RAA 2019
Potsdam

# BOOK OF ABSTRACTS
## Conference Programme

10th International Congress on the Application of Raman Spectroscopy in Art and Archaeology

September 3rd – 7th 2019 in Potsdam, Germany

Institute of Geosciences at the University of Potsdam

RAA 2019
Potsdam

Martin Ziemann (Ed.)

# Book of Abstracts
# Conference Programme

## 10th International Congress on the Application of Raman Spectroscopy in Art and Archaeology

September 3rd – 7th 2019, Potsdam, Germany

**University of Potsdam 2019**

Institute of Geosciences

www.geo.uni-potsdam.de

www.raa2019.de

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Dear participants of the RAA2019 in Potsdam,

We cordially welcome you to the 10th International Congress on the Application of Raman Spectroscopy in Art and Archaeology in Potsdam. Our congress shows once again the ongoing European and world wide interest in this field of Raman applications. This scientific congress brings together researchers from diverse areas and represents dedicated work on the use of Raman spectroscopy techniques in the fields of art history, history, archaeology, palaeontology, palaeoenvironment, conservation and restoration, museology, degradation of cultural heritage, archaeometry, chemometrics, and many other fields. As in the past years, developments of new instrumentation, in particular non-invasive methods, have received unbroken great attention. Besides ancient materials – such as pigments, dyestuffs, wood, glass, metals and others - more and more modern materials and their previously unknown deterioration processes have come into the focus of our studies – examples of these are modern colours, inks, plastics and building materials.

Previously RAA congresses were held in London (2001), Ghent (2003), Paris (2005), Modena (2007), Bilbao (2009), Parma (2011), Ljubljana (2013), Wrocław (2015), Évora (2017), and this year (2019) in Potsdam.

We open this congress that has an ambitious program, highly interesting keynotes, talks and poster presentations. We sincerely thank all contributors and scientific committee members for their great support and commitment to make the RAA2019 a success.

Furthermore, we are pleased for the financial support by our main sponsor DBU-Deutsche Bundesstiftung Umwelt, as well as the gratifying variety of exhibitors of Raman spectroscopic techniques and instrumentations: the “Sans souci” sponsors HORIBA Jobin Yvon GmbH, Renishaw GmbH, B&W Tek, Inc., Witec GmbH and the "Neues Palais" sponsor Thermo Electron GmbH.

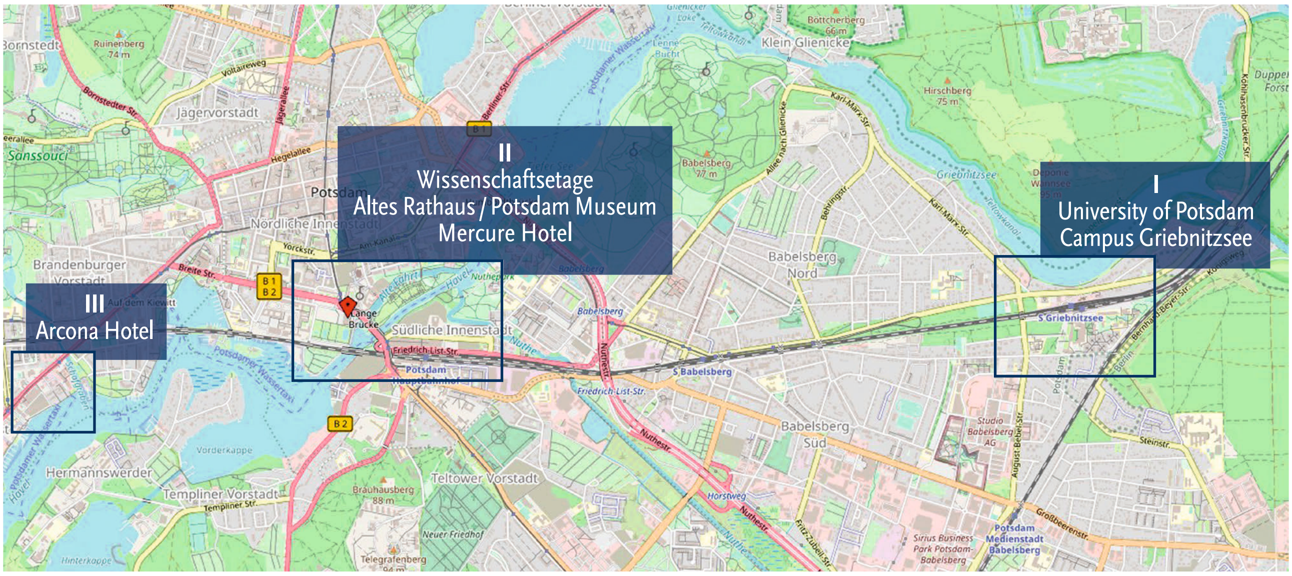
Once again, a cordial welcome to all participants and best wishes for a successful meeting and pleasant stay in Potsdam.

On behalf of the Organizing Committee

**Martin A. Ziemann**
Chairman of the RAA2019

# RAA2019 Conference Sites

## Overview



## I Conference Venue (03.–07.09.2019)

University of Potsdam – Campus Griebnitzsee
August-Bebel-Strasse 89, 14482 Potsdam | buildung 6

## II Registration (02.09.2019, 16:00–18:00)

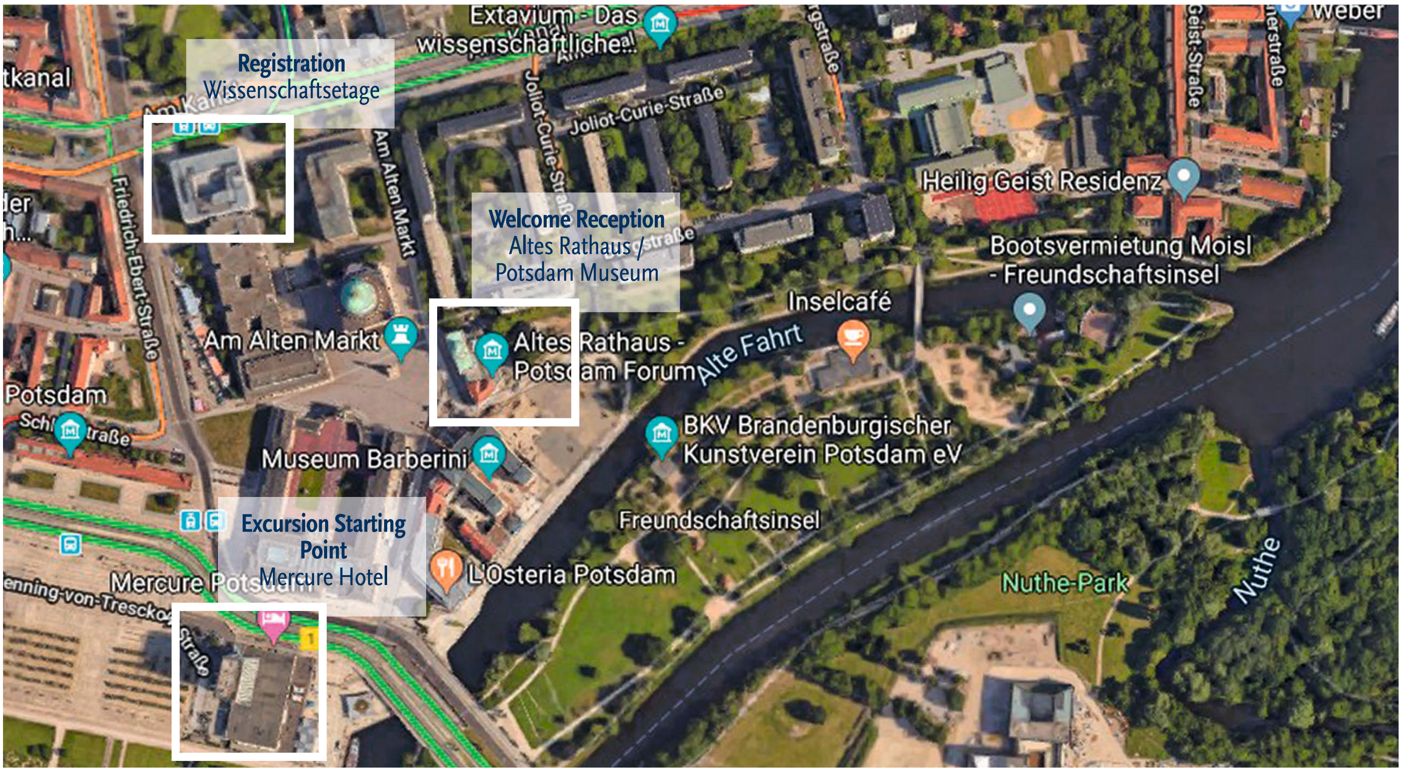
Bildungsforum, Am Kanal 47, 14467 Potsdam | 4th floor, Wissenschaftsetage

