umk.pl/konserwacja_ankieta/

Poster Session

P1

Comparisons of the signal to background ratio of Raman spectra acquired for the identification of pigments by different instrumental setups for measurements on samples and *in-situ*

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Keywords: Raman, pigments, non-invasive setups

Raman-Microscopy on micro-samples is widely used for the identification of pigments in works of art. However, *in-situ* measurements directly on the object are strongly preferred because no sampling is needed.Another important advantage is that all the areas ofa painting can be analysed providing more representative results.

In this study we compare setups for micro-Raman-measurements *in-situ* and on samples and evaluate the spectral responses. Measurements were carried out on mock-up samples and on one study-case painting.

The traditional microscope set-up (Fig. 1, 1) is compared with the use of setups where the laser path is deviated by 90° for analyses directly on the object (horizontal beam, Fig. 1, 2) and with measuring head connected to the spectrometer viafibre optics, which allows the examination of an object few metres away from the Raman instrument (Fig. 1, 3).

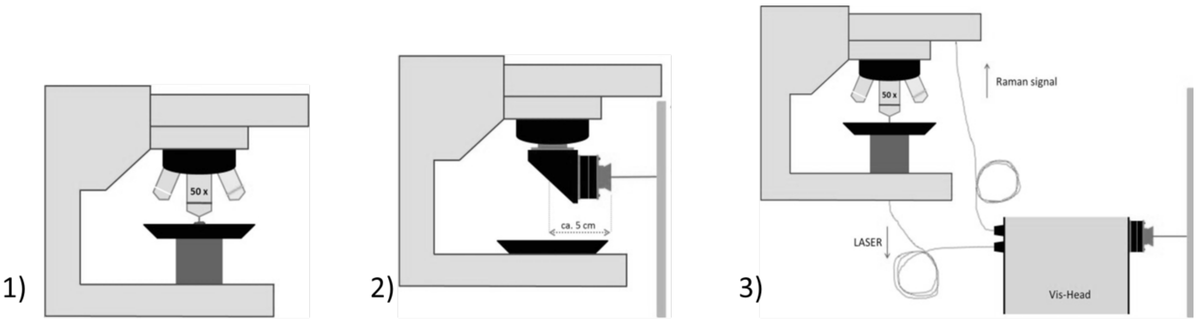

Figure 1. Three configurations of the Raman measurements: 1) traditional microscope; 2) horizontal beam set-up and 3) fibre optics

Due to the Raman microscope design, only small paintings (ca. 30 cm) without frame can be fully analysed in configuration 1. With the help of extension tubes, larger objects can be analysed. For the horizontal beam configuration different extension tubes were tested with variation in the distance between mirror and focal point (3 and 30 cm approximately).

Two lasers were used for this study, 785 and 532 nm. The lasers' wavelength has an influence, on spectral response of a pigment and intensity of interference by fluorescence, hence influencing thesignal to noise ratio.

Other parameters, such as laser intensity, objective, grating, time of acquisition and accumulations were kept constant whenever possible to obtain comparable results. The signal strengths were determined as counts (Raman signal intensity) per second of measurement and per Watt of laser intensity (Cns/s.W).

The mock-up samples consisted of pellets of pure pigments – cinnabar, red ochre, ultramarine blue, yellow chrome and phthlalocyanine blue. The choice of the pigments was based on their homogeneity and their presence in the study-case painting.

The study-case concerns a falsifiedpainting, "Cubist still life" (1913) recently dismissed as work of Fernand Léger based on previous analysis at the Rathgen-Forschungslabor of micro samples. In this work we compare the performance of the different non-destructive /non-invasive configurations described abovewith the results previously obtained on micro-samples.

On the mock-up samples the horizontal beam configurations showed spectral responsesthat were very similar to thoseof the microscope whereas the with the fibre optics the spectral response decreases drastically in comparison with the microscope.

On the painting more parameters influence the intensity of the signal, such as roughness of the surface, mixture of different materials, difficulty in focusing, presence of binding media, etc. Therefore, it is more difficult to define a trendingbehaviour and quantify the performances of the different configurations, but it can generally be said that the spectral response is similar to that observed with for mock-ups.

P2

Colombian or Not Colombian: a Confocal Raman Spectroscopy comparative study of Miniature Paintings on Ivory

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Keywords: authentication, ivory, Colombian miniature painting, micro Raman confocal spectroscopy

Through this study aimed to verify the relationship between a heritage object without identification with two renowned Colombian artist using confocal Raman spectroscopy as an analytical tool.

Miniature painting in Colombia was developed during the colonial period and continued until independence (XVII c – XIX c), when it gradually was replaced by daguerreotype images. The technique originated from Europeinvolved the use of oil and watercolor on surfaces such as ivory and copper. It was developed mainly by artists linked to the Catholic Church who used art as a way to create portraits and relics of the famous people of the region. In this research, the composition of a set of miniatures painted on ivory by two renowned Colombian artists Pio Jose Dominguez (three portraits of early XIX century Colombian heroes) and Jose Maria Espinosa (six portraits of middle XIX century Colombian heroes, Priest and independence martyrs) from the collection of the National Museum of Colombia has been investigated by Raman Spectroscopy and compared with an unattributed miniature painting by an unknown artist who some art experts believes related to the ones mentioned above.

For this study the paintworks was analyzed in situ, collecting material information of each work (pigments, support and protective glass). A confocal Olympus BX41 fluorescence microscope coupled with a Raman spectrometer Horiba® XPLORA was used, which together with a set of laser emission 785 nm, 638 nm and 532 nm, left characterized the chemical composition of the samples.

The results analyzed and compared, given a similarity in membership between the works of each artist, founding a color pallet compound of prussian blue, vermillion, lead white, ochre yellow and carbon black, however, differ in composition with the piece of the unknown artist work for the presence of red lead and the absence of yellow and white pigments, which can postulate that was not produced by none of those Colombian artists studied. It is also noteworthy that found in the work issue a red pigment (red lead) that is used in this technique mainly in Europe schools, which gives provides a point of discussion for its true origin.

Acknowledgements

This work was made possible thanks to the collaboration of the National Museum of Colombia, their Chief restorer Maria Catalina Plazas and by financial means from the Faculty of Science - Department of Chemistry of the University of Los Andes Colombia.

P3

An approach to the identification of ambers from diffrend archaeological sites

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Chemical studies on resinous materials in archaeological remains are generally aimed at identifying the origin of the materials present, at studying the production and manufacturing techniques, and at improving techniques for their conservation and restoration.
This is particularly true for ambers remains. This paper presents some significant results for a systematic characterisation of the chemical composition of ambers of different provenance. The study has been carried out by using spectroscopic techniques, Raman and FT-IR with the aim of creating or extend FT-IR, Raman, FT-Raman libraries of geological and archaeological ambers. The data could be used as references in provenance studies of archaeological amber finds.

Based on this knowledge, archaeological resinous materials, recovered in a various sites, dating back from the ninth century BC to the second century AD, have been analysed and the relevant results discussed. Comparisons of analytical detailed results enable the recent and ancient history of the materials to be traced.

It is shown that provenance can be ascertained, in addition to the classical Beck's method of FT-IR spectra (based on the special shape of the infrared spectrum in the 1500- 1000 cm-1 region), also by using Raman spectra and XRF data. The alteration of Museum preserved samples are taken into consideration for a description of the rapid changes of the spectra recorded.

P4

Characterization of the Sicilian amber by micro Raman Spectroscopy

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Keywords: Amber, Raman-spectroscopy, jewels, Simetite, Sicily.

Amber (general formula $C10H16O$) is a fossilized resin found in many parts of the world (e.g. Baltic region, Mexico and Dominican Republic). Chemical characteristics of amber are related to the biological origin and the geological conditions during the maturation process.

The simetite amber coming from the eastern and southern Sicily is one of the more precious amber characterized by colors ranging from yellow, yellow-bluish to red and black. The name derives from the Simeto River that transport the amber to the see banks where the seekers still find it. The use of simetite is attested starting from prehistoric periods as small globules. During the 18th and 19th centuries, local artisans made very impressive jewels with this material worldwide appreciated.

Despite of the importance of this amber varieties, in literature very few data are present on scientific analysis of simetite [1] due also to the difficulty of findings authentic samples, often collected in museums and mineralogical collections.

In this paper we report the micro-raman analysis of numerous samples of simetite performed on raw pieces and loose gems. Furthermore, for comparison we analyzed specimens of Baltic and Dominican ambers and synthetic resins. All the analyzed samples have been kindly provided by the gemologist Ugo Longobardo.

The analysis were carried out by micro-Raman Jasco NRS-3100 apparatus, equipped with laser excitation source at 785 nm. As well known, this technique has the advantage of being non-destructive and non-invasive making it a particularly suitable for the analysis of precious materials. Furthermore, raman spectroscopy was successfully used for the characterization of amber and copal [2].

The main aim of the research is to characterize simetites by means of raman spectroscopy and to create a database useful for future studies. and to distinguish it from less precious ambers of different geographical origin or fakes and simulants.

The results obtained on numerous ambers of certain origin, permitted to recognised a variability of simetites chemical composition, until now not evidenced. However, multivariate statistical analysis carried out on raman spectra allow us to distinguish the Sicilian natural amber from the Baltic and Dominican ones.

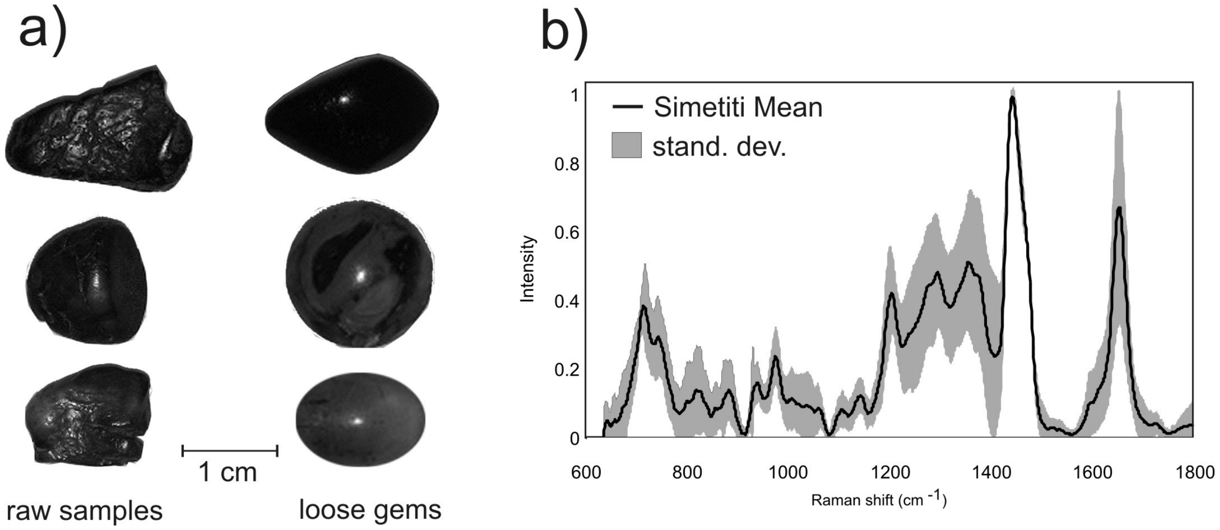

Figure 1. a) Pictures of some studied simetites, representative of the analysed set; b) mean and standard deviation of simetite raman spectra.

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P5

Red gemstones characterization by micro-Raman spectroscopy: identification, genesis and treatments in rubies and their imitations.

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Keywords: red gemstones, Raman-spectroscopy, jewels, jewellery, rubies.

In the framework of a wide project aimed to study the potential of Raman spectroscopy in characterizing gems[1,2], jewels and jewellery collections[3], in this work the results of a micro-Raman investigation on red gemstones are proposed.

The use of Raman spectroscopy as gemological tool is recently largely increased, thanks to the possibility to carry out non-invasive, non destructive, quickly and contactless measurements on precious objects and artifacts[4]; these requirements are fundamental for gems characterizations, in particular in the case of gems set in jewels and preserved in Museums. In fact, gemstones have been widely used in antiquity toadorn precious objects, such as royal insignia or liturgical objects, often having really high cultural valence. In this specific case, the use of portable equipment is mandatory[5]. Otherwise, in the case of loose gems, the possibility to analyse them with a laboratory set-up allows to go deeper inside the characterization of materials, permitting the investigation not only of the mineralogical identity but also the study of inclusions and treatments. The latter aspect represents a crucial feature in the gemmological characterization of gems in a trade context, considering the diffusion of "allowed" and "not-allowed" treatments. In addition, the possibility to identify specific solid or fluid inclusions gives back information on genesis and, sometimes, provenance of gemstones[6], supporting the gemmological attribution and solve identification problems of uncertified materials.

For aforementioned, considering the excellent results obtained on blue and green gems, a set of gems supplied by a jeweller as representative of the actual trade of the current red gems trade, have been analysed by using micro-Raman instrumentations equipped with different laser excitation sources. In detail, Raman spectra have been collected on sixteen samples of red loose gems (Table 1; Figure 1) by means a confocal Jobin Yvon Horiba Labram, equipped with the 473.1 nm excitation lines and a micro-Raman Jasco NRS-3100 apparatus, equipped with laser excitation source at 785 nm. The identification of the gemstone has been supported by the comparison between the experimental Raman spectra and reference data from various databases[7,8] and literature[9].

The results allow not only to discriminate rubies from simulant and fakes but also to achieve useful information on inclusions and treatments, obtaining a complete characterization of the studied red gems.

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Sample	*Colour*	*Weight (Carats)*	*Shape*
R1	Deep red	0.945	Oval
R2	Pale red	0.655	Oval
R3	Light red	0.230	Trapezoidal
R4	Light red	0.575	Rectangular
R5	Light red	1.715	Oval Cabochon
R6	Red	2.380	Octagonal
R7	Deep red	0.990	Drop
R8	Red	3.15	Oval
R9	Deep red	7.97	Heart
R10	Red	2.47	Round
R11	Red	0.99	Round
R12	Red	0.36	Round
R13	Pale red	1.64	Oval
R14	Pink	0.84	Oval
R15	Pink/pale red	0.38	Oval
R16	Pale red	0.43	Drop

Table 1. List of the investigated samples, together with some characteristics, such as color, weight and shape.

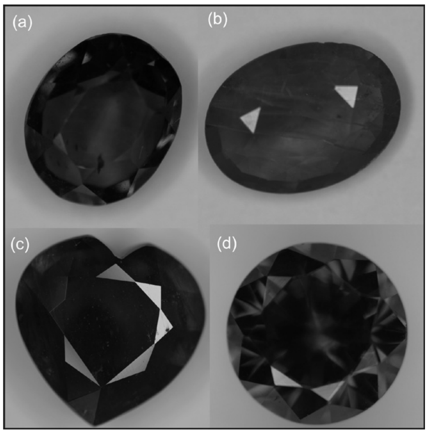

Figure 1. Pictures of some studied red gemstones, representative of the analysed set.

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P6

Lead chromate pigments and minerals: Raman identification

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Keywords: lead chromate pigments, hemihedrite, crocoite, phoenicochroite

The chrome yellow ($PbCrO_4/PbCr_{1-x}S_xO_4$) and chrome orange ($PbCrO_4 \cdot xPbO$) pigments were very popular during the Impressionism. These synthetic pigments are now intensively investigated to understand their degradation mechanisms, for an appropriate choice of the restoration treatments. Their identification is often difficult, because of the absence of a clear methodology through spectroscopic techniques.

The corresponding rare mineral species,crocoite $PbCrO_4$ for chrome yellow andphoenicochroite$PbCrO_4 \cdot PbO$ for chrome orange, have been in a few cases identified as intentionally added pigments in works of art dating back to periods well before the introduction of the synthetic pigments. Moreover, in some cases, orange colors have been assigned to even more exotic mineral species as hemihedrite$ZnPb_{10}(CrO_4)_6(SiO_4)_2F_2$, as the presence of the chromate group gives “similar” Raman spectra.