## Reception (03.09.2019, 17:00–19:00)

Old Town Hall of Potsdam, Potsdam-Museum, Am Alten Markt 9, 14467 Potsdam

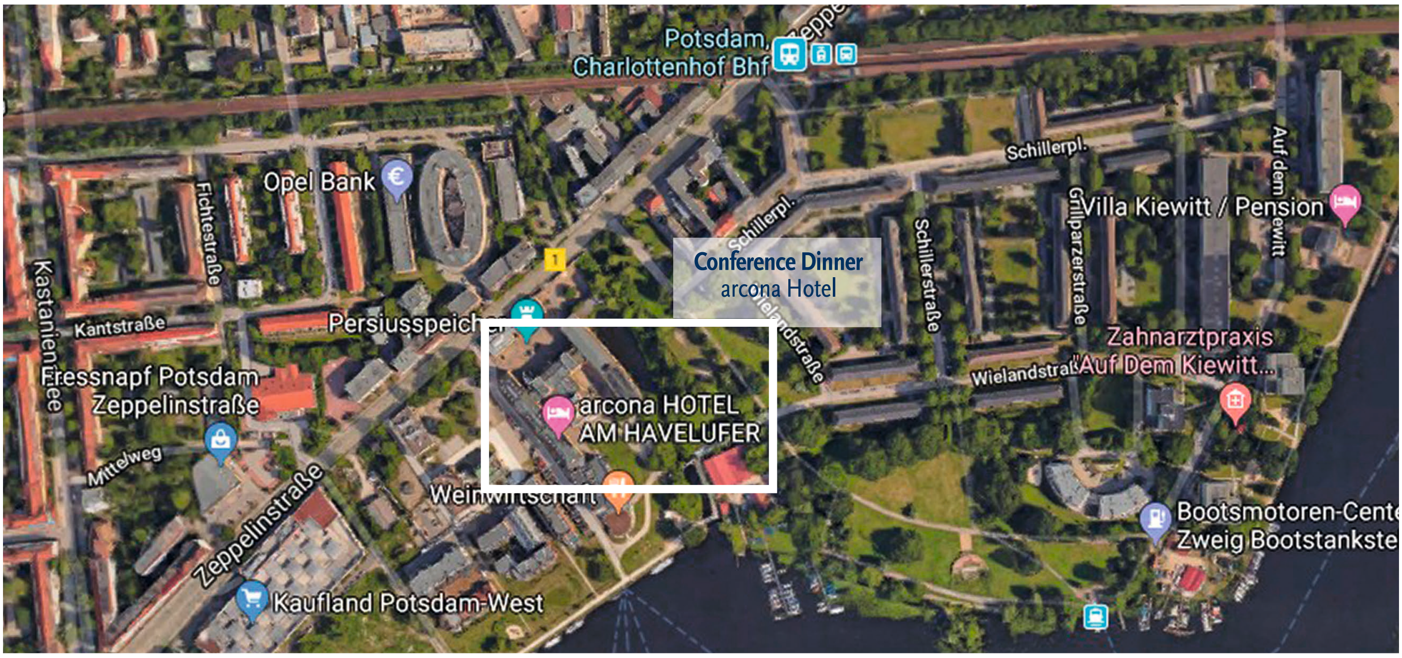
## Excursion Starting Point (06.09.2019, 08:15)

Mercure Hotel, Lange Brücke, 14467 Potsdam



## III Conference dinner (05.09.2019, 19:00–23:00)

Arcona Hotel, Zeppelinstrasse 136, 14471 Potsdam



# 3rd–7th September 2019

## Keynote lectures

RAA2019
Potsdam

# 3rd–7th September 2019

# Conference Programme

**2 September, Monday**

| | | | |
|---|---|---|---|
| 16:00–18:00 | | **Registration** (Bildungsforum, Centre of Potsdam, 4th floor, Wissenschaftsetage) | |

**DAY 1 - 3 September, Tuesday** (Conference site Campus Griebnitzsee)

| | | | |
|---|---|---|---|
| 8:00–9:30 | | Registration | |
| 09:30–10:00 | | **Opening of the RAA2019** | |

**Session 1 – Material characterization and degradation processes**

| | | | |
|---|---|---|---|
| | | **Keynote lecture** | |
| 10:00–10:40 | KL1 | Kepa Castro (Spain) | |
| | | *Unexpected degradation mechanisms in cultural heritage* | 19 |
| 10:40–11:00 | OP1 | Lucile Brunel-Duverger (France) | |
| | | *A Study of Copper Greens found on Yellow Coffins from the Egyptian Antiquities Department of the Louvre Museum* | 20 |
| 11:00–11:30 | | **Coffee break** | |

**Session 2 – Material characterization and degradation processes**

| | | | |
|---|---|---|---|
| 11:30–11:50 | OP2 | Thorsten Allscher (Germany) | |
| | | *Glass or gemstone? − A systematic review of the jewelled bindings from the collections of the Bayerische Staatsbibliothek* | 25 |
| 11:50–12:10 | OP3 | Danilo Bersani (Italy) | |
| | | *Nondestructive investigation on the 6th century Lombard jewelry collection* | 27 |
| 12:10–12:30 | OP4 | Zoltan Pal (Romania) | |
| | | *From naturally occurring aragonite to Art Nouveau decorative objects: Corund deposit, Romania and it's Aragonite Museum seen by multi-laser micro-Raman spectroscopy* | 28 |
| 12:30–12:50 | OP5 | Simona Raneri (Italy) | |
| | | *Raman spectroscopy as a tool for provenancing black limestones (bigi morati) used in antiquity* | 30 |
| 12:50–14:00 | | **Lunch break** | |

**Session 3 – Raman spectroscopy in archaeology and paleoenvironment**

| | | | |
|---|---|---|---|
| | | **Keynote lecture** | |
| 14:00–14:40 | KL2 | Alessandro Vergara | |
| | | *On the production from furnaces in archaeological sites* | 35 |
| 14:40–15:00 | OP6 | Thomas Schmid (Germany) | |
| | | *Raman band widths of anhydrite II reveal the burning history of high-fired medieval gypsum mortars* | 36 |
| 15:00–15:20 | OP8 | Martin Ziemann (Germany) | |
| | | *Calcite-aragonite transitions of an alpine stalagmite from Central Switzerland studied by Raman spectroscopy* | 38 |

|  |  |  |  |
|---|---|---|---|
| 15:20–15:40 | OP9 | Juan Manuel Madariaga (Spain) |  |
|  |  | *The influence of sediments on some extracted iron nails from the recovered Urbieta shipwreck (Gernika, North of Spain)* | 40 |
| 15:45 |  | **End** |  |
| 17:00–19:00 |  | **Welcome reception** (Old Town Hall (Altes Rathaus) of Potsdam) |  |

**DAY 2 – 4 September, Wednesday**

**Session 4 – Development of Raman techniques, new Raman instrumentation**

|  |  |  |  |
|---|---|---|---|
|  |  | **Keynote lecture** |  |
| 09:30–10:10 | KL3 | Peter Vandenabeele (Belgium) |  |
|  |  | *Comparison of Mobile State-of-the-Art Raman Instruments and New Perspectives in Cultural Heritage Studies* | 45 |
| 10:10–10:30 | OP10 | Elmar Schmälzlin (Germany) |  |
|  |  | *Ultrafast Raman imaging of large-area samples without stepwise scanning applying an integral field spectrograph from astronomy* | 46 |
| 10:30–10:50 | OP11 | Anastasia Rousaki (Belgium) |  |
|  |  | *In or out the laboratory: A direct comparison of micro- and portable Raman spectroscopy on the analysis of Patagonian rock art (Argentina)* | 48 |
| 10:50–11:20 |  | **Coffee break** |  |

**Session 5 – Presentations by sponsors**

|  |  |  |  |
|---|---|---|---|
| 11:20–11:40 | OP12 | Marc Richter, Sponsor Renishaw GmbH (Germany) |  |
|  |  | *Renishaw InVia Raman microscopy - From Basics to Applications* | 53 |
| 11:40–12:00 | OP13 | Bernd Bleisteiner, Sponsor HORIBA Jobin Yvon GmbH (Germany) |  |
|  |  | *HORIBA Jobin Yvon an archaeological company? – Celebration of 200 Years History* | 54 |
| 12:00–12:20 | OP14 | Sponsor 3 |  |
| 12:20–12:40 | OP15 | Sponsor 4 |  |
| 12:40–14:00 |  | **Lunch break** |  |
| 14:00–16:00 |  | **Poster Session with coffee and soft drinks** |  |

**Session 6 – Chemometrics in Raman spectroscopy and Material characterization**

|  |  |  |  |
|---|---|---|---|
|  |  | **Keynote lecture** |  |
| 16:00–16:40 | KL4 | Barbara Łydżba-Kopczyńska (Poland) |  |
|  |  | *Fading in the spectroscopic determination of the age of ballpoint ink* | 57 |
| 16:40–17:00 | OP16 | Enrico Pigorsch (Germany) |  |
|  |  | *New Insights into Paper. Chemical Paper Analysis by Raman Microscopy* | 59 |
| 17:00–17:20 | OP17 | Oana Florescu (Romania) |  |
|  |  | *Determining the archaeometric and chemometric characteristics of the old documents. Paper and writing support* | 61 |
| 17:20–17:40 | OP18 | Adele Bosi (Italy) |  |
|  |  | *Identification of synthetic organic pigments in Gebrüder Schmidt printing inks by Raman spectroscopy – A case study* | 63 |

| | | | |
|---|---|---|---|
| 17:40–18:00 | OP19 | Marta Manso (Portugal) | |
| | | *The colours of the Power plant in* Levada de Tomar | 65 |
| 8:00 | | **End** | |

**DAY 3 – 5 September, Thursday**

**Session 7 – Material characterization and Conservation issues**

| | | | |
|---|---|---|---|
| | | **Keynote lecture** | |
| 09:30–10:10 | KL5 | Dalva L. A. de Faria (Brasil) | |
| | | *An unlikely Modigliani?* | 69 |
| 10:10–10:30 | OP20 | Anna Rygula (Poland) | |
| | | *The conservation of 18th century gun-powder horn with amber decoration: a top-down approach* | 71 |
| 10:30–10:50 | OP21 | Danuta Stępień (Poland) | |
| | | *Raman Spectroscopy in the Restoration of an* Our Lady of Czestochowa *Icon* | 73 |
| 10:50–11:20 | | **Coffee break** | |

**Session 8 – Material characterization and degradation processes**

| | | | |
|---|---|---|---|
| 11:20–11:40 | OP22 | Camila Mortari (Portugal) | |
| | | *Micro-Raman and X-ray fluorescence spectroscopy applied to the characterization of glazes from Portuguese azulejos* | 77 |
| 11:40–12:00 | OP23 | Javier Pinto (Spain) | |
| | | *Investigating glass beads and the funerary rituals of ancient Vaccaei culture (s. IV-II BC) by Raman Spectroscopy* | 78 |
| 12:00–12:20 | OP24 | Nurdan Yucel (Turkey) | |
| | | *Raman Identification, Compositional Characteristics and Degree of Deterioration in Ancient Komana Glass Bracelets* | 80 |
| 12:20–12:40 | OP25 | Kepa Castro (Spain) | |
| | | *Raman investigation for the understanding of a blackening phenomenon on late Gothic wall paintings* | 82 |
| 12:40 | | **Lunch break** | |

**Session 9 – Material characterization, Development of Raman techniques, SERS**

| | | | |
|---|---|---|---|
| | | **Keynote lecture** | |
| 14:00–14:40 | KL6 | Stephanie Zaleski (USA) | |
| | | *Characterization of the degree of crystallinity in zinc soaps with variable-temperature Raman spectroscopy* | 87 |
| 14:40–15:00 | OP26 | Klara Retko (Slovenia) | |
| | | *SERS-procedure in the heritage science by utilising photoreduced substrates based on HPC and silver nanoparticles* | 88 |
| 15:00–15:20 | OP27 | Daniela Reggio (Spain) | |
| | | *Multipurpose SERS substrates for nanodestructive detection of small molecules in collections* | 90 |
| 15:20–15:40 | OP28 | María Vega Cañamares (Spain) | |
| | | *FT-Raman, SERS and DFT analysis of safflower red dyed Japanese paper* | 92 |

| | | | |
|---|---|---|---|
| 15:40–16:10 | | **Coffee break** | |

**Session 10 – Material characterization and degradation processes**

| | | | |
|---|---|---|---|
| | | **Keynote lecture** | |
| 16:10–16:50 | KL7 | Armida Sodo (Italy) | |
| | | *Spectroscopic investigation of Cappadocia proto-Byzantine paintings* | 97 |
| 16:50–17:10 | OP29 | Ana I. Giraldo Ocampo | |
| | | *Micro-Raman Spectroscopy and Complementary Analytical Techniques for Material Characterization of Archaeological Mural Paintings at El Alto del Aguacate, Tierradentro Cauca, Colombia* | 99 |
| 17:15 | | **End** | |
| 19:00–23:00 | | **Conference dinner** (Restaurant in the Arcona hotel Potsdam) | |

## DAY 4 – 6 September, Friday

| | | | |
|---|---|---|---|
| 8:15–16:15 | | Excursion day | |

## DAY 5 – 7 September, Saturday (Conference site Campus Griebnitzsee)

**Session 11 – Material characterization, commercial pigments**

| | | | |
|---|---|---|---|
| | | **Keynote lecture** | |
| 09:30–10:10 | KL8 | Danilo Bersani (Italy) | |
| | | *Analysis of pigments by Raman spectroscopy* | 103 |
| 10:10–10:30 | OP31 | Christoph Herm (Germany) | |
| | | *Early 20th century commercial pigments from a manufacturer’s sample collection analyzed with Raman spectroscopy* | 104 |
| 10:30–10:50 | OP32 | Lavinia de Ferri (Norway) | |
| | | *Characterization of powdered pigments for pictorial retouching by Raman spectroscopy* | 106 |
| 10:50–11:20 | | **Coffee break** | |

**Session 12 – Material characterization and degradation processes**

| | | | |
|---|---|---|---|
| 11:20–11:40 | OP33 | Stefano Legnaioli (Italy) | |
| | | *New evidence for the intentional use of calomel as a white pigment* | 111 |
| 11:40–12:00 | OP34 | Teresa Madeira (Germany) | |
| | | *Tubes of paint used by Vieira da Silva (1908-1992): Application of Raman spectroscopy and complementary techniques* | 113 |
| 12:00–12:20 | OP35 | Eva Mariasole Angelin (Portugal) | |
| | | *A closer look at red in Portuguese historical plastics: a Raman microscopy study* | 115 |
| 12:20–13:00 | | **Discussion and concluding remarks** | |

| | | | |
|---|---|---|---|
| 13:00–14:00 | | **Coffee** | |
| 14:00 | | **End** | |

## Poster

# Session 1

# Material characterization and degradation processes

# Unexpected degradation mechanisms in cultural heritage

**Kepa Castro**

Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country (UPV/EHU), P.O. Box 644, 48080 Bilbao, Basque Country, Spain,
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**Keywords:**, pigments, Raman Spectroscopy, in-situ analysis, degradations.

The degradation mechanisms of cultural heritage are diverse and sometimes unknown. Fortunately, Raman spectroscopy has become in a very valuable technique to characterise the cultural heritage and to describe the degradation products and mechanisms that take place.

The threats faced by cultural heritage are complicated, with the need to study a large number of variables. Even if we consider that atmospheric pollution [1], together with wars, fires, catastrophic natural events and vandalism, is the most important factor of cultural heritage decaying processes, which promotes the precipitation of soluble salts, the degradation of pigments, the destruction of sculptures and mortars, etc, there are many others, such as the decomposition of corps, agricultural activities, the effects of animal depositions, biodeterioration due to microorganisms, biopatinas, incompatibility among original components, bleaching of the colour caused by the impact of ultraviolet radiation (light fastness), etc. However, it is usual to attribute many fading processes to air pollution and the ubiquitous acid rain. In any case, whatever the degradation is, Raman spectroscopy can be use to deduce its origin.

Another important factor of deterioration is the use of unsuitable conservation treatments, which at the beginning seem to conserve and preserve, but that become harmful with the past of time. This is due to undesirable ageing of conservation materials and even to unexpected chemical reactions between the conservation materials and original constituents. In the same way, the restoration works are, in many cases, used to mitigate the visible consecuences of the problems, but not to solve the problems that are causing the deterioration. This fact is tricky but unfortunatelly happens when an incomplete diagnosis has been done.

Independent of the cause threatening the cultural heritage, the use of Raman spectroscopy has become indispensable to obtain a good diagnosis.

**Acknowledgements.**

This work has been financially supported by MADyLIN project (BIA2017-87063-P) funded by the Spanish Agency for Research AEI (MINEICO/FEDER-UE).