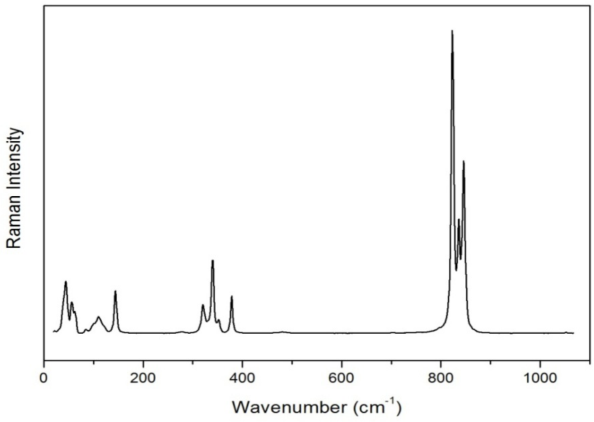

Figure 1 – The Raman spectrum of phoenicochroite

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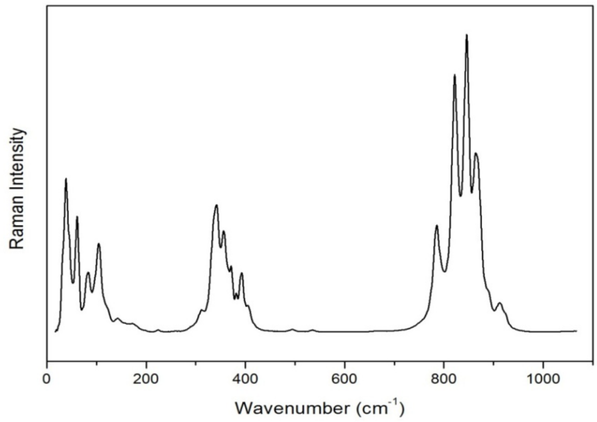

Figure 2 – The Raman spectrum of hemihedrite

We report accurate polarized Raman spectra (taken at 623.8 nm and 473.1 nm), including the low-wavenumber region down to 25 cm^{-1}, of crocoite, phoenicochroite (Figure 1) and hemihedrite(Figure 2) crystals, not easily found in databases. In some cases, the spectra have been takenby "angle-resolved polarized Raman spectroscopy".The characteristic features that allow a definite identification of the minerals specie are indicated[1-2].

Synthetic lead chromate pigments of different hues, produced by different manufacturers, were investigated to characterize their composition. "Chrome yellow" is generally found as lead chromate/sulphate$PbCr_{1-x}S_xO_4$: the X-Ray diffraction peaks are shifted and the Raman bands are broader with respect to the bands in pure crocoite. "Chrome orange" pigment is normally the synthetic equivalent of phoenicochroite, with composition $PbCrO_4{\cdot}xPbO$, while "chrome red" pigment is a mixture of lead chromate/molybdate/sulphate$Pb(Cr_{1-x-y}Mo_yS_x)O_4$ and lead chromate/sulphate.

A case study, chrome yellow and orange pigments found in a degraded environment in the wall paintings in the Santa Vittoria Chapel in San Lorenzo de' Picenardi castle (Cremona, Italy),is finally discussed.

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P7

In-situ studies of inks, pigments and parchment in manuscripts by portable Raman spectroscopy

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Keywords: Raman spectroscopy, pigments, parchment, iron-gall inks, degradation

Raman spectroscopy has been widely applied as non-invasive and non-destructive spectroscopic technique for the identification of pigments and inks in manuscripts. It enables compound specific identification of pigments of the same color, determination of the way of their production and in specific cases even the raw materials used and hence their origin [1]. Usually it is applied in combination with other complementary techniques such as XRF and/or FTIR.

Raman spectroscopy has also proven to be successful for the study of the degradation and aging phenomena occurring on parchment that is stored in libraries or private collections for several hundred years [2]. Numerous documents, manuscripts and artworks are now suffering varying degrees of degradation due to the corrosive nature and color instability of many iron gall inks, widely applied in the middle ages. The ability to identify an ink on an item as iron gall is therefore useful not only from a historical and curatorial perspective but for conservation and preservation purposes too. It can be used to confirm the ink type of an already corroded item for treatment purposes or to identify items to be monitored for potential risks of deterioration in the future [3].

Systematic studies were performed for both, the identification of inks and pigments as well as for the evaluation of degradation processes on parchment of manuscripts. Raman measurements could be carried out in-situ with the ProRaman-L-Dual-G of EnwaveOptronics, USA, a fully integrated and portable instrument. The excitation source applied for this investigation was a Diode Laser at 785 nm (~350 mW) with a narrow line-width of 2.0 cm^{-1}. The instrument is based on a two dimensional CCD array detector which is temperature regulated (-60°C). The integrated microscope is equipped with a 1.3 Mpixel CMOS camera with In-Line LED illumination.

Mock-ups were prepared on calf parchment, following traditional methods of production using black-brown inks such as iron gall ink, sepia and carbon black as well as red inks such as minium (Pb_3O_4) and cinnabar (HgS). Raman spectra of these samples were acquired as reference and investigations have been carried out on Glagolitic, Greek and Latin manuscripts in the Austrian National Library in Vienna. In the Glagolitic manuscripts mainly lapis lazuli, malachite, vermillion and iron-gall inks could be identified whereas the spectrum of pigments was different in Greek and Latin miniature paintings, where mainly lead white, minium and also azurite could be identified.

Additionally, small samples of fresh parchments from different animal skins (sheep, goat, calf) were artificially aged under defined environmental conditions (temperature, humidity and UV-light). The deterioration of the parchment is a complex process depending on the environment, display and storage during the centuries. Collagen degradation processes are in general gelatinization and hydrolysis. Within Raman investigations, the ratio and difference of Amide I and Amide II bands can give a very clear overview of the degradation pathway [4]. Amide I Raman shift can be identified in the region between 1660–1670 cm^{-1} (C = O stretching vibration) whereas at around 1555 cm^{-1} the Amide II (bending vibration of the N-H bonds) can be detected. Gelatinization (**ΔE)** corresponds to an increase in the position of Amide I and Amide II bands; the value for the samples used in this study was considered to be around 112 cm^{-1} for new manufactured parchments. Hydrolysis (AI/AII) corresponds instead to peptide links breakdown to form amino acids. The AI/AII ratio is about 1.07 for new parchment used for this evaluation [5].

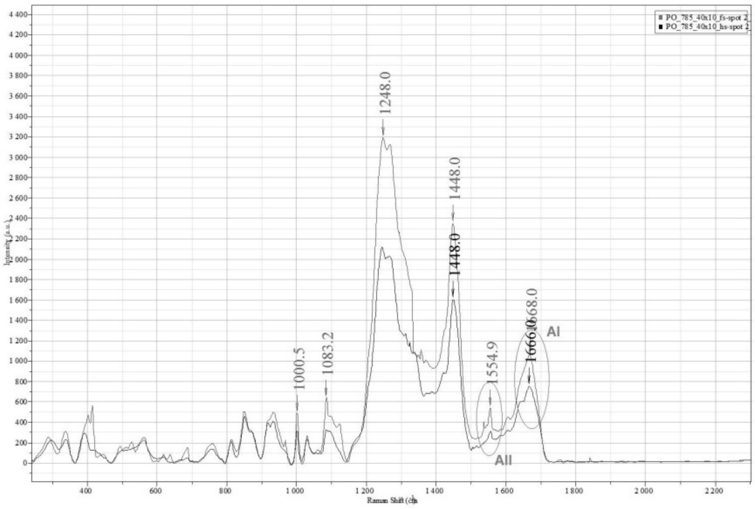

Figure 1. Raman spectra of parchment, flesh and hair sides. Amide I (AI) and Amide II (AII) bands are shown

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P8

Multimethod studies on document ageing: time-induced changes in composition of triarylmethane ballpoint ink dyes

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Keywords: Raman spectroscopy, chromatography, mass spectrometry, document authentication, ink writing age determination.

The determination of document origin and actual time of preparation is a complex task involving identification of writing materials and establishing the uniformity and age of writing. The questioning of provenience of both personal and official documents falls into the area of forensic science, from modified text to antedated contracts.

Ball point inks contain dyes and pigments as colorants, and solvents, resins, dispersants and various modifiers. Several analytical methods are used in identification of inks and the processes involved in their ageing on paper [1], including gas chromatography of residual solvents and chromatographic methods (TLC, HPLC) or capillary electrophoresis for identification of dyes [2,3]. All these methods combine separation and identification of dyes, but they require samples of questioned documents (destructive methods).

Spectroscopic analysis (UV-VIS, IR, RAMAN) of ballpoint dyes in documents is prefered because of non-destructive character, however, in complicated cases sample pretreatment and separation are required [4,5].

Crystal violet is a triarylmethane dye frequently used in ballpoint inks. It undergoes slow degradation due to contact with air and light, and the products of demethylation could be detected by various methods [6].

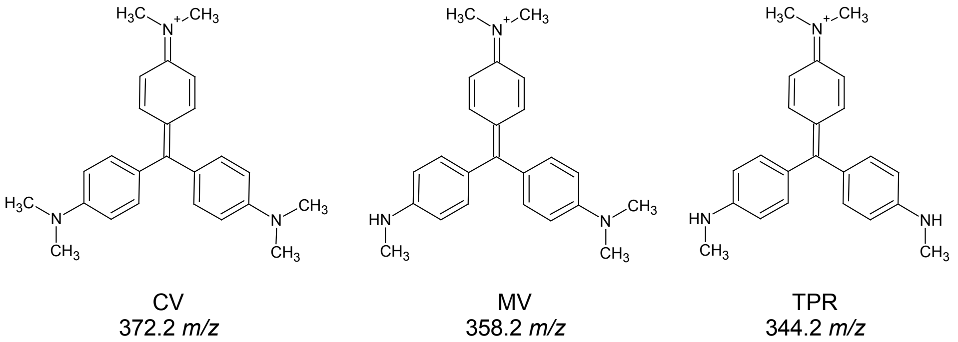

Figure 1. Components of blue writing ink: crystal violet (CV) and products of its degradation: methyl violet (MV) and tetramethyl pararosaniline (TPR). Masses of monovalent ions observed in MS spectra are indicated as *m/z* values.

We investigated a series of ballpoint ink writings using a multimethod approach. The writing samples obtained during a four-month storage in natural light or darkness were subjected to spectroscopic analysis (polymorphic scanner 2D VIS/NIR and Raman), as well as electrospray mass spectrometry (ESI-MS) and chromatographic separation (HPLC with UV-VIS detection), analyzing the degradation of crystal violet (*m/z* 372), to develop a scale of accelerated ageing for comparative writing analysis.

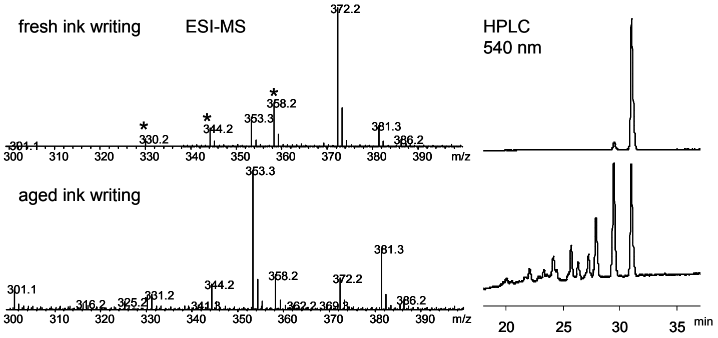

Figure 2. Mass spectra and HPLC-VIS chromatograms of samples of fresh (top panels) and aged (bottom panels) ballpoint ink writing samples.

The combination of spectral methods with separation and MS identification leads to reliable comparison of writings and allows analysis of influence of storage conditions on dye composition. The time-dependent deterioration of ballpoint inks based on crystal violet could be analyzed by mass spectrometry, the results obtained by MS are in agreement with changes in spectral properties of writing traces. Chromatographic separation of ink extracts reveals changes in composition of dyes with increased sensitivity due to low background in VIS range. The observed changes are more pronounced in MS and chromatography than in spectral analysis, partially because of pre-sample treatment nad separation. The development of accelerated ageing procedure could be based on combination of chromatographic and MS analysis, providing suitable time-scale to non-destructive Raman analysis.

Acknowledgements

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P9

Raman database of green pigments

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Keywords: green pigments, archaeometry, green earths

A comprehensive Raman study of green pigments is still missing in the literature. Raman spectra of green pigments of archaeological and art historical significance have been collected (in the range 80-3500 cm^{-1} for the 785 nm diode laser and 60-3700 cm^{-1} for the 532 nm Nd:YAG one) in order to establish a database. The spectra have been compared with existing literature, both archaeometrical and strictly mineralogical. All the studied pigments were purchased from Kremer Pigmente, Germany.

The studied materials can be divided in groups according to the cationspresent, which determine the green colour: mainly copper (two examples are given in Figure 1) and iron for the historically known green pigments; while copper, chromium and cobalt based pigments have been synthesized more recently[1].

It is important to point out that some of these materials might be degradation products of other copper based pigments (for example Cu oxalates) or copper containing works of art such as metal objects[2].

It has to be noted that the literature about green pigments and materials related to works of art is wide, yet not all of the spectra of copper containing pigments, such as salts of organic acids, chlorides, silicates, carbonates, phosphates and sulphates, are extensively discussed[1]–[3].In more recent times, copper based green pigments were synthesized belonging to the group of phtalocyanines, azo pigments and arsenites[1].

As regards different natural green earths, again, not many spectra are published. Iron based pigments are mainly silicates, such as the green earths glauconite and celadonite[4], [5]. These minerals are commonly found throughout Europe. Different reference materials (Bavaria, Bohemia, Cyprus, France, Northern Italy, Russia) have been collected to try to evaluate the feasibility of provenance studies.

On the other hand, geological publications exist for those materials of mineralogical importance.

The present research will provide the archaeometrist a useful guide, in terms of Raman spectra and literature, about identification of green pigments.

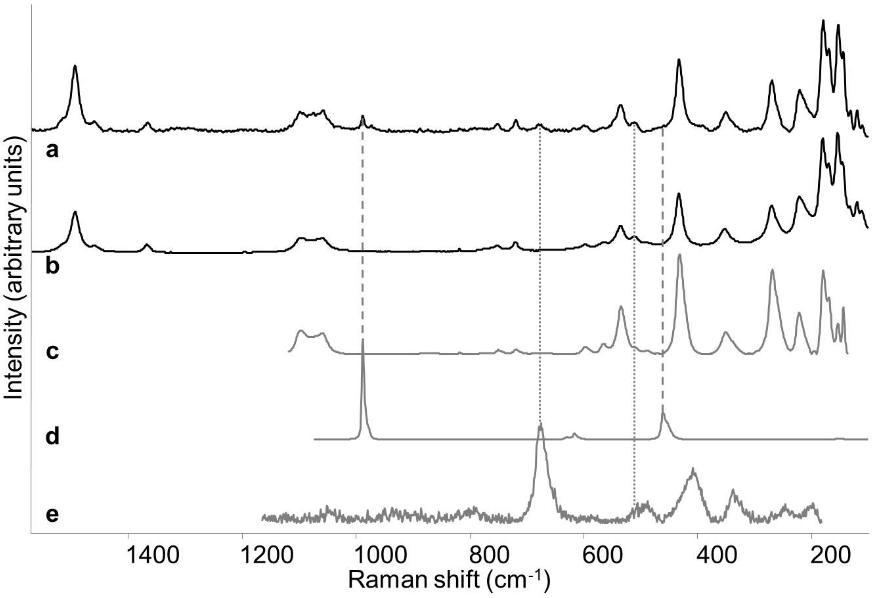

Figure 1. Raman spectra of Kremer pigments chrysocolla K1035 (a) and malachite K10310 (b) (532 nm laser). RRUFF reference spectra: (c) malachite (R050508),$Cu_2CO_3(OH)_2$, (d) baryte (R050335), $BaSO_4$, (e) chrysocolla (R050053), $(Cu_{2x}Al_x)H_{2x}Si_2O_5(OH)_4{\cdot}nH_2O$.