**References.**

[1] Impacts of air pollution on cultural heritage corrosion at European level: What has been achieved and what are the future scenarios, Francesca Di Turo, Chiara Proietti, Augusto Screpanti, M. Francesc Fornasier, Irene Cionni, Gabriele Favero, Alessandra De Marco, Environmental Pollution, **2016**, 218, 586-594

# A Study of Copper Greens found on Yellow Coffins from the Egyptian Antiquities Department of the Louvre Museum

**Brunel-Duverger Lucile**[1,2,3], **Coquinot Yvan**[1], **Duranton Maroussia**[5], **Tremoureux Elie**[1], **Brodie-Linder Nancy**[3,4], **Pagès-Camagna Sandrine**[1,2]

[1] Centre de Recherche et de Restauration des Musées de France, Research Department, Paris, France, email : lucile.brunel@culture.gouv.fr
[2] PSL-PCMTH UMR8247 CNRS
[3] Laboratoire de Chimie Biologique, Université Cergy Pontoise, France
[4] Laboratoire Léon Brillon CEA, Saclay, France
[5] Institut National du Patrimoine, Restoration Department Laboratory, Aubervilliers, France

**Keywords:** copper green, egyptian pigment, spectroscopic analysis, altered materials.

Egyptian yellow coffins from the 21st Dynasty are a very specific production only found in the Theban area and reserved for the priests and priestesses of the Amon Temple. The study of these objects, which is part of the Vatican Coffin Project, targets the identification of all the materials used in the yellow coffins fabrication. The main goal of this venture is to determine the manufacturing processes in order to acquire a global view of the characteristics of production and then eventually to isolate specific workshops. For this purpose a methodological protocol has been developed at the Centre de Recherche et de Restauration des Musées de France. We are studying a dozen of the funerary sets, complete or not, of the Yellow Coffins from the Egyptian Antiquities Department of the Louvre Museum. The work on the 32 green samples has highlighted the complexity involved in identifying precisely by classical methods the chemical nature of the copper-green pigments.

The SEM-FEG imaging of green samples provides new information concerning texture layer and grain morphologies. Two morphology groups have been identified: 1) a compact mass of tiny grains less than 1µm (fig.1.a) and 2) grain remains between 2-5 µm and external crowns (fig.1.b). Both these textures suggest a pigment largely altered. It is well known that copper greens are quite unstable, and specific environments (salts, humidity and/or presence of organic materials [1, 2]) are conducive to their alteration. The first elementary analyses obtained by SEM-EDS showed in all cases, besides the presence of copper chlorides and copper sulfides, tin or lead traces. This last point suggests a synthetic extraction of copper from bronze scraps. In the literature copper chlorides newly formed are often proposed as the most stable phases.

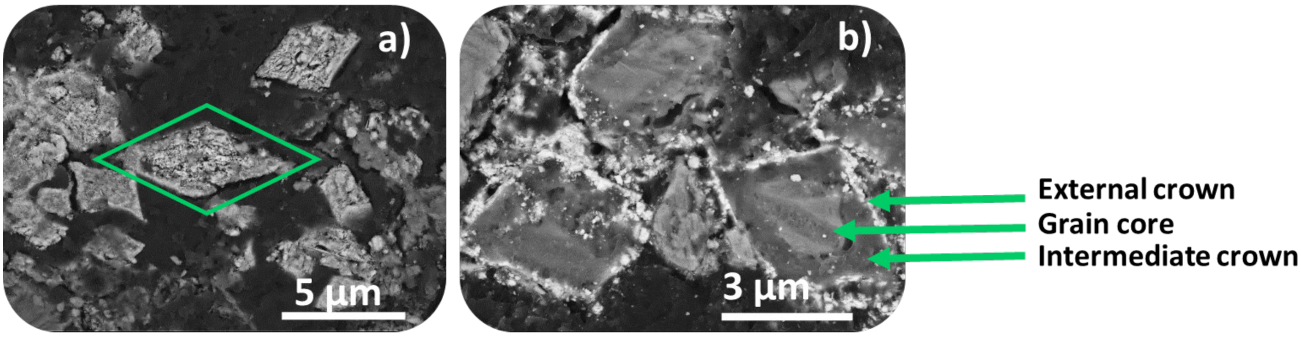

**Figure 1.** SEM-FEG imaging of green altered pigments (left) a) AF9590-Co5 observation of diamond shape grain remains composed of tiny grains ; (right) b) AF9593-Co4 observation of external crowns of degradation on diamond shape grains with compact cores.

However, other studies have not only shown the possible formation of copper-protein complexes, like copper-proteinate, but also the possibly alteration to copper oxalate [3, 4, 5]. The difficult point of this study lies in the fact that all these different materials listed are in the same range of colors between blue and green and are very close to the initial hue of our unaltered copper pigment. The visual identification of the altered areas is then not possible ; response that can only be achieved through analysis.

In order to address the identification complexity, assuming that we have organometallic materials, it was necessary for us to use vibrational techniques to go further and get complementary information about the precise chemical and structural composition of our complex green pigments. Direct measurement on micro-flakes using FT-IR analysis with an diamond ATR accessory gave us interesting first results indicating a possible existence of copper sulfates and chlorides with moolooite copper oxalates. This information has been confirmed by IR microscopy on cross-sections obtained using a specific sample preparation. This particular sample preparation allowed us to obtain their distribution with respect to each other. This technique has also provided data which was unexpected. Indeed, we also have detected the presence of calcium oxalate inside the white preparation layer. This coupling of IR methodologies has given precious information necessary for understanding the degradation processes taking place in the green layer. To go even further, we have prepared samples to imitate the copper compound mixtures in order to mimic alteration mechanisms and then to try to understand the degradation phenomenon.The µRaman spectroscopy applied to the laboratory samples confirmed our first assumption of initial green materials. All the data obtained and combined finally allowed us to propose the nature of the synthetic copper green used by egyptian craftsmen 3 000 years ago.

## Acknowledgements

This work is supported by the Fondation des Sciences du Patrimoine/EUR-17-EURE-0021. Thanks to the Egyptian Antiquities Department from the Louvre Museum.

## References

[1] Svarcova, Hradil, Hradilova, Koci, Bezdicka - Anal. Bioanal. Chem., **2009**, *Micro-analytical evidence of origin and degradation of copper pigments found in Bohemian Gothic murals*

[2] Gunn et al., Studies in Cons, **2002**, *Copper ions appear to play an important role in the degradation of the organic constituents in various layers of paintings, as well as of a number of materials such as wood, canvas, paper or leather.*

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# Session 2

# Material characterization and degradation processes

# Glass or gemstone? − A systematic review of the jewelled bindings from the collections of the Bayerische Staatsbibliothek

**Thorsten Allscher**[1]

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**Keywords:** gemstone analysis, jewelled bindings

A number of world-famous gospel books with jewelled bindings which are kept in the collections of the Bayerische Staatsbibliothek. These bindings are known not only for their outstanding goldsmith work, but also for their rich gemstone stocking. Over the centuries, the bindings have been damaged, restored and reworked, so that only in rare cases the original set of gemstones is present. In other cases, glass stones were already used in the production, as matching gems were obviously not available.

The Codex Aureus (Clm 14000), the jeweled book box of the Uta Codex (Clm 13601), the Evangeliary of Henry II (Clm 4452), the Gospel book of Otto III (Clm 4453), the Reichenau Gospel book (Clm 4454) or the Gospel book from Wessobrunn (Clm 22021) and other famous books with jewelled bindings have been systematically investigated. All the gemstones were analyzed by Raman spectroscopy, glass replacements were revealed and the gemstones were identified by comparison with the RRUFF database [1].

**Figure 1.** Four examples from the jewelled bindings of the Bavarian State Library: A crystal clear sapphire, a barely recognizable doublet, a glass stone and a calcedon to imitate a sapphire.

In Figure 1 four examples of “gemstones” are shown that can mislead the viewer when only investigated visually. Raman spectroscopy was an indispensable tool for identifying the true nature of the gemstones. Not only for the subdivision of glass or mineral the Raman spectroscopy was helpful, also a more accurate determination of the gems could be made as shown in figure 2.

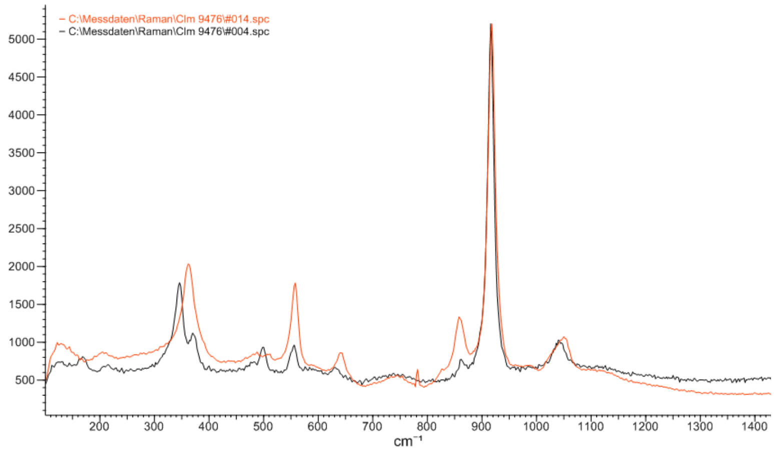

**Figure 2.** The identification of garnets, pyrope and almandine.

The lecture should not only present the results of the systematic investigation but also discuss the reliability of the results of the identification via a database as a function of the spectral quality. Also, the project database of the Bayerische Staatsbibliothek will be presented in which every single Raman spectrum is registered to the measured gemstone on the binding and can be downloaded in the JCAMP-DX format.