Acknowledgements

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P10

Raman spectroscopy of the works of Rafał Hadziewicz (1803-1886) from the collection of the National Museum in Kielce

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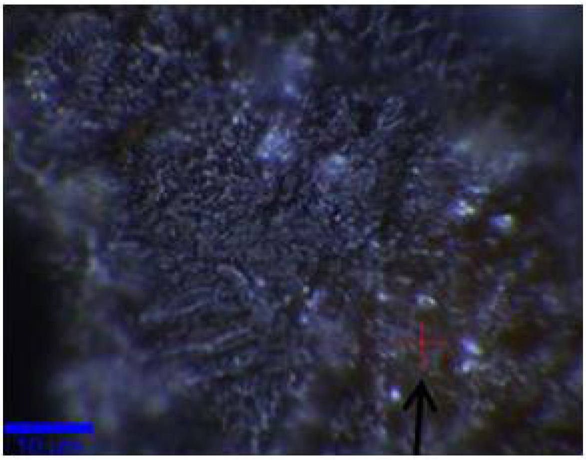
Keywords: authentication, painting analysis

Rafał Hadziewicz is a Polish 19th century painter. Graduate of the Fine Arts Faculty of the Warsaw University. After receiving a scholarship from the State Commission for Religious Confessions and Public education in 1829 he left for Dresden and later Paris where he studied at the École des Beaux-Arts under Antoine-Jean Gros. Then he studied and made drawings in the French Academy in the studio of Bertel Thorvaldsen. During his stay in Rome (until 1833) he studied the paintings of the old masters in museums, galleries and in studios of renowned Italian artists. In 1834 he arrived in Kraków, where he painted for churches. Five years later he went to Moscow. There he became a drawing professor at the Faculty of Mathematics of the Moscow University in the period from 1839 to 1844. In 1844 he moved to Warszawa and there (in the period 1846-1864) he taught as a professor at the School of Fine Arts. Towards the end of his life, in 1871 he moved to Kielce, where he died in 1886. He educated many eminent Polish artists. His works include altar and religious paintings as well as portraits. He also painted historical compositions, taking inspiration from Italian renaissance and baroque art. He was interested in ancient culture.

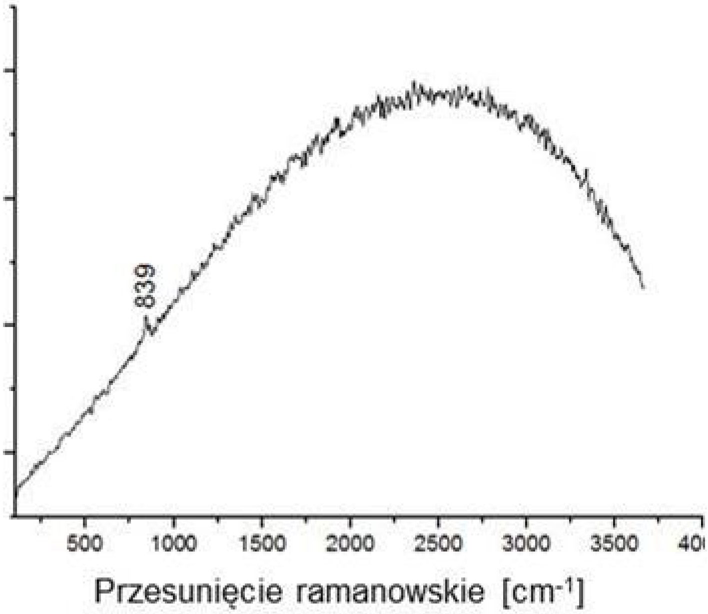
Monographic exhibition of the artist's *oeuvre* planned for the end of 2015 at the National Museum in Kielce was the inspiration to undertake studies on his palette. In the scope of preparations for the exhibition, in the period from 2010 to 2014, 10 paintings of the artist from the collection of the National Museum in Kielce were subject to "false colour", ultraviolet and infrared tests. Samples were also taken for specialist tests. Samples were used to prepare a cross-section which was subjected to SEM-EDS and ATR-FTIR tests. If any of the analysis gave ambiguous results micro-Raman tests were used for clarification. They were used mainly for research of cross-sections, but also for powders. The registration of Raman spectrums were recorded using WITec Alpha 300 microspectrometer with a CCD camera and a laser with excitation of 532.8nm. All spectres were analysed in order to identify pigments present in the painting layers. The most significant pigments identified by Raman were: prussian blue, ultramarine, chrome green and yellow, massicot, mars red, brown ochre, charcoal, barium sulfate, chalk, gypsum, verdigris and probably copper blue.

Mutually complementary analysis of the artist's work allowed characterising the painter's palette.

P10



The sample No. 11 from the picture *Maria wstępująca do świątyni.*



Raman spectrum

P11

A comparison of pigments applied in two gothic wall paintings in Slovenia using Raman microspectroscopy

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Keywords:wall paintings, pigments, gothic, gilding, Raman microspectroscopy

The present study deals with the identification of pigments in order to identify differences in the technology used for two gothic wall paintings from the former 13th century[1] Minorite church of St. Francis of Assisi (Koper, Slovenia). During the building's research in 2007 prior to the renovation (2012-2014) an important find was made. In a deep walled-in niche of the former sedilia in the choir two layers of gothic wall paintings were discovered.

The lower, older layer dates to the 14th century and was damaged by chiselling and hammering in preparing the surface for the new layer of render. The main figure is the Madonna Enthroned with the Child, flanked by two saints. On the sidewall of the niche two additional saints and a medallion with the Lamb of God are still preserved. The idealised rendering of faces, almond-shaped eyes, green underpainting, soft drapery folds, and colour modelling speak of strong Italian Trecento influences, characteristic of the Slovenian coast. The second layer dates to the 15th century and was applied to a thin render that was, at its discovery, already partially detached from the surface. The scene of the death of St. Francis, accompanied with friars and nuns, is set in a church interior, depicted in perspective. The composition and formal elements speak with the new renaissance spirit.

The younger wall painting was detached, restored, and returned to the opposite side of the presbytery in a special construction, mirroring the original niche, while the older wall painting was conserved and preserved in situ.

Samples of paint layers were analysed using Raman microspectroscopy, supported with SEM-EDS analysis, to identify pigments and painting techniques.

Results revealed that the older mural was painted mainly in *a fresco,* with final elements in *a secco,* which is a typical technique for Italian Trecento mural painting. On the other hand, the younger one was executed mainly in *a secco*technique, often applied in Northern Europe, especially in the Alpine region.[2] On the older wall painting mostly a single paint layer was discovered, while on the younger up to three layers were identified, which is due to *a secco* technique.

On both wall paintings pre-drawings were made with carbon black; on the older one also red ochre was used. The differences between the two paintings are especially observed in pigments applied. Azurite on the background, carbon black, red and yellow ochre, lime white, and green earth are characteristic for the older one.

The pigment palette used for the younger wall painting is much broader. Besides the already mentioned pigments, applications of not only expensive pigments, such as cinnabar, azurite and malachite, but also of rare ones, such as orange yellow vanadinite, were identified. Furthermore, lead pigments such as lead white, red lead, and lead tin yellow type I were also determined. As in the older painting, azurite was applied *a secco* for the background area, while the architectural and other elements were painted with the rest of the identified pigments.

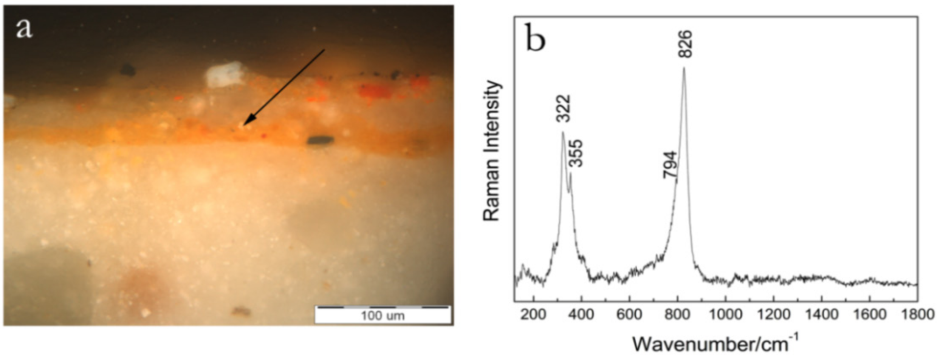

Figure 1. Yelloworangepaintlayerwithvanadinite. (a) Opticalmicroscopy, reflectivelight. (b) Ramanspectrumofvanadinite (laser 785 nm).

For both layers the gilding technique with the application of gold leaf was used for the haloes of the saints, which is however quite rarely found in gothic wall paintings from Slovenia. For the older wall painting gold leaf was applied on a layer of red ochre (bole), while for the younger on a layer of lead pigments(mixtion) that was a common gilding technique in Italy between the 14th and 16th centuries[3].

The comparison of materials and painting techniques of both murals confirms the art-historical identification, that the older one shows a strong influence of the Italian Trecento, while the younger one is closer to North-European tradition with *a secco* painting technique and the selection of pigments. It is an important addition to the knowledge of Slovenian mediaeval mural painting, which is stylistically and technically situated on the crossroads between Italian and North-European artistic currents.

Acknowledgements

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P12

Potentialities and Limitations of Raman spectroscopy in the analysis of iron gall inks

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Keywords: Raman, iron gall ink

Since early Middle Ages iron gall ink belongs to common writing materials in the production of manuscripts. Our research focuses on the questions of material composition, provenance and attribution of iron gall inks. Since 2006 Raman spectroscopy has become a routine technique for iron gall ink identification [1]. In this work we probed Raman and FTIR-ATR spectroscopy for characterization and differentiation of self-made iron gall inks resulting from the reaction between ferrous sulfate and tannins from oak gallnut. Our study set consisted of a series of iron gall inks that differed in their composition with respect to: a) metal sulfates that were added in different proportions to imitate natural vitriol; b) vinegar and c) red wine that were added in accordance with historic recipes. It is noteworthy, that though addition of red wine influenced the viscosity of the inks, their properties such as the colour, writing quality and ageing effects were found to be identical.

We conducted the Raman measurements with a modified Raman inVia Spectrometer (Renishaw) with spectral resolution of 2 cm^{-1} using a laser line of 785 nm and 50x lens. The infrared spectra were collected with ExoScan 4100, a handheld spectrometer (Agilent) using an ATR sampling interface that results in the spectral resolution of 4 cm^{-1}.

Figure 1 shows three Raman spectra of the inks that differ only in their organic solvents. We observe three identical spectra whose pattern matches that of the inks based on Aleppo gallnuts from the ref. [2]. On the other hand, the peak positions of the characteristic bands in the fingerprint region at: 1579 cm^{-1} v(C=C) ring; 1475 cm^{-1} scissor (CH2), v(C=C) ring, v(C-H); 1426 cm^{-1} symmetric v(COO-), v(C-H), v(O-H); 1327 cm^{-1} v(C-O) (carboxylic); 1233 cm^{-1} v(C-H), v ring, v(C-O) (ester); 1094 cm^{-1} v(C-O) (alcoholic) and 960 cm^{-1} w(CH2) only roughly coincide with the assignments given in [2].
The ink complex seems to dominate the spectrum so that no contributions from the red wine (ink 51) or acetic acid (ink 46) could be detected. Curiously enough, also the non-reacting metal sulfates could not be detected by Raman or IR-spectroscopy.

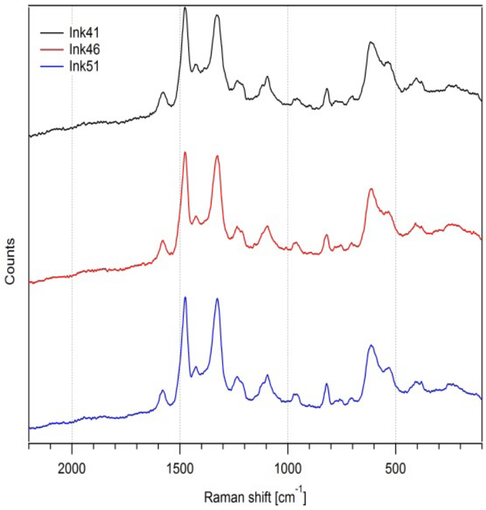

Figure 1: Raman spectra from iron gall inks with different additives

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P13

Micro-Raman and other spectral studies on dinosaur fossils

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Keywords: dinosaurs, Raman identification, elemental and chemical group mappings

Dinosaurs had been once living beasts which played very distinguished role inside whole animal world before they became extinct 65 Ma ago. Paleontologists find recently many remains joined to dinosaurs. The fragments of bones and teeth prevail in the material due to much greater resistivity of hard tissues in comparison with soft tissues. However, it is strong controversy whether the hard tissues are more or less original apatite sample or not the geological cast. The significant diagenesis changes were noticed in discovered material[1]. Still another problem is preservation of soft tissues. Some announcements inform that such matter was found in special conditions[2,3].

Figure 1. Fragment of the bone under scrutiny. It is a top part of 6.5 kg weight, cut off from the whole preserved bone of weight of 820 kg.

Our sample is the fragment of hip of unidentified dinosaur, most probably sauropod, found in Jurassic Morrison Formation, Colarado and Utah states. It is dated on Upper Jurassic, but not later than 147 Ma. The formation is famous of the dinosaur discoveries which occurs even contemporarely[4]. The whole fossil involves the fragments which can be initially described as the fossilized remains or casts of the bone, muscles, fat and skin. The aim of the paper was the determination of different phases and potential coupling them to the anatomical parts mentioned and looking for potential organic material preserved. We cut off some strips of the sample and they were one-sided polished with corundum and diament polishing wheels. The samples after such a preparation were examined with v|tome|xmX-ray tomographmanufactured by General Electric, Energy Dispersive X-Ray Probe coupled with Field Emission Scanning Electron MicroscopeMIRA produced by Tescan, X-ray diffractometerEmpyrean produced byPANalyticaland Dispersive Raman MicroscopeInVia manufactured by Renishaw with exciting laser785 nm.

Hydroxy- and fluorapatite, calcite and fractions of silica were detected among studied mineral phases. Perhaps the most interesting discovery was the detection of remains of organic matter in bone fractions of the sample. It was done due to Raman spectra (Fig.2).

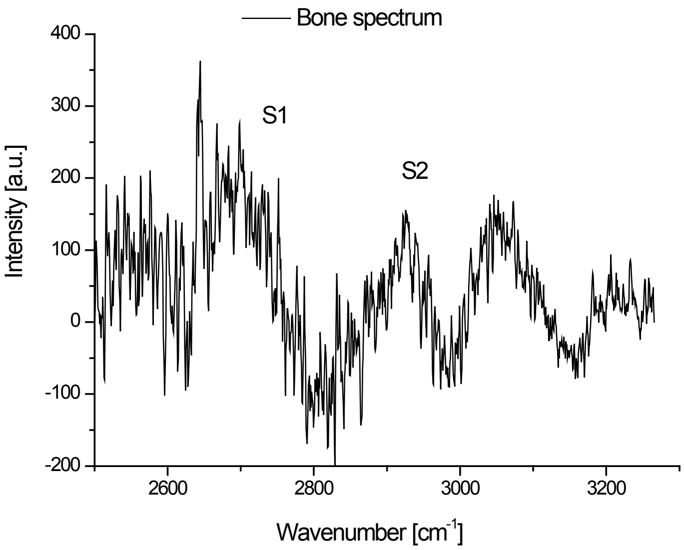

Figure 2. S1 and S2 modes according to Beyssac et al.[5]in a fragment of Raman spectrum of bone material.

The sample is still studied to determine the strict distribution of remains of organic matter.