## Acknowledgements

This work was funded within the project "Digitization and Cataloguing of Book Covers as autonomous objects d'art" by the Deutsche Forschungsgemeinschaft (DFG).

## References

[1] B. Lafuente, R.T. Downs, H. Yang, N. Stone, *The power of databases: the RRUFF project. Highlights in Mineralogical Crystallography,* T. Armbruster and R. M. Danisi, eds. W. De Gruyter: Berlin, **2015**, p. 1-30.

# Nondestructive investigation on the 6th century Lombard jewelry collection

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**Keywords:** Raman spectroscopy, portable instrumentation, X-Ray fluorescence, jewels

A Lombard treasure in form of grave goods was found during archaeological excavations in Lodi Vecchio (North of Italy). It is a very important finding for its historical value and the preciousness of its items, dated the end of the VI century and now preserved in the archives of Superintendence of Milan. As a symbol of the Lombard culture, it includes many pieces of jewelry, like necklaces and pendants, gold objects as coins and a cross and a couple of impressive blue glass drinking horns. The findings were analysed *in situ* using portable instrumentation: Raman spectroscopy with two different excitation wavelengths (785 and 532 nm), and X-ray fluorescence (XRF). The goal was the identification of the materials, including gems, minerals, glasses and metals, to catalogue the Lombard treasure for its exhibition in the *Laus Pompeia* Museum (Lodi Vecchio, Italy). Results show the presence of quartz, chalcedony and other more precious minerals and stones like lapis lazuli. The analyses of the golden pendants, realized with the cloisonnè technique, underline the amazing talent of Lombard goldsmiths. The Raman spectra of the red stones present in the pendants show typical signals of garnets with very similar composition for all the stones (around 70% almandine and 30% pyrope) suggesting a common provenance. Among them, a red fragment, cut to imitate a garnet, is identified as a "fake" as its spectrum shows the characteristic glass features. Drinking horns and other glasses were analysed. They have similar chemical composition and structure and can be classified as soda-lime glasses, little polymerized and low-melting. The results suggest that this grave and its findings could have belonged to a rich family, buried in the most significant place of the town, near the Episcopal palace and cathedral. Combining a molecular technique (Raman spectroscopy) and an elementary technique (XRF) in portable modes, it was possible to characterise all the materials (amorphous as well as crystalline) present in the trousseau. This work underlines the importance and the advantages to use complementary and portable techniques to study archaeological items with a high historical value that cannot be moved or sampled. Using two Raman instruments with two different laser wavelengths showed that the 532 nm laser yielded for these materials (in particular silicate gems) superior results, compared to 785 nm.

# From naturally occurring aragonite to Art Nouveau decorative objects: Corund deposit, Romania and it’s Aragonite Museum seen by multi-laser micro-Raman spectroscopy

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**Keywords:** aragonite, calcite, Corund deposit, multi-laser micro-Raman spectroscopy, semiprecious stones analysis, Aragonite Museum of Corund

Coexistence of calcite and aragonite polymorphs in naturally occurring carbonate rocks from a famous aragonite deposit in a protected area in Corund, Romania was subject of few controversial, early studies, yet uncompleted according to the current standards [1],[2].

A unique aragonite exploitation facility founded by Czech engineer Knop Vencel at the beginning of twentieth century gave rise to small aragonite decorative objects production facility, employing fine polishing of various coloured carbonate mineral resources (Fig. 1). Despite the difficulties caused by two world wars and the economic recession, it succeeds to maintain production of decorative and household objects in Art Nouveau ornamental style. Aristocracy, politicians, royal families, advocates, doctors, churches were ordering customized aragonite products. Unfortunately, the communist regime declined all the extraction and polishing activity by nationalization and unprofessional exploitation of the unique local carbonate resources. Currently, a small, but deeply thematic Aragonite Museum is running in the original building of the former factory, and expose for public a collection that is continually enriched with creations from the former Corund Factory and other aragonite pieces collected around the world.

The criticism raised the question on the aragonite identity and suggested that the deposit is actually calcite [3]. A further opinion on the available calcite-aragonite mineral has been released supported by mineralogy techniques [4].

Accurate information on the local mineral deposit and objects composition and polymorphism has been recently obtained employing multi-laser micro-Raman spectroscopy and imaging on representative and systematic samples collected in the area.

Figure 1. Left:The panoramic interior of the Aragonite Museum of Corund, Romania (upper) and several exposed objects. Right: A naturally occuring mineral showing joint regions of aragonite (white) and calcite (grey).

To be able to get insight into the geochemistry of the region, a comprehensive and systematic Raman spectroscopy study is underway to unveil the spatial diversity of the local

Corund carbonate deposits (coexistence of aragonite-calcite polymorphs in a reduced spatial range). Additionally, Raman methods elucidated the nature of various coloured minerals from the exploited rocks and the objects exposed in the Aragonite Museum. An example of Raman signal collection within 1 s and its dependency on the excitation wavelength, collecting optics and applied power on a white aragonite counterpart from a mixed rock is showed in the Fig. 2.

Carbonate minerals polymorphs of $CaCO_3$ are easily identified according to their characteristic Raman feature in the low wavenumbers range. The symmetric bending mode of carbonate ion occurs as a distinct band at 712 $cm^{-1}$ in calcite and as a doublet at 701–706 $cm^{-1}$ in aragonite [5], [6].

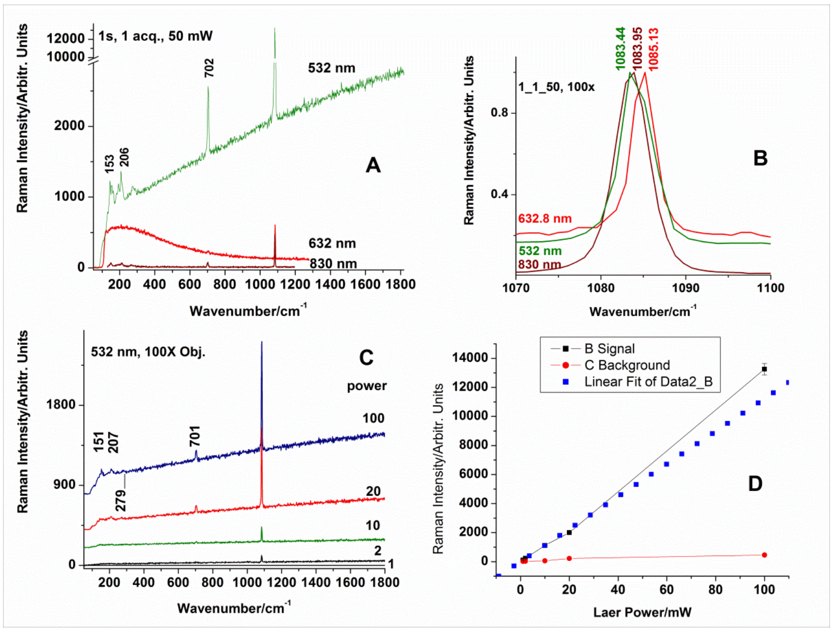

Figure 2. Wavelength excitation dependence Raman spectra of naturally occurring aragonite from Knop Vencel's first quarry in Corund area, Romania A); slight variation of the carbonate stretching mode (B); Raman signal dependency on the applied laser power (C) and the plot of signal and background intensity against applied power (D) for the 532 nm line. Exposure time was 1s in all the measurements.

Raman excitation profile, collecting optics and laser excitation power, all influenced the decision-making when it comes about correct identification of naturally occurring carbonate minerals sometimes covered with biofilms.

Field measurements of the decorative objects need a strong experimental background to identify the proper excitation power, optics and excitation profiles for non-destructive field use of Raman spectrometer.

Detailed spectroscopic data of several decorative objects (one ordered by the last Romanian Queen, Maria de Edinburgh) hosted in the Aragonite Museum in Corund, Romania will be discussed.