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P14

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

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Keywords: Mobile Raman spectroscopy, mapping system

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

Until now, Raman mappings are only performed in laboratory experiments: by using an XY stage the investigated object is moved step by step under the microscope attached to the spectrometer [6]–[8] for example, obtaining information on the samples' layering structure is necessary. This paper reports on the development of a Raman mapping approach based on a set of scanning mirrors that direct the laser beam in two spatial directions, vertically through the microscope head or through a horizontal exit on the Raman microspectrometer. The first configuration still has limitations in terms of the size of the work of art that can be analyzed, as it has to fit under the microscope objective, but considerably larger objects can be studied when using the scanning mirrors placed in the horizontal exit. In this paper, the advantages and limitations of these two Raman mapping approaches are compared and discussed on the basis of an example of a contemporary oil painting on canvas. . The main limitation of this approach is the restriction of the sample size: the object has to fit under the microscope and should be sufficiently flat, even if an autofocus system is present [6]. In this project, we want to implement this approach outside the laboratory and use it in the field.

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

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

Not only is the set-up of the instrumentation of great importance, data quality and data treatment are important aspects. Model painting sare analysed to test whether good spectra can be obtained with (very) short measuring times, combined with multivariate analysis.

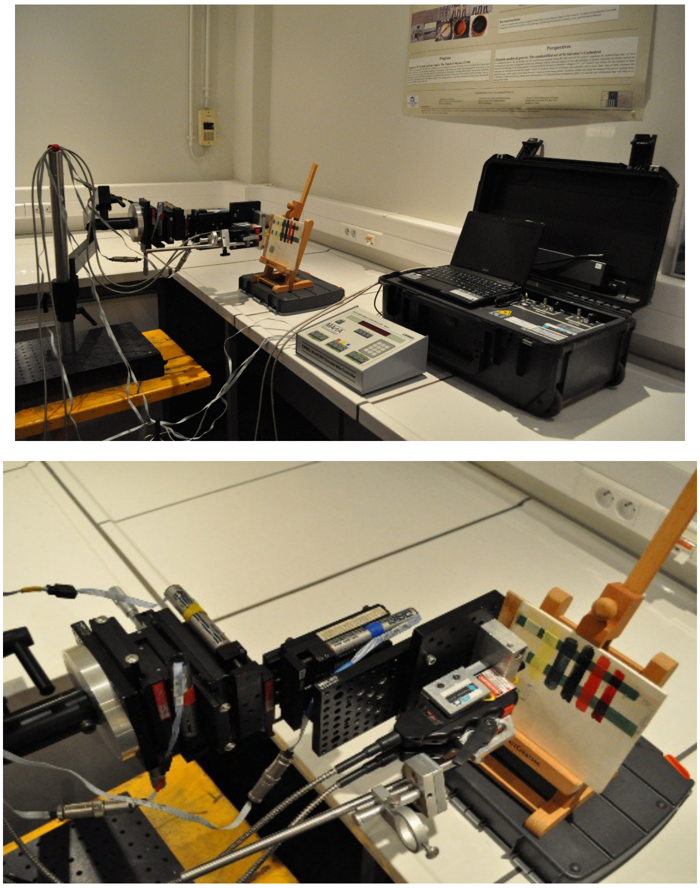

Figure 1. Preliminary result of the in-situ set-up, developed in-house

Conclusion

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

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P15

Wrocław-Partynice amber depots - the application of the comprehensive spectral database of succinite and fossil and subfossil resins

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Keywords: multispectral database, provenance of amber,

The success of provenance investigation of amber is determined by the adequate choice of the method and the usage of the reference spectra database. Raman spectroscopy is widely recognized as an effective technique used in the provenance investigation of the amber[1], which allowed us to perform *in situ* measurements without any preparation of the sample. Unfortunately, more that often the archeological amber objects are covered by the weathered layer which becomes the origin of the strong fluorescence obscuring Raman spectra. In many cases this outer layer cannot be removed without the damage to the object. It appeared that the implementation of supplementary techniques is necessary in order to determine the provenance of such amber objects. The applicability of the annihilation spectroscopy (PAS) in the analysis of the raw material was proved during investigations of the amber objects discovered in the archaeological excavations in Domasław (Poland)[2]. Moreover, in the identification of amber other methods are also used: transmission infrared spectroscopy and ATR, but they require preparation of samples. In the cases when the surfaces of amber objects are weathered and the preparation of the sample is possible, the information about the provenance might be delivered by SEM-EDS analysis.

The second important condition of the successful investigation is the access to the adequate database. The Cultural Heritage Research Laboratory at the Faculty of Chemistry, Wrocław University developed the Raman spectra database of amber and copal which was successfully applied in the provenance study of archaeological amber objects discovered in Poland [3,4]. The developed comparative spectral database is based on reference spectra of fully documented samples of succinite, fossil resins, subfossil resins and imitations from the comprehensive collection of The Museum of the Earth's Amber Department, Warsaw, started in 1951. The database is systematically developed and recently was extended to incorporate ATR, annihilation positronium reference spectra and also SEM-EDS data of amber and copal.

The aplicability of this comprehensive scientific database was verified during provenance investigation of enormous amber deposits discovered in 1906 and 1936, nearby the horse racing track in Wroclaw-Partynice (Ger. Breslau-Hartlieb)[5]. The total weight of the raw material accumulated in them amounted from 1240 to 1760 kg, according to various estimates, which so far is the biggest find of this type in the world[6]. Many archaeological studies conducted in that area[7] showed the relationship of these findings with an extensive settlement of the population of the Przeworsk culture and perhaps the La Tène one, which functioned in the first century BC. The analysis of the findings indicates that they had character of storage pits[8], not „treasures" as they were often determined. Moreover, the findings of pieces of raw material and semi-finished products of amber in the settlement suggest that its inhabitants practiced both the amber trade and its processing. The discovery of the amber commercial and craft center in Partynice plays important role in history in Silesian archaeology and is still the most convincing evidence concerning the course of the Amber Road and the role that the Wrocław area played on it.

As a method of choice, the FT-Raman spectroscopy, PAS and SEM-EDS were implemented in the investigations. Due to the huge number of the objects varying in colour, the analyses were carried out after the selection of the reference samples. The data obtained as a result of the analysis of chosen reference amber objects were compared with the reference data from the Laboratory database. It is highly probable that the archaeological amber originated from tertiary deposits of Baltic amber (succinite) but due to the localisation of the finds, other possible amber deposits have also to be considered, from Moravia (valchovite and/or neudorfite) and from Germany. The comprehensive results completed during the comparative analysis indicate the Baltic origin of the investigated amber objects. However, due to the enormous number of discovered objects and the fact that some part of the finds nowadays is inaccessible, we cannot exclude the possibility that not only succinate formerd in the Wrocław-Partynice depots.

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P16

Micro-Raman study of the carbonationdepth of a lime paste produced by a traditional technology

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Keywords: lime mortar, carbonation depth, $CaCO_3$ polymorphs, micro-Raman

Lime is an important material forrestoration and conservation of cultural heritage. It has been produced and used by mankind over centuries as a binder in mortars for brickwork, stonework, rendering and plastering[1]. Historically, lime was used in different forms such as quicklime, hydrated powder and/or putty, and its quality varied according to local geology and composition of raw materials, and production technology. Unlike many products obtained from modern plants, the use of traditional technologies can ensure a better compatibility with historic lime based materials [2]. A similar composition of lime to historic binders can be achieved by using limestone from local quarries.

A key factor affecting the properties of lime-based materials is the rate of carbonation. Carbonation is the reaction between atmospheric CO_2 and $Ca(OH)_2$ in an aqueous medium, resulting in the formation of $CaCO_3$[3].It is an exothermic process mainly controlled by two mechanisms: the diffusion of the atmospheric CO_2 gas into the pore structure of the mortar, and the chemical reaction between the dissolved CO_2 and $Ca(OH)_2$. Calcium carbonate can occur as three anhydrous crystalline polymorphs (calcite, aragonite, vaterite), two hydrated crystal forms (calcium carbonate hexahydrate (ikaite) and calcium carbonate monohydrate) and as amorphous $CaCO_3$ [4, 5].

In this work the study of the carbonation depth was performed using micro-Raman spectroscopy on cross sections of lime samples produced in a traditional kiln[6]. The carbonation was studied on the samples of a hydrated lime paste aged for various times in a climatic chamber. The samples were impregnated with cyclododecane prior to cutting them into sections. Raman spectra were collected in the spectral range 1400 – 50 cm^{-1}, with the laser beam (wavelength 532 nm) focused with 20x objective (N.A. 0.40).The spectra were collected as matrices of 57x10 points with the steps of 500 μm, covering a depth of 28.5 mm from the sample surface. Micro-Raman spectroscopy allows to draw maps showing the presence of different $CaCO_3$ polymorphs as well as the ratio between $CaCO_3$ and $Ca(OH)_2$ in the sample. This method proved to be more reliable and accurate with respect to the phenolphthalein indicator. The detailed reconstruction of the carbonation profile with a micrometric resolution in conjunction with built-in optical microscopy is a useful tool for the study of microstructural and mineralogical aspects affecting the hardening process of lime-based materials.

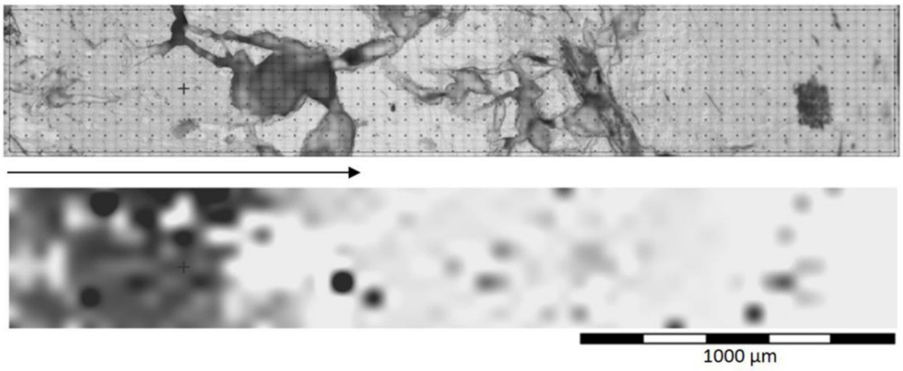

Figure 1. The area of the sample with the matrix of measured points (top) on the surface of cross section and the map of intensities of $CaCO_3$ (bottom), where the black colour corresponds to the regions with the highest concentration of $CaCO_3$. Carbonation develops at the sample surface (the left end of the picture).

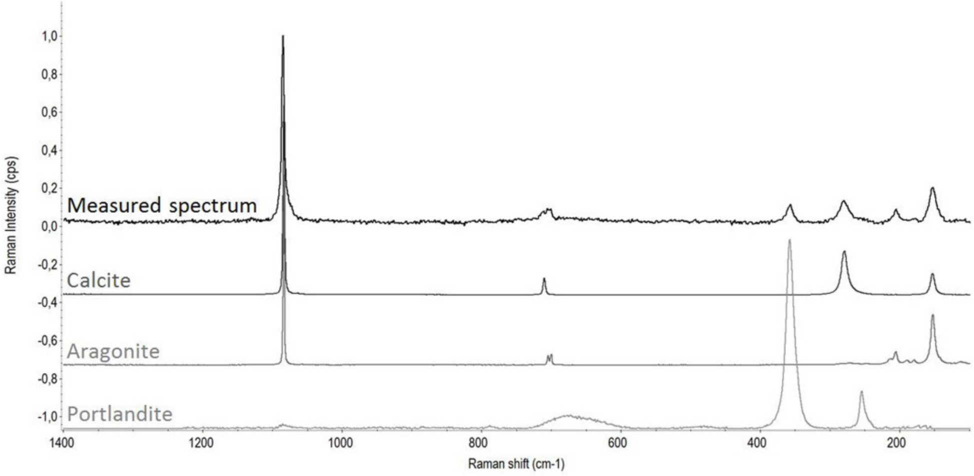

Figure 2. Aselected spectrum (top) in comparison with the spectra of pure phases. In this spectrum there is evident the presence of the $CaCO_3$ polymophs (calcite and aragonite) and $Ca(OH)_2$(portlandite).

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P17

Comparison of semi-quantification experimental methodologies using micro-Raman spectroscopy: PALME software as an alternative tool for the study of salts efflorescence

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Keywords: Raman spectroscopy; soluble salts; quantitative analysis

As demonstrated in the bibliography, the most widespread method used for semi-quantification with Raman spectroscopy is based on the so-called external calibration curves, especially after the work of Giles et al. demonstrating how it is possible to obtain linearity in the spectral response as a function of the concentration [1]. Normally this method takes time for the preparation of pellets composed both by mixtures of standard and or by real samples. Moreover, it is also necessary to evaluate the integration area of the selected Raman band assigned to a given compound and/or the height of those bands for each Raman spectrum collected.

Recently, the PALME software (Programme d'AnaLyse de spectres de Melange), developed at MONARIS (UPMC, Paris), has been developed in order to obtain the same quantitative information from the vibrational spectrum using a multivariate linear regression approach. It considers a mixture spectrum as a linear combination of the suspected pure materials spectra and in the field of Cultural Heritage studies it has been applied to various contexts: Raman quantification of dyes in textiles [2] ; extract quantitative parameters from Raman hyperspectral maps for iron corrosion products [3] as well as to detect and quantify mixtures in model historical varnishes (colophony/linseed oil) using non-invasive techniques like FT-Raman and IR analyses using ATR and non-invasive reflectance modes [4].

The aim this work is to use experimental methods, both, external calibration and PALME quantification, on real samples in order to compare the results obtained and verify which method can be considered the more reliable. Both methodologies have been tested on efflorescence salts sampled in the San Esteban church (Ribera de Valderejo, Basque Country, Spain). In this church the crystallization of salts is causing serious damages that compromise even the stability of the structural walls. The study of the degradation process and the identification of the causes is a fundamental step in order to limit further damages and preserve artworks belonging to the cultural heritage.

In the first part of the work micro-Raman spectroscopy was carried out in order to identify the compounds present in the collected samples. Raman spectra showed the presence of calcium carbonate ($CaCO_3$), calcium sulfate as gypsum ($CaSO_4.2H_2O$) and potassium nitrate (KNO_3) as the main compounds in the efflorescence samples.

To perform the quantification of each compound in the samples by using the first quantification method, pellets composed by mixtures of the three pure (standards) salts at different concentrations were prepared. Several calibration curves have been constructed considering either the areas or the height of the main Raman band for each salt. Accordingly pellets of the real samples were prepared and analyzed by Raman, referring the area or the height to the respective calibration curve for quantification of each compound.

For the second quantification method, the PALME software was used directly on the Raman spectrum of the different real efflorescence samples to quantify each compound through a fitting by a linear combination their main Raman spectra for 700 to 1400 cm^{-1}.

The results obtained from both quantification methodologies were comparable in statistical terms (95% confidence interval of the concentration values for each compound), revealing that both, the external calibration and the PALME software methods, are reliable and repeatable.

As the PALME procedure does not require any prior preparation and can be directly applied on the Raman spectra of the known samples (PALME requires the knowledge of which are the compounds present in the sample and their reference spectra as pure products) with unknown concentrations, we can propose the use of such software as a viable alternative to the external calibration curve procedures as it allows to obtain comparable quantitative information in a very short space of time. Moreover, it can be implemented not only in the laboratory but also in the computer controlling the portable Raman spectrometer, to perform quantitative estimations of compounds in real time during field analysis campaigns.

Acknowledgements

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P18

The role marine aerosol in the formation of sulphate and double sulphate nitrate salts in gypsum based materials of plasters from the inner areas of the Igueldo Lighthouse (San Sebastian, Basque Country, north of Spain)

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Keywords: Gypsum plaster, humberstonite, marine aerosol, sulphates, nitrates, Raman Imaging

Salt crystallizations in the interior of the pores or on the surface of building materials are one of the principal pathologies of many historical buildings. During decades the use of gypsum plasters in many constructions has been very common. The poorly crystallized gypsum can loses its hydration waters faster than a well crystallized one. Sometimes, solutions containing NaCl, $MgCl_2$, $CaCl_2$ can dehydrate gypsum as a result of their lower water vapour pressure, promoting the change of gypsum solubility [1].