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# Raman spectroscopy as a tool for provenancing black limestones (*bigi morati*) used in antiquity

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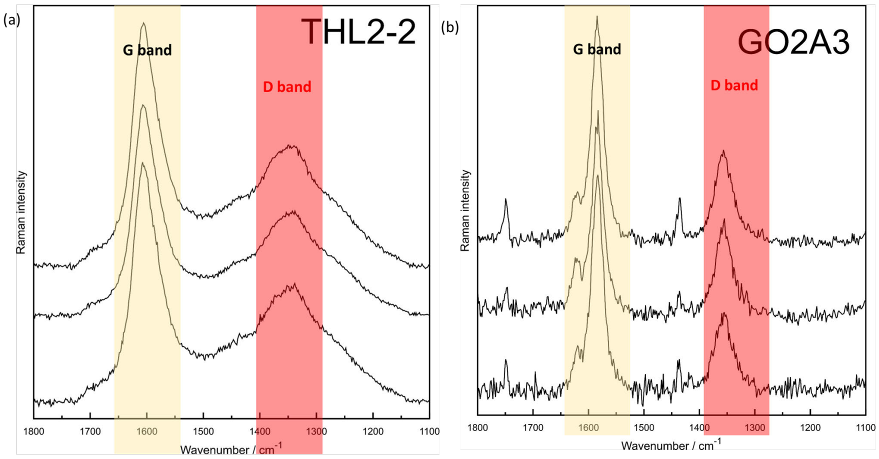
**Keywords:** *bigi morati*, black limestone, carbon, Raman spectroscopy, provenance

The use of black stones in antiquity has often been associated with symbolic meanings such as those connected to funerary practices (tombs, stelai, etc.), and in representing African men and animals (sculptures), as well as in contrast colouring of architectural elements (columns, capitals., bases, *opera sectilia*, mosaics). Among the many different types of stones employed in classical times for such purposes, limestones (*bigi morat*i) were by far the most used materials, followed by true black marbles (*bigi antichi*). Both lithotypes, often referred as *neri antichi,* are not easily distinguished autoptically, especially if the surface of their artifacts is covered (as is very frequent) by a pervasive grey natural patina. The Greeks in the Hellenistic period, and the Romans in Imperial times opened many limestone quarries throughout the Mediterranean provinces, the most important being located in Italy (e.g. in the Tolfa area, Latium), Greece (in Peloponnesus, especially in the Mani peninsula and in the island of Chios), North Africa (in Tunisia, such as at Ain el Ksir, Djebel Aziz, Thala, etc.), and Asia Minor (in Adapazari, ancient Bithynia, and Ionia). Most of the limestones quarried in these sites have been so far only preliminarly archaeometrically characterized, so that the provenance determination of ancient artifacts, an high demanding question in archaeological documentation, is now quite difficult.

The creation of a reference database and analytical criteria able to positively discriminate black limestone is a must in the light of the scientific debate. Unlike white marbles, for which an extensive literature provides minero-petrographic and isotopic methods for provenancing [1], the availability of data on black limestones from ancient quarries is currently not exhaustive [2]. A first attempt of multidisciplinary database is represented by a complete petrographic, isotopic and electron paramagnetic resonance (EPR) study on black limestones from some of the geographic locations mentioned above [3], whereas another dataset has more recently concerned the *neri antichi* from the Göktepe area, in Turkey [4]. However, the material characterization is always based on the use of micro-destructive methods, limiting the application of the proposed discrimination criteria in the case of very valuable artifacts for which sampling is normally difficult to obtain.

In this respect, Raman spectroscopy offers a challenging opportunity in non-destructive studies of objects made of black limestones. Bearing organic, carbonaceous matter conferring them the typical black-dark grey color, the Raman features of its D and G bands might provide information on the geological origin and history of the limestones. In fact, the Raman spectrum of carbonaceous matter provides valuable information of geological relevance allowing to describe carbon structure and possible presence of structural defects [5].

In this paper we present the preliminary results of a methodological approach based on Raman spectroscopy analysis of carbon in black limestone for provenance determination. Raman spectra, collected in the range 1000-1800 $cm^{-1}$ by using a Raman microspectrometer equipped with a 514.5 nm excitation, were exploited to inspect disordered carbon or defective graphitic structures in some Greek, Numidian and Microasiatic black limestones, previously characterized from the petrographic and mineralogical point of view. The obtained results indicated that Raman spectroscopy may be an effective tool for provenance discrimination of *bigi morati*; actually, experimental data suggest that G and D bands spectroscopic features, (I)D/(I)G Raman ratio and FWHM(G) and FWHM(D) values varies with provenance (Fig. 1), assessing a possible discrimination criteria among black limestones in non-destructive and non invasive way.



*I(D)/I(G) = 0.8; FWHM(D) = 188.9; FWHM(G) = 59.9; FWHM(D)/FWHM(G) = 3.2*    *I(D)/I(G) = 0.9; FWHM(D) = 39.4; FWHM(G) = 23.3; FWHM(D)/FWHM(G) = 1.7*

**Figure 1.** Raman spectra collected on (a) North African and (b) Microasiatic black limestones, exhibiting different Raman fingerprint, (I)D/(I)G Raman ratio, FWHM(G) and FWHM(D).

The initial research results therefore encourage the enlargement of the existing dataset in order to provide reference data on a larger number of samples from other Mediterranean sources

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# Session 3

# Raman spectroscopy in archaeology and paleoenvironment

# On the production from furnaces in archaeological sites

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**Keywords:** Furnaces, lime, ceramics

The knowledge on the material production from archaeological sites contains valuable information on the technological advances and on the commercial routes of a civilization. Archaeologists can face some ambiguities in the assessment of the productive function of furnaces emerging from excavation. An easy non-destructive protocol to discriminate among production of lime, ceramics or metals is the aim of this work. Indeed, the work addresses the possibility to assist archaeologists in a vibrational spectroscopy-based identification of the production from furnaces. Reference cases of well-known productive function were used to identify the best vibrational markers of productive and technological interests. The analysis was applied to two unknown cases of interest form Velia [1] and Roscigno [2] (South Italy), archeological sites below briefly introduced.

Velia is a Greek colony, in southern Italy, which in Roman age retains its importance for the productive and commercial activities along the Tyrrhenian coasts. The furnace analyzed is built, perhaps in the middle or late Imperial age, on the fortification of the Hellenistic age.

Roscigno is an ancient settlement in the innermost area of Cilento, in a position dominating the routes connecting Paestum and the Tyrrhenian coast to the Vallo of Diano; dated from the first half of the seventh until third century BC.

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# Raman band widths of anhydrite II reveal the burning history of high-fired medieval gypsum mortars

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**Keywords:** analytical methods, gypsum dehydration, high-fired gypsum mortar, thermal anhydrite, Raman band width determination

The use of high-fired gypsum as binder for masonry and joint mortars or stuccowork in Central Europe in the Early and High Middle Ages was a regional specific as it depended on local gypsum deposits. The calcination technology possible at the time resulted in an assemblage of calcium sulphate phases dehydrated to different degrees and partly thermally damaged accessory minerals of the raw gypsum. Because of the absence of medieval textbooks, the observation of high-temperature, low-pressure mineral transformations and the correlation of phases coexisting in not hydrated binder relicts in the gypsum matrix to the mineralogy of the raw material and the burning conditions constitute the only source to the historical technological know-how.

The $CaSO_4$–$H_2O$ system consists of five crystalline phases, which can be discriminated by structural analysis methods, such as Raman spectroscopy, due to obvious differences in their spectroscopic data: gypsum ($CaSO_4 \cdot 2\ H_2O$), bassanite (hemihydrate, $CaSO_4 \cdot \frac{1}{2}\ H_2O$), anhydrite III ($CaSO_4$), anhydrite II ($CaSO_4$), and anhydrite I ($CaSO_4$). Only recently, it was possible to demonstrate that small spectroscopic variations exist also within the relatively large stability range of anhydrite II from approx. 180°C to 1180°C: all Raman bands narrow with increasing burning temperature applied in the synthesis from gypsum powder [1]. The determination of band widths of down to 3 $cm^{-1}$ and differences between them of a few tenths of a wavenumber is not a trivial task. Thus, this contribution discusses peak fitting and strategies for correction of instrument-dependent band broadening [2].

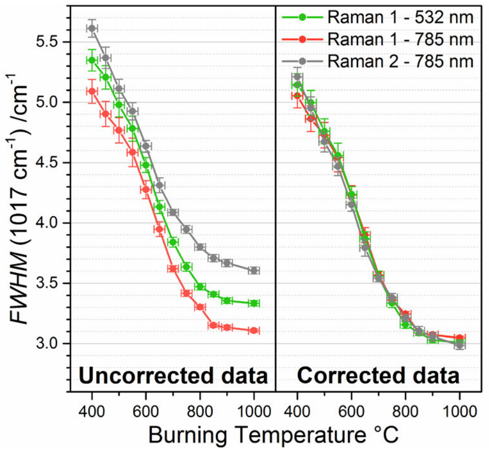

**Figure 1.** Full widths at half maximum (*FWHM*s) of the most prominent band at 1017 $cm^{-1}$ in the room-temperature Raman spectra of anhydrite II after burning from gypsum at different temperatures. Data measured with two different instruments and excitation wavelenghts, and shown prior to (left) and after correction of instrument-related band broadening (right) [2].