Building materials from the inside of Igueldo Lighthouse (San Sebastian, Basque Country, north of Spain) show different kind of pathologies, which were evaluated in a previous works [2,3]. In some areas, the tiles covering some walls are being detached due to the formation of new salts in the gypsum plaster placed under the tiles which weaken its role as a joint mortar. After a preliminary characterization of the gypsum plaster [3], in the present work, an in-depth study was carried out in order to characterize the nature of these salts and to propose a degradation mechanism leading to their formation. For that purpose, micro Raman spectroscopy (point-by-point and imaging) was applied. This technique was useful to identify the presence of the two dehydrated forms of the original gypsum from the plaster: bassanite ($CaSO_4·½H_2O$) and anhydrite ($CaSO_4$).

Regarding the new salts crystallized in the plaster, it was possible to obtain additional Raman spectra showing bands at 1067, 1048 and 1013 cm^{-1}, that correspond to the Raman features of the double sulphate-nitrate salt humberstonite ($K_3Na_7Mg_2(SO_4)_6(NO_3)_2·6H_2O$). Further X-Ray Diffraction (XRD) and Attenuated Total Reflectance Infrared (ATR-FTIR) analyses confirmed the presence of the salt humberstonite. This double salt can be formed as a consequence of the reaction between dissolved sulphates coming from the plaster (gypsum, bassanite and anhydrite are partially soluble) and sodium, potassium, magnesium and nitrate coming from the marine aerosol [4]. The presence of nitrate salts in the inner areas of the lighthouse was also proven in the previous works on this construction [2,3], assigning the band at 1067 cm^{-1} to sodium nitrate and that at 1048 cm^{-1} to potassium nitrate. The wavenumber at the maximum for both nitrates coincided with two bands of humberstonite, but the Full Width at Half-Maximum (FWHM) do not coincide, being greater those of humberstonite as it can be seen in Figure 1C, in comparison with Figure 6 of ref. [3].

Apart from humberstonite, glauberite ($CaNa_2(SO_4)_2$, main band at 1001 cm^{-1}), syngenite ($K_2Ca(SO_4)_2{\cdot}H_2O$, main bands at 981 and 1006 cm^{-1}) and polyhalite ($K_2Ca_2Mg(SO_4)_4{\cdot}2H_2O$, main bands at 989 and 1016 cm^{-1}) were also identified by means of Raman spectroscopy. The presence of these salts was also corroborated by means of XRD, ATR-FTIR and SEM-EDS. Therefore, the combined use in this work of Raman spectroscopy, together with XRD, ATR-IR and SEM-EDS was proven to be an adequate analytical methodology to avoid inaccurate assignments that can be done using only Raman spectroscopy, especially regarding the variety of salts that could be formed in such plaster bodies and environmental conditions.

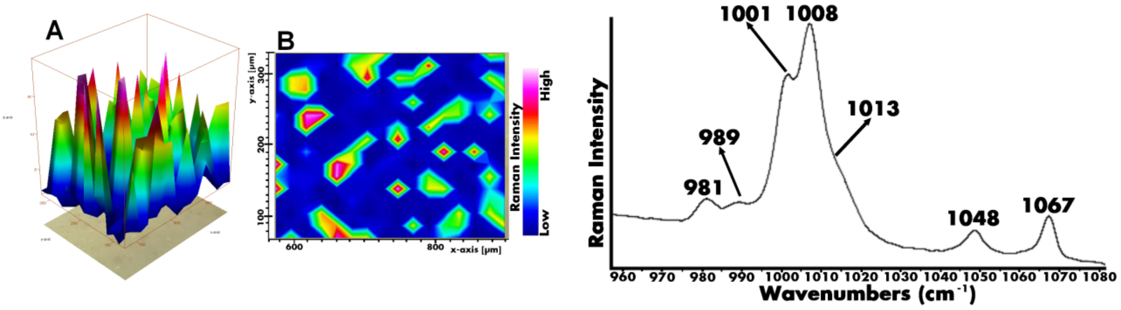

Figure 1. (A and B) Raman distribution of humberstonite in the gypsum plaster (C) Raman spectrum showing the presence of humberstonite, gypsum , glauberite, polyhalite and syngenite crystallizations in the gypsum plaster from the interior areas of Igueldo Lighthouse.

Using XRD and SEM-EDX three chloride salts were also identified in the samples from gypsum plaster. Therefore, the input of sodium and magnesium, also present in the new crystals, can come from the chlorides carried in the marine aerosol (e.g. NaCl, $MgCl_2$, KCl, etc.) [1]. Considering all the new mineral phases identified, a complete reaction scheme was proposed. In this scheme, anhydrite is the precursor of the new crystalline phases. The dehydrated calcium sulphate, in continuous contact with marine environment and other surrounding sources can experiment different reactions giving rise to new sulphates and double sulphate nitrate salts.

Acknowledgements

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P19

Portable Raman and Raman imaging usefulness in emergency analyses to detect decaying on building materials from Punta Begoña Galleries (Getxo, North of Spain)

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Keywords: Raman imagining, mortars, concrete, sulphates, black crusts

Punta Begoña Galleries were built in 1918 in Getxo (Basque Country, North of Spain) as a retaining wall of a hillside where it was located the mansion of Horacio Echevarrieta, an important tycoon of that time. Although, he was the head of one of the most important families of the 20th century aristocracy of the area, the Galleries were abandoned in the fifties and nowadays the building belongs to the town of Getxo, being their conservation state very poor. To recover its historical memory, a multidisciplinary research team including chemists, geologist, architects, archaeologists, historians, etc. researchers of the University of the Basque Country and technicians of the City Council of Getxo are working together. This work summarizes some of the results related to the characterization of the original materials and the identification of the decayed products as part of the emergency analysis to detect in short time the decaying of the building.

In the development of these tasks, Raman spectroscopy played an important role, because its portable versions allowed us performing the evaluation of these materials composition. Moreover, the obtained results are the key for the selection of the most appropriate sampling points, minimizing the deterioration generated during the sampling.

Two portable Raman spectrometers (innoRam model, $B_{\&}WTEK_{INC}$, Newark, EEUU) equipped with 785 nm and 532 nm lasers respectively were used. In the laboratory, a RA100 spectrometer and a confocal inVia Raman microscope (Renishaw, Gloucestershire, UK) were used, respectively. With the confocal microscope, apart from point-by-Raman analyses, Raman imaging was also performed.

In the outer areas of the Galleries, stones, different mortars (joint, rendering and decorative) and the cement from the cornice of the building were analyzed. The coincident composition of these materials was calcite ($CaCO_3$), quartz (SiO_2), different kind of aluminosilicates and hematite (Fe_2O_3). With respect to the degradation products, gypsum ($CaSO_4{\cdot}2H_2O$) and amorphous carbon were identified as the main constituents of the black crusts that cover these materials. The formation of sulphates and carbon can come from the impact of atmospheric SO_2, road traffic/industry emissions respectively. Biological patinas were also identified, in which scytonemin and other biogenic pigments were characterized.

In the cements from the cornice, nitratine ($NaNO_3$) was determined, probably formed due to the reaction of sodium carbonates from the cement and the oxidized NO_x coming from the polluted atmosphere and/or with the NH_4NO_3 input coming from rinsing waters from the upper garden. The principal problem of all these mortars is the formation of efflorescences including gypsum, but mainly thenardite (Na_2SO_4)-mirabilite ($Na_2SO_4{\cdot}10H_2O$), which caused their detachment when the cements lost their binding capacity.

In the inner areas of the Galleries, decorative and rendering mortars from the wall and those covering the reinforced concretes from the ceilings were characterized (see Figure 1 A and B). The main components of wall mortars were calcite and gypsum. In some cases, alite (Ca_3SiO_5) and belite (Ca_2SiO_4) were identified. These components are characteristic of Portland Cement clinker that could have remained unreacted in the hydration process of it. In these mortars, apart from nitratine, other nitrates such as niter (KNO_3) and/or nitrocalcite ($Ca(NO_3)\cdot 4H_2O$) were also distinguised. The main components of the mortar that covers the concrete and the one that acts as the binder of the concrete itself were calcite, quartz, aragonite ($CaCO_3$) and gypsum. The aragonite identification confirms the use of beach sand as an aggregate, shell fragments can even be observed in the mortar. The concrete from the ceiling of the lower Gallery is covered with three different mortar layers (see Figure 1 C). The outermost layer (calcite, quartz and gypsum) is covered with a black crust (gypsum, calcite and amorphous carbon). In the inner layers calcite and aragonite were identified. In the case of the layer in contact with the reinforcement, the presence of calcite is lower, but a high presence and distribution of silicates was observed thanks to Raman imagining. In the outermost layers, dolomite ($[Ca(Mg(CO_3)_2]$) was also identify. Attending to gypsum distribution, it is observed that it is principally present in the outermost layer, but it is also present in the next one in a lower extend (see Figure 1 D). Regarding the aggregate used in the outermost layer, it belongs to calcite. As in the mortars from the outer areas of the Galleries, in the inner areas, thenardite and gypsum were identified on the efflorescences over mortars. In this case, apart from these salts, calcite and natron ($NaCO_3\cdot 10H_2O$) were also identified by Raman spectroscopy. The presence of these efflorescences is also causing the detachment of the mortars, leading to the loss of the steel reinforcement alkaline protection against oxidation processes. Chlorides from marine aerosol can also accelerate this oxidation process. In the steel reinforcement samples using Raman spectroscopy, it was possible to identify the presence of different iron oxides [hematite and lepidocrocite, (α- Fe(O) OH)] due to the oxidation process they are suffering. In addition, calcite stalactites are formed in the ceiling of the lower Gallery due to the dissolution of original calcite (and/or gypsum) coming from the mortars.

Figure 1. (A) A detail of the ceiling from the Punta Begoña inner areas where the concrete sample (B) was taken, (C) A cross section of the three mortar layers (L2, L3 and L4) over the concrete and the black crust formed over mortar layer L2, (D) Distribution of gypsum throughout the cross section of the three mortar layers over the concrete obtained using Raman imaging.

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P20

Analysis of the Raman spectra of various inks on the documents from the court cases

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Keywords: Raman spectroscopy, forensic science, spectra of inks, spectrum of paper

Raman spectroscopy is becoming a useful tool of major importance in forensic science and in related aspects. This is a non-destructive and non-invasive analytical method, where the samples can be examined without previous preparation.

We have obtained and analyzed 64 Raman spectra of documents from the court cases and herein report the selected data. The samples of documents printed in black, blue, green and red inks and toners have been examined. The dispersive Raman microscope with 633 nm wavelength laser was used for analysis of the blue and green colours. FT-Raman spectrometer with a germanium detector cooled by liquid nitrogen and 1064 nm Nd:YAG laser was used for black and red inks. The comparison included printouts of two inkjets and two laser printers. All investigated samples of the documents were measured in standard conditions and used as the reference spectra. Afterwards, the printouts were kept under different conditions, for instance in the darkness, in the place with a high humidity or they were irradiated with UV light, and then compared with the reference spectrum of the examined colour.

The spectra of documents printed in the same colour and on the same type of printers have reveled some changes depending on the applied external conditions. The most significant differences have been noticed in the cases when the samples were kept under high humidity conditions.

P21

Red organic dyestuff analyses of the Jan Matejko (1839-1893) preserved historical paints from tubes by means of HPLC-DAD-MS broadened by XRF and SEM-EDX techniques

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Keywords: organic dyestuff, extraction, paints, liquid chromatography mass spectrometry

Analysis of natural dyes in historical objects is important for the development of effective and appropriate conservation strategies and to determine the origin of the artifacts. It provides historical information necessary for the documentation of the artwork and sometimes is decisive in establishing the work's authenticity. Identification of a particular dye is usually based on the presence of its main components, while minor components are important for differentiating between dyes originating from closely related sources [1]. Examination of the dyestuff components was for many years generally unfeasible as the size of sample required to solubilize the contained dyestuffs prior spectroscopic or chromatographic analysis was unacceptably large. Determination of the dyes extracted from paint samples became possible as these methods became more sophisticated and the sample size could be reduced, following methods similar to those already used for textile dyestuff samples [2]. Hyphenated techniques (high performance separation techniques coupled to extremely sensitive and selective spectrometric detectors) seem to be the most efficient tools for the analysis of very small samples of materials of complex matrices [3]. Among them, reversed phase liquid chromatography with electrospray mass spectrometric detection offers solutions of difficult problems encountered in the analysis of real samples of unknown composition, when subsists the lack of proper standards. The sample preparation procedure is apparently of great importance as it can have crucial effects on the analytical results obtained by HPLC. Most of the natural dyestuffs are of the mordant type in a lake form obtained by co-precipitation with an inorganic substrate, in which the dyes are chemically bound by difficult to dissociate chelate bonds. Mixtures of organic solvents and strong acid such as HCl or H_2SO_4 are successful in extracting the dyestuffs from lakes but hydrolyze many of them into less informative aglycones [4]. Alternative effective method is based on the hydrofluoric acid, which is both a weak acid and a strong aluminum -complexing agent, for extraction of mordant-type dyestuffs with preservation of glycoside bonds [5]. The Krakow collection of painting materials used by Polish 19th century most famous historic academic painter Jan Matejko consists of nearly 300 tubes. Most of them are oil paints of Richard Ainès company, formerly Mulard, owned before him by recognizable French art materials supplier Eduard. Red colorants within the collection vary in hue from warmer and lighter to deep dark red or even slightly purple or violet in hue.

Aim of the study is the identification of organic dyestuffs in red oil paints used by Jan Matejko, using LC-UV/MS. While HPLC-MS has been extensively used for the identification of natural organic dyes in the historical textile samples, this method has not been widely employed for samples extracted from oil paints.

In the present work, an analytical protocol for the identification of red dyes using liquid chromatography-mass spectrometry with atmospheric pressure electrospray ionization is presented and it was successfully applied to identification of the main components of Madder lake (purpurin, alizarin and its isomers, rubiadin, pseudopurpurin, munjistin, nordamnacanthal) and Cochineal (carminic acids) in the historical sample s of 19th century lakes from the National Museum in Krakow, Poland.

The extraction methods of the dyes were critical for this analysis. The use of HF to extract intact colorants from lake ensures non-destructive extraction of acid-labile components, while the strong mineral acid HCl hydrolyzes not only the metal-dye complex but also decomposes the glycosidic dye into the parent aglycon and causes formation of many undesirable side products which may hinder proper identification of the dye.

Apart of indication of the red colorants, the carriers for the dye as well as fillers within the paint were investigated by means of XRF and SEM-EDX. Both aluminum aluminum hydroxide and tin oxide or tin chloride) containing carriers were identified as well as chalk and silica, aluminosilicates or lead white and zinc white as additional fillers.

sample	Elements (XRF, SEM-EDX)	Dyestuffs (HPLC-DAD-MC)	Result
M 31	Al, P, Sn Si, Pb, Sb, S, K	nordamnacanthal, alizarin and its isomers, purpurin, rubiadin, pseudopurpurin, munjistin	Madder lake, aluminum hydroxide and tin oxide substrate, silica, lead white fillers
M 31B	Al, P, Sn, As Si, Ca, S Sb?	purpurin, alizarin and its isomers, nordamnacanthal pseudopurpurin, munijstin, rubiadin	Madder lake, aluminum hydroxide, tin oxide, chalk substrate with silica fillers
M 48	As, S, Ca, Co, tiny amounts Zn, Fe	purpurin, alizarin and its isomers nordamnacanthal rubiadin, munijstin, pseudopurpurin, lucidina, damnacanthal	Madder lake, precipitated on chalk, zinc white filler
M 49	**Sn**, **Ca**, As, P, Fe, trace Cu, Si	purpurin, alizarin and its isomers carminic acid in tiny amounts	Madder lake Cochineal tin based substrate, chalk
M 51	**Sn**, Al, Ca, P, K Fe, Cu, As	purpurin, alizarin and its isomers, nordamnacanthal rubiadin, munijstin, pseudopurpurin, lucidina, damnacanthal	Madder lake tin based and aluminum substrate, chalk
M 52	K	purpurin, alizarin and its isomers nordamnacanthal	Madder lake

Table 1. Results of identification of the red dyestuffs, dyes' carriers and fillers

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P22

Investigating the use of pink and violet hues on Greek figurines

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Keywords: Greek, dyes, anthraquinones, VIL, FORS, UV, IRTF, Raman

Funerary terracottas from fifth to three century BC created in Great Greece (including Italy, Turkey and part of Africa) were painted with vividic colours, specific depending the area of creation. Even if the mould and the model were similar, each part of the Mediterranean basin employed various materials for the coloured decorations.

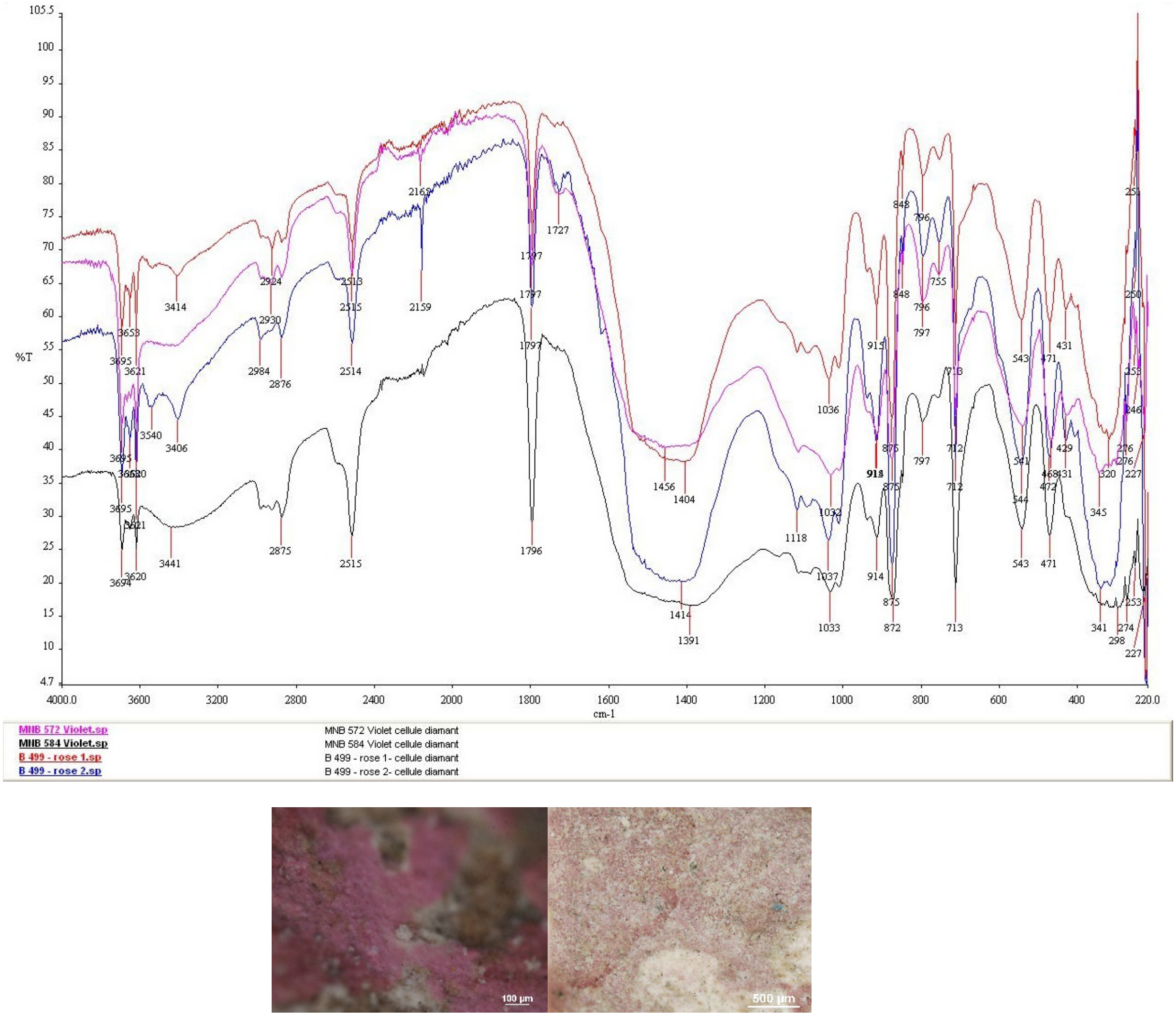
The research performed on the precious colours for the Greek artists – pink-violet, green and gilding – aims to distinguish workshop and tradition and to determine local use. This present work will be focused on the violet and pink hues.More than twenty figurines stored in the Greek, Etruscan and Roman Antiquities Department from the Louvre Museum, with precise origin, were studied.

By combining multispectral images (UV, VIL, IR), XRF spectroscopy and in-situ and microsampling spectroscopies (FORS, IRTF, µRaman), identification of various dyes was realised. Quinone family is the main source of these dyes, sometimes in so few quantity, so HPLC is not enough sensitive. FORS permits to distinguish some family or mixture.

Terracotta figurine under UV and natural light; pink decorations are visible in orange fluorescence.

Depending on the location of the creation, animal or vegetal dyes were used, orange fluorescence under UV is characteristic of some pink, identified as kermes or madder.For the violet, no conchylian purple is characterised; Egyptian blue is mixed with pink dye in Eastern Greece or pure vegetal colorant, orcein, is employed. The white support for the pink dyes is always an aluminosilicate wherever is the workshop, and the violet dye is fixed on calcite.

These first results without samplingconstitute the first step to identify dyes used as pigments. They could permit to precise, with all the materials data (preparation, composition of the mineral polychromy) the origin of some pieces and the trade roads during Antiquity.



Purple and pink samples and IR spectra of some of them

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P23

Libs and microscopy analyses of five 17th century oil paintings from the king Jan III's palace museum in Wilanow

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Keywords: painting analysis, LIBS, multivariate analysis

This paper presents the selected results of the analysis of the 17th-century paintings from the Museum of King Jan III's Palace's at Wilanów collection. The works chosen for examination are of great importance to the Museum, as they might have been painted by court artists of King Jan III.

Jan Sobieski was a broadly educated art lover and a patron of artists. He engaged foreign artists at his court; there were, among others, French and Italian artists. The king also funded foreign scholarships for talented Polish artists as he wanted to educate masters for his own academy of arts which he intended to establish. His protégés were: Jan Reisner (1655-1713) and Jerzy Eleuter Szymonowicz-Siemiginowski (1660-1711), who were given scholarships to study at St. Luke's Academy in Rome.

The erudite king was also a staunch art collector who looked for works of art in entire Europe. Unfortunately, after his death, the valuable collection was divided between his heirs and over the years it became more and more dispersed.

From 2012 a new project was launched which aims to collect comparative materials in order to establish and classify differences between the technique and technology of the unsigned portraits of Jan III and his family, which were, presumably, painted in the king's lifetime and which appertained to royal collection.

The aim of the study is to determine the technological structure of the paintings, to gather comparative material that would serve to conduct further multidisciplinary attributive research.The research is carried out with active participation of art historians, conservators and experts in conservation science. Because of the large field and numerous threads to follow, the research will be conducted stage by stage and traditional research methods as well as the most advanced ones, e.g. based on the spectroscopy, will be employed. One of the latter is laser-induced breakdown spectroscopy (LIBS).

Five oil paintings, portraits of king Jan III family were tested using LIBS method and digital 3D microscopy. Results were compared with SEM/EDS and XRDP data available for some paintings. The results obtained allowed us to find stratigraphy distributions of elements in selected parts of paintings as well as to identify pigments used in tested points. Evident differences and similarities were found in grounds deposited on particular paintings. During these latest investigations conducted in 2013 and 2014, we concentrated on comparison of some elements like: Ba, Li, Ti, identified in grounds layers. Basing on this, we tried to classify the paintings following the character of the ground layers.

The analysis was additionally supported by statistical multivariate analysis. Presented results exhibit also a scale of micro-destructibility introduced by LIBS.

Finally, results showed reasonable agreement with SEM/EDS and XRDP data and gave some indications related to workshops and authorship of the paintings.

The research will be continued. Further studies will include more methods based on spectroscopy e.g. RAMAN.

P24

Influence of UV light on the stability of synthetic ultramarine blue pigment in modern and contemporary art

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Keywords: Ultramarine blue, UV ageing

The stability after different periods of exposure to UV light of synthetic ultramarine blue pigment (Color Index name: PB 29) mixed with two different type of synthetic binders (acrylic and alkyd) widely used in modern and contemporary arthas been investigated by Raman spectroscopy, and complemented by FTIR-ATR, colormeasurements, and SEM-EDX analysis..

Based on sodium alumina-silicate sulfate with the empirical formula ($Na_6Al_6Si_6O_24S_4$), ultramarine blue is characterized by a sodalite framework where S_3^- radical anions are mainly responsible for the blue color of the pigment while S_2^- radical anions represent the yellow chromophores. Some indications of the low stability to the UV light of the ultramarine blue pigment when mixed with synthetic binding media have been obtained in UV ageing studies of modern paints [1,2].

For this study, several mock-ups were carefullyprepared by mixing pure ultramarine blue pigment with each type of binder, for example acrylic (Plextol® D498, Kremer PigmenteGmbh& Co. KG, Germany), in a mixing ratio of 3:1 and prepared on glass slides obtaining a film thickness of approximately 30-40 µm. Commercial acrylic ultramarine blue paints from four different companies (Liquitex®, Lukas®, Lascaux®, and Rembrandt®) and alkyd from Winsor & Newton®were also considered. The prepared mock-ups were allowed to dryat room temperature and then aged for 31 and 83 days in the UVACUBE SOL 2/400F chamber (Dr. Hönle GmbH UV-Technology, Germany), which provides radiation with wavelengths between 295 and 4000 nm.

After UV ageing, Raman measurements recorded a decrease of the ratio of S_3^- and S_2^- radical anions in some of the mock-up samples as well as in some commercial blue paints while an increase of the S_3^-/S_2^- was observed in other specimens, indicating a variation of the content of S_3^- and S_2^- chromophores in the sodalite cage. Additionally, a color change was determined by color measurements by showing a shift in the *a**(redness/greenness) and *b** (yellowness/blueness) values of the aged samples. An increase in *L** (lightness/darkness) value of some commercial blue paints was also determined by color measurements, corresponding to a brightening of the samples. On cross-sectioned samples of the mock-upsSEM-EDX analyses displayed the formation of cracks through the aged paint film as well as the agglomeration of the ultramarine blue pigment particlesatthe surface in contrast to the unaged samples. On the other hand the infrared bands of the blue ultramarine detected by FTIR-ATR remained unchanged after UV exposure.

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P25

Optimisation and characterisation of HPC-based photoreduced SERS active substrate and its use for analysis of organic colorants present on cultural heritage objects

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Keywords: organic dyes and pigments, madder lakes, cross sections of the samples, SERS, photoreduction

Surface Enhanced Raman Spectroscopy (SERS) was proven to be an efficient method for detection of organic colorants which are present in low concentrations in paint layers. The method shows the compatibility with other analytical methods and its high-performance in examination of priceless objects of cultural heritage.[1,2]Due to Raman signal enhancement and high sensitivity, the amount of sample required for the SERS measurement is reduced. Moreover, due to fluorescence-quenching properties of SERS substrates, it is possible to identify colorants whose signals are obscured by this phenomenon in conventional Raman spectra. Nevertheless, interferences for unambiguous identification can still arise due to intrinsic properties of SERS substrates and/or components of the paint layers. For instance, the binding medium often contributes to additional luminescence, overriding the spectral features and reducing the intensity of vibrational modes of target organic colorants. Several studies in conservation science focused on optimisation of the strategy by adapting extraction and hydrolysis procedures and by proposing new and/or modified SERS substrates. In addition, minimal or even non-invasive approach techniques for the examination of paint layers present in the finishing layers are being developed, but they also do not provide enough information on sample's stratigraphic properties.

Therefore, a hydroxypropyl cellulose (HPC)-based photoreduced silver substrate for the analysis of organic colorants was proposed.[3] It showed promising results in the investigation of samples' stratigraphy, as the increased viscosity of the substrate offers the ability to maintain a better control when applied to minute samples prepared in cross sections. In the present study the photoreduced substrate was used for detection of the organic dye alizarin red S (alizarin carmine) on the cross sections of the samples taken from the mock-up panels exposed to well-controlled artificial ageing environment. Several types of samples were prepared (combinations of binders and varnishes); the dye was bound in linseed oil as well as in proteinaceous media (fatty and unfatty egg tempera) with or without egg white varnish applied atop. Non-invasive infrared spectroscopy measurements, performed directly on the surface of the samples, showed a significant rate of paint layer degradation (compared to respective control, non-aged samples). Degradation was defined according to significant changes of the bands, assigned to binder components, and undistinguishable spectral signatures of the dye (i.e. shifts and overlapping of the bands). In spite of the deteriorated paint layers, SERS analysis successfully accomplished the organic dye identification without interfering signal of the binder.The advantage of SERS analysis in such cases is attributed to high sensitivity of the method for identification of organic pigments and dyes.

Furthermore, the present study was also dedicated to optimisation and characterisation of the substrate to gain a better insight into substrate's properties. The optimisation steps consisted of varying the initial concentrations of Ag salt and the polymer (HPC), changing the reaction conditions (e.g. wavelength and the intensity of incident irradiation, time of the exposure) with the aim to achieve optimal properties with regard to viscosity, durability and sensitivity. SERS-activity was evaluated through the enhancement of alizarin reference dye's signal. In many cases, substrates showed an incomplete reduction and,as a probable consequence, an in-situ formation of silver nanoparticles caused by laser irradiation[4,5] during Raman measurement. Both processes were taken into consideration in the signal intensity comparison. To obtain a better understanding on reduction, nanoparticle formation, the role and the behaviour of HPC, different methods were complemented, including spectroscopic, chromatographic and microscopic investigations.

Separately, a part of the research addressed also SERS analysis of several commercially available madder pigments and compared to ground madder roots. It is known that the colour of the madder lake pigments depends greatly on the preparation path of the lakes using different recipes and ingredients and therefor on the content of different colouring substances.[6]This was an attempt to contribute to the assessment of the lake preparation and to understanding of technological aspect of artist's materials.

Acknowledgements

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P26

On "*Viridis color cum sale*". New approach on its composition

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Keywords: pigments, verdigris, Raman spectroscopy, FTIR-ATR, XRD, SEM-EDX, LM

Verdigris is an historical pigment widely used in easel painting, wall painting and to prepare inks used on manuscripts. There are many recipes and processes for obtaining it, so it can be constituted by several compounds. Anyway, they are cooper(II) salts: acetates or hydroxyacetates with different hydratation grades, or hydroxychlorides, or a mixture of these compounds. The majority of recipes refer to the obtaining from copper plates and vinegar. Some of them have been reproduced and products obtained have been analyzed by different analytical techniques, such as, XRD [1,2], Raman spectroscopy [3] and a combination of XRD and vibrational spectroscopy techniques [4]. There are other recipes which refer to the use of common salt (NaCl) or ammonium chloride (NH_4Cl), combined with urine or vinegar vapors, on copper plates. In this case, the result obtained is a complex mixture of copper(II) hydroxychlorides and other substances [5-7].

In this paper are presented the results corresponding to the reproduction of recipe XXXVIII of *Ms. Heraclius* (10th-13th c.), referred to *viridis color cum sale* [8], which is similar to the recipe given by Theophilus on the preparation of "green salt" [9]. In both, vinegar vapours act on a copper plate impregnated with honey and powdered common salt (NaCl). After 25 days, different morphologies and colors (green, bluish green and blue) appeared on the corroded plate. Samples were taken from these different areas and they were analyzed by light microscopy (LM), SEM-EDX, ATR-FTIR, Raman spectroscopy and XRD.