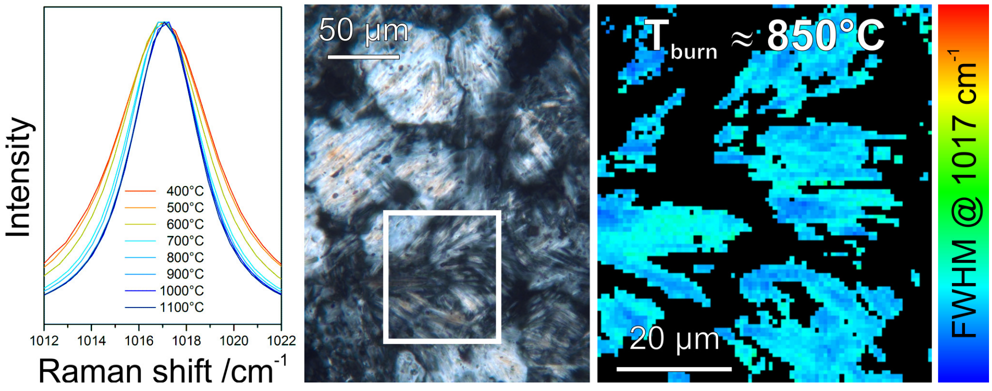

**Figure 2.** Shape of the most prominent Raman band of anhydrite II as a function of burning temperature (left), polarised light micrograph (crossed Nicols) of a cluster of firing products in a high-fired medieval gypsum mortar (centre), and Raman band width distribution map of the highlighted area (right). The mean band *FWHM* relates to a burning temperature of approx. 850°C [3].

Raman maps of polished thin sections of gypsum mortars provide access to the burning histories of individual remnant thermal anhydrite grains and enable the discrimination of natural anhydrite originating from the gypsum deposit. This novel analytical method was applied to samples from medieval South Tyrolean stucco decorations and sculptures. Beyond that, Raman microspectroscopy was employed for following pyrometamorphic reactions in natural impurities of the raw material. In the presented examples mineral thermometry indicates process temperatures above 800°C: the breakdown of magnesium-rich chlorite led to the formation of forsterite $Mg_2SiO_4$, while the thermal decomposition of dolomite $CaMg(CO_3)_2$ yielded – after hydration and carbonation – magnesite $MgCO_3$, $CaCO_3$ polymorphs and magnesian calcite. Lower burning temperatures, which leave the accessory minerals in their pristine form, can be traced by measuring the spectra of anhydrite crystalites in grains of firing products and evaluating Raman band widths. Throughout the applications of this analytical method so far, calcination temperatures ranging from approx. 600°C to 900°C were determined [3].

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# Calcite-aragonite transitions of an alpine stalagmite from Central Switzerland studied by Raman spectroscopy

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**Keywords:** stalagmite, calcite-aragonite transition, Raman mapping

Stalagmites can be precisely dated by means of U-Th disequilibrium methods which make them an valueable archive to investigate climate variability. They can grow up to several thousands of years, their climate information is well preserved due to their protected environment. Generally, a large toolbox of common proxies is available to reconstruct climate variability. The absolute values of the proxies depend on the speleothems polymorph, which is commonly calcite (Cal) or aragonite (Arg) [1].

In this work, we investigate the potential of a new proxy to decipher climate information from Cal to Arg transitions in a stalagmite found in a cave of the northern rim of the Swiss Alps. This stalagmite is already well investigated in terms of its U-Th based chronology and its stable isotope composition [2]. The Cal-Arg transitions occurred along the growth axis and laterally, along individual growth layers. Especially the lateral type of transitions occurs only very rarely in natural carbonates. However, they provide the potential to study the mechanisms responsible for the polymorph change during precipitation from carbonate containing solutions. In contrary, transitions along the growth axis enable to study the water film thickness of speleothem surfaces during growth. We applied high resolution Raman spectroscopic mapping on the Cal-Arg transitions [3].

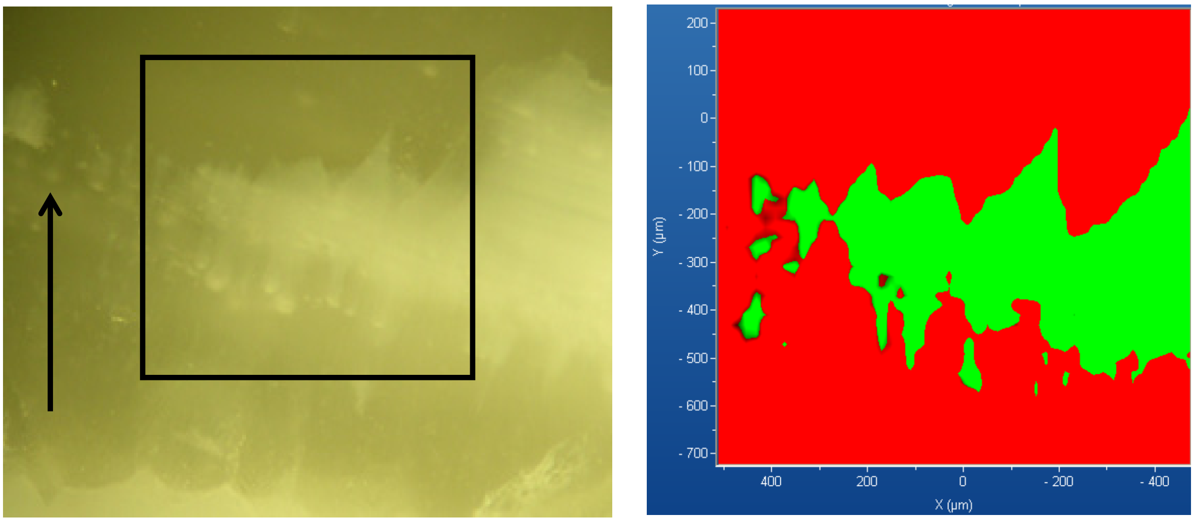

**Figure 1:** (left) Detail of the stalagmite using oblique illumination (field of view 2 mm x 2 mm). The arrow indicates the growth direction. The growth axis of the stalagmite is to the left. (right) Raman map of this area (1000 µm x 1000 µm in overview mode with 20 µm step width. Colour coding: red: calcite, green: aragonite).

The Raman maps (Fig. 1) reveal that Arg-Cal transitions occur abruptly, starting from single Cal nucleation seeds within a closed Arg layer and spreading fan-like in growth direction to build within less than ~50 µm a closed Cal layer. Transitions from Cal to Arg occur not as abrupt as the Arg to Cal transitions, as single Cal structures seem to stop growing at various locations and are replaced by Arg needles. The high resolution maps with 3 µm step width indicate that water film thickness was at least ~ 200 µm, which is about double of the generally accepted value.

## Acknowledgements.

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# The influence of sediments on some extracted iron nails from the recovered Urbieta shipwreck (Gernika, North of Spain)

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**Keywords:** Archaeological samples, Underwater Cultural Heritage, Raman Spectroscopy, iron, Raman Spectroscopy.

Cultural Heritage often brings to mind artefacts like sculptures, paintings, monuments and buildings as well as archaeological sites. Today, Underwater Heritage and the natural environment are also considered part of cultural heritage since communities identify themselves with the natural landscape. “Underwater Cultural Heritage” means that there is a cultural, historical or archaeological value, which has been partially or totally underwater, periodically or continuously, for at least 100 years[1].

This is the case of a shipwreck, belonging to the second half of the 15th century that was discovered in 1998 by chance in the sediments of the Urdaibai estuary, in Urbieta near Gernika (Basque Country), at 4 meters underground[2]. The scientific study presented in this work was considered important as this archaeological site is absolutely out-of-context and our aim was to shed light on it. Pursuing this objective, a first analysis on three selected groups of iron nails from the Urbieta shipwreck, which are currently preserved in the Archaeological Museum of Bilbao, was performed. Those nails were grouped as a function of the classical conservation treatments on archaeological iron objects: (a) the group of the no-treated nails, (b) those treated with tannic acid, and (c) those with polyethylene glycol (PEG). By analysing these three groups of samples, our aim was to define the raw materials used, to identify possible degradation problems and to assess the performance of the applied treatments. To our surprise, an unexpected element was observed around the corroded body of the three groups of nails, Zn. The common features are shown in Figure 1 (a sample treated with PEG) showing also some of the unexpected mineral phases. Zinc is only observed in the outer layer of the iron samples, but it is not metallic. Actually, Raman spectroscopy confirmed the presence of zinc hydroxides and sulphates.

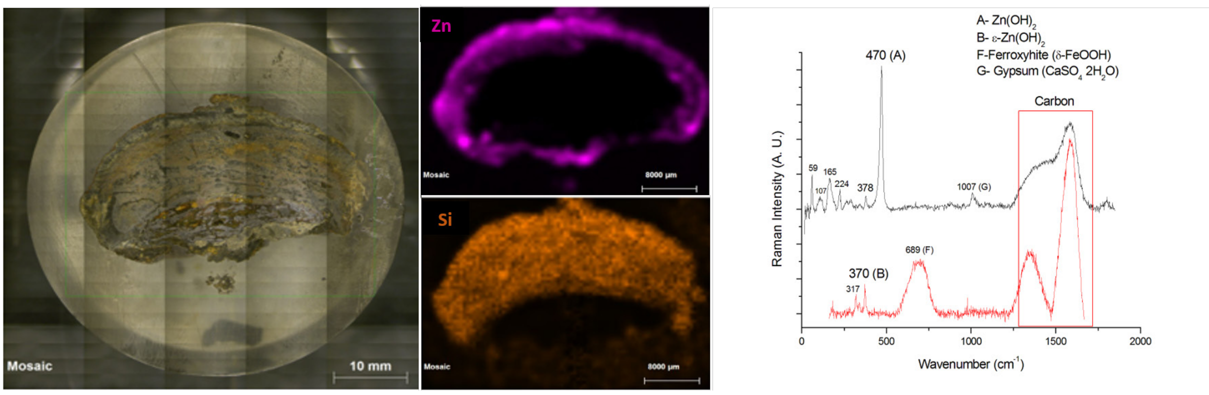

Fig. 1 – The extracted nail treated with PEG together with wood (left), XRF images showing the presence of zinc and silicon around the nail (middle) and Raman spectra (right) from outside (black) and inside(red).