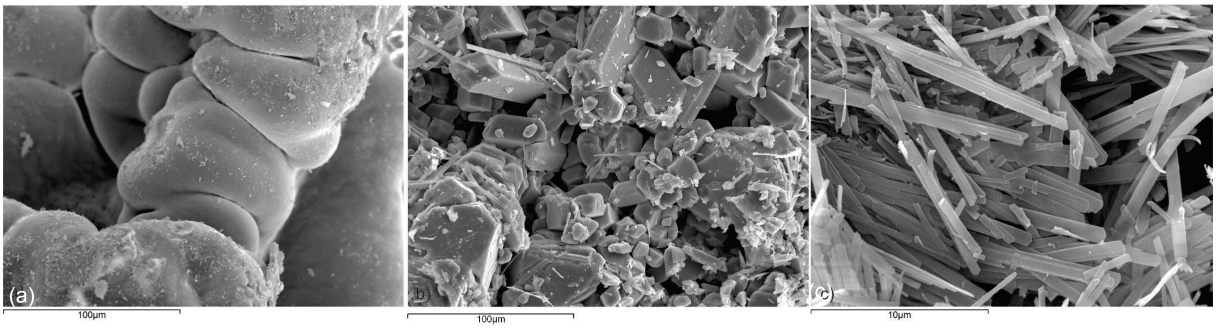

Fig. 1. SEM(SE) images. Samples taken from green area (a), green-bluish area (b), blue area (C)

The green colour sample (ref. HE.13) is formed by globular particles forming botryoidal aggregates (Fig. 1a). It is a mixture of atacamite and clinoatacamite, both of them are idiomorfics responding to the composition of [$Cu_2Cl(OH)_3$]. The bluish green sample (ref. HE-12) presents prismatic and tabular particles and it is a neutral verdigris [$Cu(CH_3COO)_2 \cdot H_2O$]. Blue sample (ref.HE-11) is formed by aggregates of acicular particles (Fig. 1c). This is basic verdigris [$xCu(CH_3COO)_2yCu(OH)_2zH_2O$], but its exact composition could not be confirmed, because there are no JCPDS identification patterns coincident. Figure 2 shows examples of the results obtained with the different analytical techniques used in this investigation.

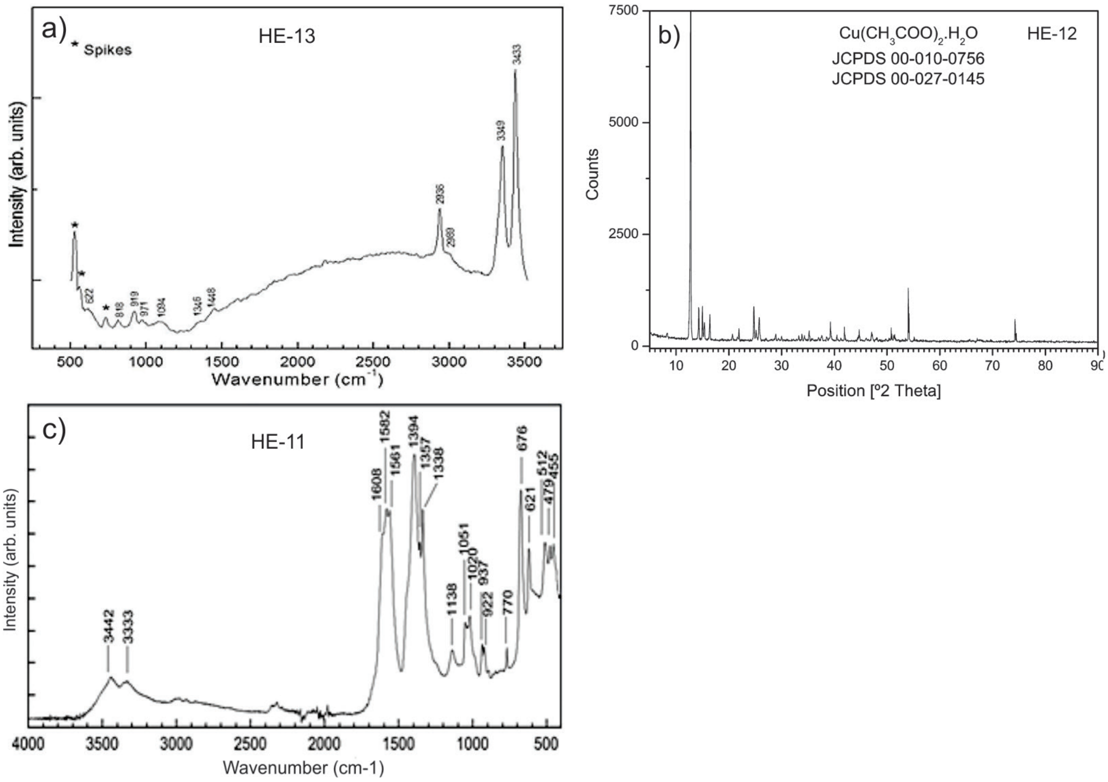

Fig. 2. a) Sample HE-13 (green area). Raman spectrum; b) Sample HE-12. XRD results (bluish green area); c) Sample HE-11 (blue area). ATR-FTIR spectrum

P27

Application of Raman spectroscopy to investigate the Bohemian medieval panel painting 'Votive Panel of Jan Očko of Vlašim'

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Keywords: Raman micro-spectroscopy, pigment identification, Bohemian panel paintings, medieval period, GC-MS, binding media.

The aim of this paper is the summarisation of results obtained by the investigation of the exquisite Bohemian medieval panel painting '*Votive Panel of Jan Očko of Vlašim*' (canvas-covered fir wood, 181.5×96.5 cm, before 1371, Inv. No.: O 84) from the collections of the National Gallery in Prague, during which the Raman spectroscopy was employed in the characterization of inorganic substances. The largest panel in Bohemian gothic painting was probably executed for the private chapel of the archiepiscopal country residence in Roudnice nad Labem by an artist from the studio of Magister Theodoricus. The picture dated into the period 1370-1371 is depicting the second Prague archbishop Jan Očko of Vlašim with Bohemian patron saints in the lower band and Virgin Mary with Charles IV and Wenceslas IV with their personal patron saints in the upper level. The style of the painting marks late imperial style of Emperor Charles IV and signalizes the beginning of the Beautiful Style in Bohemian painting [1].

For the revision of the painting technique and characterisation of the pigments and binding media, the samples from the chemical-technological laboratory archive of the National Gallery were studied within the recent project 'Historical technologies and modern methods of research'.

A representative range of micro-samples, collected and archived in the 1990's in context of the panel restoration, was investigated by the optical microscopy on polarizing microscope (OM), by micro-chemical analysis and by the element analysis using the scanning electron microscope with X-ray microanalysis SEM/EDS. Molecular analysis was recently accomplished using micro-Raman spectroscopy (MRS) and Infrared spectroscopy with Fourier transformation (FTIR). The gas chromatography - mass spectrometry (GC-MS) technique was applied to specify the presence of lipid and protein binding media. Recently, the investigation was also enlarged by the non-invasive analysis by means of mobile X-ray fluorescence allowing the determination of inorganic pigments and metal plates in the whole area of the painting.

The use of Raman spectroscopy was crucial for the analysis of some pigments or dyes (for example lead-tin yellow type II or indigo) in non-destructive way. The measurements were performed on the individual pigment grains or on the cross-sections using the mapping mode for better observation of individual components present in colour layers.

Thanks to the analytical methodology carried out, 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 as lead white, lapis lazuli, indigo/woad, vermilion, red lake, earth pigments, red lead, lead-tin yellow type II, copper-based green and carbon-based blacks were detected. The studies also enabled to specify the admixtures of pigments in the painting layers, and determine the pictorial technique used in the process of creating this work of art. One of the focuses of this research was also the survey on decorative technique and gilding on the black poliment [2]. The gilding on the black poliment is a rare method observed in the Bohemian panel paintings, apart from the Votive Panel of Jan Očko of Vlašim, it was found on the artworks of the Master of the Třeboň Altarpiece [3] or on the Triptych with the death of the Virgin Mary, known as the Roudnice Altarpiece [4]. The gilding technique is connected also with the realization of brocade textile imitation found on the cloaks of Charles IV, Wenceslas IV, St Wenceslas and St Adalbert. The Raman spectroscopy in mapping mode was used to show the distribution of the individual pigments in the cross sections what revealed the construction of the brocade.

In addition, the survey on binding medium in combination with different pigments is demonstrated. It seems that the *tempera grassa* paining technique was applied on the panel in yellow and green tones. The binder composition is based on the presence of drying oil, egg yolk, pine and elemi resin. The last two components are likely to originate from the restoration interventions. Higher value of the P/S ratio indicates the presence of egg yolk, which was confirmed by a series of cholesterol oxidation products as well. At the same time, the abundant amount of azelaic acid, the product of drying mechanism of oils, shows that drying oil is also present. Diterepenes as dehydroabietic acid (DHA) and its oxidation products confirmed the pine resin (*Pinus* species), while triterpenes as α-amyrin and α-amyrin proved the presence of elemi resin (Burseraceae). On the other hand, the blue is mostly based on drying oil with additions of pine and elemi resins. Also here the origin of the resins can be expected to be from the restoration. In this case, egg yolk was not confirmed, however, the simultaneous excess of beeswax altered not only the oil identification, but plausibly also might disguised the presence of egg.

The Raman spectroscopy in the combination with other analytical methods helped to better understand the gilding technique, the composition of decorative motives and the sophisticated use of pigments – use of the precious pigments like lapis lazuli or the pigments typical for the Bohemian Gothic paintings of the 14th century like lead-tin yellow type II [5]. The investigation fully confirmed the extraordinary artistic value as well as the technically-high performance of this panel painting, which is considered as one of the most important testimony of the medieval art in Bohemia and Central Europe. The results and their interpretation were achieved within the close collaboration of conservation scientists, conservator and art historian.

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P28

Non-invasive XRF research of the evolution of the 19th century pigments, identified in situ on more than hundred representative Polish painters' paintings

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Keywords: 19th century pigments XRF, non-invasive painting analysis, artists' palette

In order to create comparable database of the implementation of the exact pigment on paintings, not relying only on the dates of invention of pigments based on written sources, but on the real moment of application on paintings, more than 100 certainly dated paintings of various Polish artists, from the period 1800-1900 were investigated using portable XRF spectrometer (researched included works by J. Szermentowski, J. Matejko, W. Gerson, A. Gierymski, W. Weiss, Leon Wyczółkowski and others). When sampling was possible complementary research by means of Raman spectroscopy, SEM-EDX and XRD was conducted.

The research demonstrated real dates of the first appearance on paintings of individual pigments by chosen artist, sometimes significantly shifted in time in comparison to the dates of the invention and implementation to the mass production. The evolution of the use of range of pigments exchanged with time with newly invented other ones within the whole period was followed on real paintings of exact painters. When there were more paintings of one painter investigated, some changes were discovered during individual artist lifespan for example lead white was replaced by zinc white and chrome yellows by cadmium yellows in the case of Leon Wyczółkowski. Some pigments appeared to be characteristic for the exact painter as for example Naples yellows containing zinc white as their admixture in wide range of five different hues of this yellow pigments found on Jan Matejko (1838-1893) paintings and in his preserved historical paint tubes. Pruszkowski preferred synthetic copper blue verditer in opposite to other painters mostly using cobalt blue and artificial ultramarine. Rarely used pigments like cobalt violet, found only in some works by Jacek Malczewski and Wojciech Weiss at the end of the 19th century, and manganese violet on paintings of Leon Wyczółkowski, present different approach of various artist to the new pigments appearing on the market – more open or more conservative. Characteristic trace elements in some pigments, like special additions respectively of molybdenum, arsenic or nickel in the different hues of cobalt blue were observed, enabling in some cases identification of the exact pigment of the individual producer or supplier, supporting significantly authentication. Significant number of paintings shown possibility of preliminary characterization of organic dyes based paints by the identification of their substrates and fillers. The XRF examination was broadened in some cases when sampling was possible, especially on the paints from historical tubes and palettes, with SEM-EDX, Raman spectroscopy, XRD.

The research allowed recognition of the real dates of the implementation of the newly discovered pigments onto artists palettes. The extreme wide range of modifications even within one pigment kind, related to admixed fillers and other pigments was indicated. Unexpectedly rich number of pigments and their ready made producers' modification and mixtures as well as the continuous evolution of composition was uncovered. Cobalt blue was neighboured by more common use of artificial ultramarine since about half of the century, and rare exceptional use of the cerulean blue took place in the last quarter of the 19th century. Yellows evolved from pure lead antimonite yellows, in the beginning of the 19th century, replaced by lead chromates identified since 40-ies, subsequently more wide use of different kinds of chromates with various fillers and admixtures starts, till the introduction of the cadmium yellow in the late sixties. Greens based on copper and arsenic shown diversity of kinds illustrated in different ratio of one element to the other changing also the hue of the pigment. Viridian and chrome greens basing both on Prussian blue and chrome yellow and later on Prussian and cobalt blue and cadmium yellow mixtures were found.

Some unexpected results were gathered as surprisingly early use of cerulean blue by academic painter Jan Matejko or range of colour used by one artist reaching in some cases sixty different paints. Above mentioned amount and complexity of information deepened the knowledge on the workshop practice of the second half of the 19th century and enabled creation of database for more reliable comparison of data concerning pigments characteristic for individual painter, real date of their execution and popularity of use of various pigments by Polish painters in this period. These helped in some case studies of authenticity assessment showing possibilities and limits, and to draw real time of turning points in evolution of use of the exact pigments by individual painters, enabling to propose wider "technological panorama" of the 19th century, creating comparative background data for further studies of Polish and European paintings from this period. Properly used portable XRF spectrometer proved to be powerful tool in recognition of non-organic ingredients of paints, what was indicated by complementary methods used for identification

Acknowledgements

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P29

Corals and shells in museum collections: µ-Raman mapping ofcarbonates and pigments

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Keywords: corals, precious shells, pigments

The nature of the pigments in marine and terrestrial biogenic carbonates found in corals, shells or pearls is still debated and, in addition, a deeper understanding of the intricate biomineralization processes [1] is looked for a better conservation in museum collections.

Raman microscopy is a powerful technique to investigate both the spatial distribution of the inorganic phases (calcite, aragonite or vaterite) and to define the nature of the organic pigments in corals, shells and pearls, especially when resonance conditions are attained [2-5]. Mixtures of methylated (carotenoids) or non-methylated polyenes with different UV-VIS absorption spectra and chain lengths (i.e. number N of C=C bonds) are responsible for the colors and their variations in mineralized organisms [4-5].

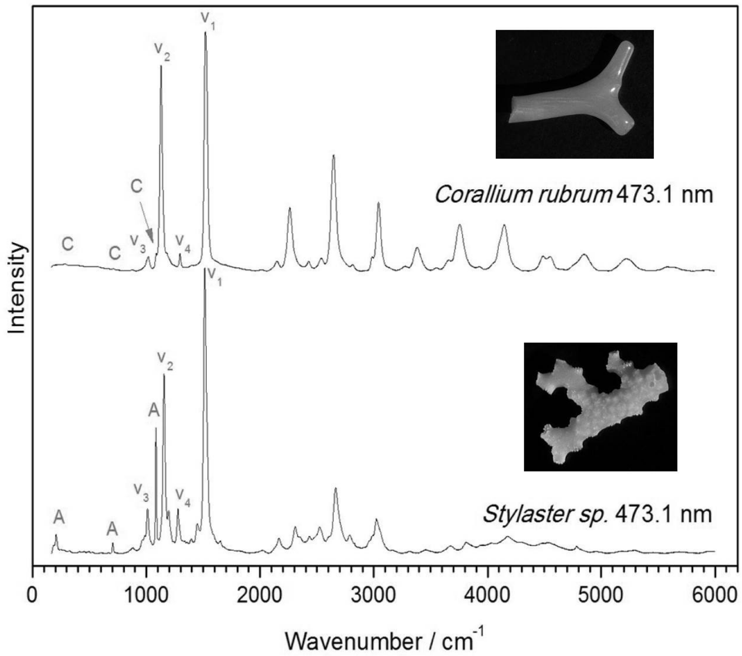

Figure 1 – The Raman spectra of *Coralliumrubrum* and *Stylaster* sp.

Here we report on Raman mapping measurements at 632.8 nm and at 473.1 nm (resonance) in calcitic and/or aragonitic samples: terrestrial pulmonate gastropod mollusk shells of the Liguusvirgineus species (family Orthalicidae) and marine shells (*Bractechlamysvexillum*) compared with corals (*Stylasterroseus*and*Coralliumrubrum*).

P29

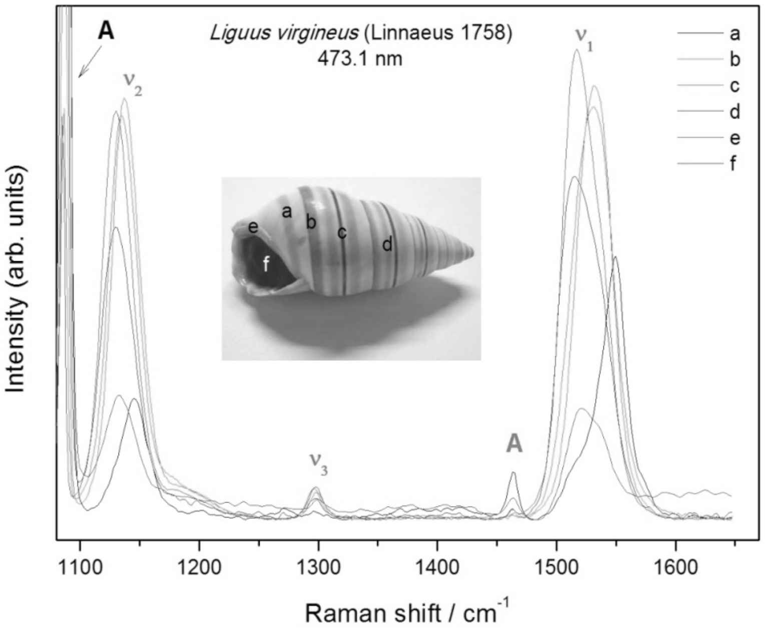

Figure 2 –Raman spectra of different color lines in *Lyguusvirgineus*.

The pigment in *Coralliumrubrum* (calcitic) shows Raman frequencies typical of polyenicunmethylated chains whereas in *Stylasterroseus* coral (aragonitic) the spectrum is similar to that found in a methylated carotenoid pigment as astaxanthin or canthaxanthin. On the other hand, for the peculiar *Liguusvirgineus* shells investigated (mainly aragonitic), the pigments show both methylated and unmethylayedpolyenic nature. The results of the Raman mapping distribution of carbonate species are discussed and compared with those found in marine gastropoda or bivalve shells, where methylated polyenes are hardly found.

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Portable Raman and Raman imaging usefulness in emergency analyses to detect decaying on building materials from Punta Begoña Galleries (Getxo, North of Spain)

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Keywords: Raman imagining, mortars, concrete, sulphates, black crusts

Punta Begoña Galleries were built in 1918 in Getxo (Basque Country, North of Spain) as a retaining wall of a hillside where it was located the mansion of Horacio Echevarrieta, an important tycoon of that time. Although, he was the head of one of the most important families of the 20th century aristocracy of the area, the Galleries were abandoned in the fifties and nowadays the building belongs to the town of Getxo, being their conservation state very poor. To recover its historical memory, a multidisciplinary research team including chemists, geologist, architects, archaeologists, historians, etc. researchers of the University of the Basque Country and technicians of the City Council of Getxo are working together. This work summarizes some of the results related to the characterization of the original materials and the identification of the decayed products as part of the emergency analysis to detect in short time the decaying of the building.

In the development of these tasks, Raman spectroscopy played an important role, because its portable versions allowed us performing the evaluation of these materials composition. Moreover, the obtained results are the key for the selection of the most appropriate sampling points, minimizing the deterioration generated during the sampling.

Two portable Raman spectrometers (innoRam model, $B_{\&}WTEK_{INC}$, Newark, EEUU) equipped with 785 nm and 532 nm lasers respectively were used. In the laboratory, a RA100 spectrometer and a confocal inVia Raman microscope (Renishaw, Gloucestershire, UK) were used, respectively. With the confocal microscope, apart from point-by-Raman analyses, Raman imaging was also performed.

In the outer areas of the Galleries, stones, different mortars (joint, rendering and decorative) and the cement from the cornice of the building were analyzed. The coincident composition of these materials was calcite ($CaCO_3$), quartz (SiO_2), different kind of aluminosilicates and hematite (Fe_2O_3). With respect to the degradation products, gypsum ($CaSO_4{\cdot}2H_2O$) and amorphous carbon were identified as the main constituents of the black crusts that cover these materials. The formation of sulphates and carbon can come from the impact of atmospheric SO_2, road traffic/industry emissions respectively. Biological patinas were also identified, in which scytonemin and other biogenic pigments were characterized.

In the cements from the cornice, nitratine ($NaNO_3$) was determined, probably formed due to the reaction of sodium carbonates from the cement and the oxidized NO_x coming from the polluted atmosphere and/or with the NH_4NO_3 input coming from rinsing waters from the upper garden. The principal problem of all these mortars is the formation of efflorescences including gypsum, but mainly thenardite (Na_2SO_4)-mirabilite ($Na_2SO_4{\cdot}10H_2O$), which caused their detachment when the cements lost their binding capacity.

In the inner areas of the Galleries, decorative and rendering mortars from the wall and those covering the reinforced concretes from the ceilings were characterized (see Figure 1 A and B). The main components of wall mortars were calcite and gypsum. In some cases, alite (Ca_3SiO_5) and belite (Ca_2SiO_4) were identified. These components are characteristic of Portland Cement clinker that could have remained unreacted in the hydration process of it. In these mortars, apart from nitratine, other nitrates such as niter (KNO_3) and/or nitrocalcite ($Ca(NO_3)\cdot 4H_2O$) were also distinguised. The main components of the mortar that covers the concrete and the one that acts as the binder of the concrete itself were calcite, quartz, aragonite ($CaCO_3$) and gypsum. The aragonite identification confirms the use of beach sand as an aggregate, shell fragments can even be observed in the mortar. The concrete from the ceiling of the lower Gallery is covered with three different mortar layers (see Figure 1 C). The outermost layer (calcite, quartz and gypsum) is covered with a black crust (gypsum, calcite and amorphous carbon). In the inner layers calcite and aragonite were identified. In the case of the layer in contact with the reinforcement, the presence of calcite is lower, but a high presence and distribution of silicates was observed thanks to Raman imagining. In the outermost layers, dolomite ($[Ca(Mg(CO_3)_2])$) was also identify. Attending to gypsum distribution, it is observed that it is principally present in the outermost layer, but it is also present in the next one in a lower extend (see Figure 1 D). Regarding the aggregate used in the outermost layer, it belongs to calcite. As in the mortars from the outer areas of the Galleries, in the inner areas, thenardite and gypsum were identified on the efflorescences over mortars. In this case, apart from these salts, calcite and natron ($NaCO_3\cdot 10H_2O$) were also identified by Raman spectroscopy. The presence of these efflorescences is also causing the detachment of the mortars, leading to the loss of the steel reinforcement alkaline protection against oxidation processes. Chlorides from marine aerosol can also accelerate this oxidation process. In the steel reinforcement samples using Raman spectroscopy, it was possible to identify the presence of different iron oxides [hematite and lepidocrocite, (α- Fe(O) OH)] due to the oxidation process they are suffering. In addition, calcite stalactites are formed in the ceiling of the lower Gallery due to the dissolution of original calcite (and/or gypsum) coming from the mortars.

Figure 1. (A) A detail of the ceiling from the Punta Begoña inner areas where the concrete sample (B) was taken, (C) A cross section of the three mortar layers (L2, L3 and L4) over the concrete and the black crust formed over mortar layer L2, (D) Distribution of gypsum throughout the cross section of the three mortar layers over the concrete obtained using Raman imaging.

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Analysis of Flint Industry from Giurgiu-Malu Rosu, Romania Paleolithic site by Raman Spectroscopy

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Keywords: compositional analysis, lithic industry

Compositional analysis of raw materials and tools found at Giurgiu-Malu Rosu settlement and observations on its flint industry are reported. In the past researches it was established that at Giurgiu a large number of raw lithic material and a very small number of tools are found [1]. Despite this, the tools were obtained by a good Upper Paleolithic technique and the huge quantity of rests is related to the quality of the used raw material.

The compositional analysis of silicolites of different provenance (Fratesti Formation or Danube Valley) taking into account the type of raw material and artefacts categories permitted the description of Superior Paleolithic population from Romanian Plain concerning the areal, techniques and predominant raw material exploitation.

Two nondestructive vibrational spectroscopy methods were used for the compositional analysis of the archaeological materials: NIR FT-Raman and micro Raman.

The raw material consists almost entirely of a bluish silex (A), a reddish silex (M) (only 4.8 %) and an insignificant number of other rocks (black schist, sandstone and quartzite).

The identification of minerals using the position of the Raman bands of alpha-quartz (465, 206 and 128 cm^{-1}), moganite (502 cm^{-1}), calcite (713, 1086 and 281 cm^{-1}, anatase (397 and 515 cm^{-1}) and aragonite (1086, 706 and 155 cm^{-1}) was made [2].

The small shifts in the alpha-quartz vibration bands position and the alpha-quartz:moganite bands intensity ratio as well as other spectral parameters were used for provenance studies. In the Raman spectra of M type silicolites the presence of the 396 cm^{-1} peak of anatase titanium dioxide, a heavy mineral of earths may indicate a raw material of higher quality.

The composition of Giurgiu-Malu Rosu flint industry and different mineralogical constituents of A and M major types of silicolites were emphasized [3]. The physicochemical properties of the raw material were correlated with the characteristics of the flint industry.

The wide heterogeneity of raw material and high percentage of "lower quality" silex could explain the vast quantity of rests. The flint industry of Giurgiu-Malu Rosu belongs to an Upper Paleolithic facies characteristic for the Romanian Plain.

Acknowledgements

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Using FT-Raman and Reflectance Spectroscopy in the Restoration Process of Polychrome Wood Panel

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Keywords: chromatic integration, painting analysis, FT-Raman spectroscopy, DRIFT spectroscopy, VIS reflectance spectroscopy

Chromatic integration of painted panel is the key operation in conservation restoration process with the ability to enact the original aesthetics. Through scientific investigation, the color integration process becomes a method of objective aesthetic restoration providing the working parameters: the nature of the pigments and the surface application mode.

In this work FT-Raman, DRIFT and Visible reflectance spectroscopy were used for quantification of the chromatic integration [1]. Experimental panels with various pigments: cadmium yellow medium, emerald green, madder lake red light, ultramarine, neutral black applied in several layers were analyzed. Accelerated aging and gamma irradiation of the wooden panels were performed to follow the stability of the watercolors in time. Raman spectroscopy was used to determine the chemical composition of watercolors used in conservation-restoration and in conjunction with visible reflectance spectroscopy to quantify the chromatic integration.

Obtaining spectral parameters-pigment concentration calibration curves allowed the interpolation of data obtained from the original panel with those obtained from the experimental panels.

Acknowledgements

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Vitruvius' recipe for Egyptian Blue and the Analysis of samples from the Italian territory

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According to Vitruvius Pollio (De Architectura) Egyptian blue can be synthesized by grinding together some sand with "aes" that is copper or bronzescraps, and natrum, that is a fluxingmean and then shaping the mixtureasballs and putting them in a pot inside a furnaceat the proper temperature. Some years ago were peated in the laboratory the preparation of this pigment with different copper salts and different fluxesat different temperatures. In all cases the silicate was obtained, as a consequence of its high thermodynamic stability.

The story tells about Vestorius coming from Alexandria in Roman Egypt and preparing in a factory at Puteoli (now Pozzuoli) the first "Italic" Egyptian blue. Some decades ago in an excavation carried out at Pozzuoli a few small blue balls were found and let a side in a repository. On reading the passage from Vitruvius, wehad the idea of checking whether the balls were consistent with the recipe reported and whether the data could confirm the presence in Puteoli of the factory reported.

In order to give a wide picture of the problem, we considered more than one hundred of samples coming from different regions of Italy, both in a powdery state and in a ball shape form. The samples were analysed by FT-IR spectroscopy, Raman microscopy and X-Ray fluorescence in the aim of observing the main elements and those present at a trace level. Moreover, we checked also the appearance of other compounds connectable to the reaction precursors.

The data obtained show that the powders named "Egyptian blue" could be divided into some groups: one with a consistent percentage of tin, another one with a consistent percentage of zinc and another without both the elements mentioned. The pigment balls with tin, that is found in some of the mas cassiterite could be related to the use of bronzescraps, those with zinc, that is rarely found as oxide or other compounds, could be related to the use of orichalcumscraps, coming from the alloy used in the minting of coins. All the other samples could be those obtained from more recent preparations from Cuma or Liternum in Southern Italy, where historic alkilns have been identified works of art.

LA-ICP-MS and Raman spectroscopy as the complementary instrumental methods in historic wall-paintings analysis

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Keywords: LA-ICP-MS, wall-paintings analysis

In the 60-ties of 20th century during the so-called Nubian Campaign various historic buildings dated back to 7th – 14th century covered by wall-paintings were excavated in different archaeological sites in today's Sudan (Old Dongola, Banganarti, Faras). In the presented investigations fragments of those wall-paintings have been thoroughly analyzed to: (I) study the Nubian wall-paintings technology, (II) determine the materials used and (III) evaluate the quality of different Nubian workshops.

The information about the exact chemical composition of each layer of wall-paintings was obtained on the basis of Raman spectroscopy analysis (Almega Thermo Scientific Nicolet). In the majority of the pigments analysis 532 nm laser wavelenght was used. In the case of some blue and green pigment layers 800 nm laser was needed to eliminate the fluorescence of the sample. Elemental analysis of murals fragments cross-sections was performed to facilitate the interpretation of the obtained Raman spectras. The use of laser ablation inductively coupled plasma mass spectrometry (Perkin Elmer ICP-MS NexION300 + CETAC laser ablation system LSX-213) enabled to obtain the information about the distribution of selected elements over analyzed inhomogeneous multilayered samples on the basis of registered transient signals for ^{11}B, ^{12}C, ^{23}Na, ^{26}Mg, ^{27}Al, ^{29}Si, ^{31}P, ^{32}S, ^{35}Cl, ^{39}K, ^{42}Ca, ^{45}Sc, ^{49}Ti, ^{51}V, ^{53}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{65}Cu, ^{66}Zn, ^{85}Rb, ^{88}Sr, ^{89}Y, ^{90}Zr, ^{111}Cd, ^{118}Sn, ^{121}Sb, ^{133}Cs, ^{137}Ba, ^{139}La, ^{140}Ce, ^{178}Hf, ^{202}Hg, ^{208}Pb, ^{232}Th, ^{238}U.

Among red pigments haematite (Fe_2O_3, 226, 293, 404 cm^{-1}), magnetite (Fe_3O_4, 663 cm^{-1}), litharge (PbO, 143 cm^{-1}) and cinnabar (HgS, 251, 343 cm^{-1}); among white pigments gypsum ($CaSO_4$, 1009 cm^{-1}), calcium carbonate ($CaCO_3$, 1087 cm^{-1}), huntite ($Mg_3Ca(CO_3)_4$, 272, 1123 cm^{-1}) and hydromagnesite ($Mg_5(CO_3)_4(OH)_2\cdot 4H_2O$, 202, 1123 cm^{-1}) were identified. Atacamite ($Cu_2Cl(OH)_3$, 511, 3350, 3435 cm^{-1}) was determined in green fragments of murals, massicot (PbO, 143 cm^{-1}) in yellow, egyptian blue ($CaCuSi_4O_{10}$, 110, 430, 475, 571, 1086 cm^{-1}) and lapis lazuli ($Na_{8-10}Al_6Si_6O_{24}S_{2-4}$, 259, 548, 1094 cm^{-1}) in blue and soot (C, 1330, 1584 cm^{-1}) in black ones. Wide variety of mainly natural mineral pigments identified led to refute the hipothesis about the poor artistic level of the Nubian workshop, inferior to then Byzantium.

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