Moreover, the presence of silicon is around the less corroded part of the nail. We obtained some features of silicates (clays), amorphous carbon and gypsum, clearly indicating an important impact of the contaminated sediments deposited in the last 80 years (coming from the industrial activity upstream of the river in the Gernika area [3] ) on the upper part of the burial in which the shipwreck was located.

Some results obtained from the untreated nail are shown in Figure 2, where selected Raman Spectra are included along with the distribution of Fe, S and Zn by X-Ray Fluorescence Spectroscopy. In these images a small area of concentrated Fe (without S nor Zn) is observed in the central-down part of the sample, suggesting the presence of less corroded iron. However, the main body is non-compact in iron indicating the presence of other elements. Sulphur is wide spread distributed (rozenite was systematically detected) although is more concentrated outside the nail, as two different zinc sulphates, gunningite ($ZnSO_4 \cdot H_2O$) and Goslarite ($ZnSO_4 \cdot 7H_2O$) in the areas where zinc is located. Besides, carbon, gypsum, calcite, pyrite ($FeS_2$) and marcasite (orthorhombic $FeS_2$) were detected.

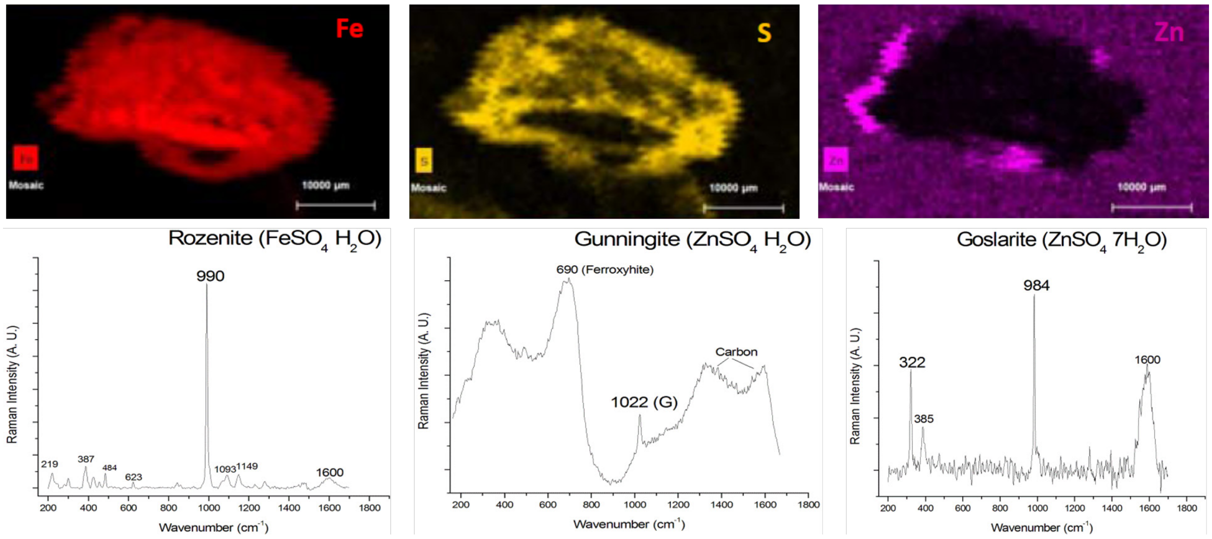

Fig. 2. Three XRF images of a non-treated nail (Fe, S and Zn) together with some selected Raman spectra.

Literature refers that nails from the subaquatic site differ from the terrestrial burials by the presence of pyrite globules in the iron body [4]. The presence of organic matter (wood from the shipwreck) is assumed as the source of sulphur. Moreover, the formation of iron sulphides (marcasite and pyrite) can also be explained by the presence of sulphate-reducing bacteria in the sediments that are able to transform the sulphates, coming from the upper parts of the burial, into iron sulphides by reaction with ferrous cations produced during the anodic dissolution of the nails [5] .

With regard to the preservation issue, it was observed that samples treated with tannic acid shown a lower amount of degradation compounds, suggesting that it could be the best conservation procedure.

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# Session 4

# Development of Raman techniques, new Raman instrumentation

# Comparison of Mobile *State-of-the-Art* Raman Instruments and New Perspectives in Cultural Heritage Studies

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**Keywords:** Raman spectroscopy; mobile spectrometers; cultural heritage; *in situ*; non-destructive

Nowadays, Raman spectroscopy is considered to be one of the first choice techniques for cultural heritage studies. Although micro-Raman spectroscopy, performed with benchtop Raman instruments, is a well established technique, it often requires samples to be taken from the artefact and positioned under the Raman microscope. From the analytical point of view investigations performed with laboratory instruments yield high quality results, although the work of art is jeopardised and possed under risk. The need for conducting non-invasive and non-destructive analysis, positioned mobile spectrometers on the forefront of Raman analysis. Indeed, the number of studies performed with mobile Raman instruments has increased during the last years. These include research on a variety of artistic works from prehistory to mediaeval times, to Renaissance, to modern art and to contemporary street art.

Technological advantages shaped Raman spectroscopy and produced a variety of approaches. These approaches or techniques were designed primarily for benchtop instruments, but today they are successfully implemented on mobile Raman spectrometers. Over the coarse of the years, mobility of the Raman systems became essential. Therefore, Raman spectrometers, became compact and light-weighted, with a miniaturised geometry including advanced software to ease the measuring procedure.

The advantages and possible drawbacks of progressing to mobile Raman analysis, and as a consequence from the laboratory to the field, will be discussed and illustrated with several examples from field campaigns.

**Acknowledgements**

Anastasia Rousaki greatly acknowledges the Research Foundation–Flanders (FWO-Vlaanderen) for her postdoctoral fellowship, number 12X1919N.

# Ultrafast Raman imaging of large-area samples without stepwise scanning applying an integral field spectrograph from astronomy

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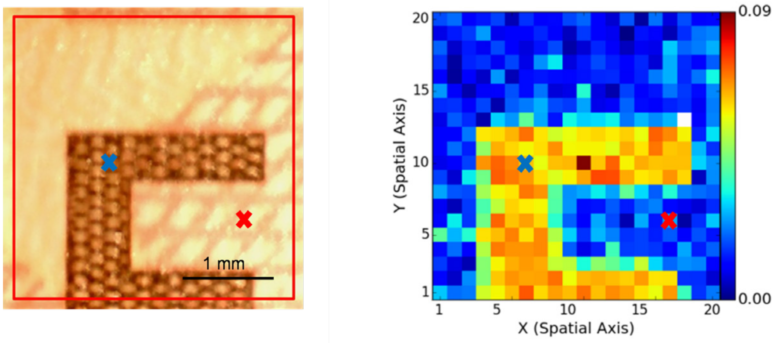
**Keywords:** imaging Raman, multichannel astronomy spectrographs

Time consuming step-by-step scanning of the sample is still common in imaging Raman spectroscopy. A radical decrease in measurement time can be achieved by applying multichannel spectrographs that are successfully used in astronomy to save scarce observation time at observatories. These high-performance spectrographs are capable to record thousands of spatially resolved spectra of a two-dimensional image field within one single exposure. Transferring this technology to imaging Raman spectroscopy allows a considerably faster acquisition of chemical maps.

The function principle of a multiplex spectrograph, also called integral field spectrograph, is slicing the image. This can be done by use of a fiber optic cross section converter. At the image plane on the sample side, the fiber front surfaces of a fiber bundle are arranged in a two-dimensional array. At the spectrograph's input, the fibers are rearranged in a one-dimensional row forming a pseudo slit. Every fiber represents a certain pixel in the image plane and produces an individual intensity- and spectrum-dependent light trace at the CCD chip. A software converts the CCD signal into a data cube that contains the entire spectral and spatial information. The setup works in essence as if every single fiber were connected to an individual single-channel spectrograph, i.e. the entire image can be captured within one single shot without any scanning procedure.

The unique fast acquisition speed makes this technique promising for medical diagnostics within the daily routine of a hospital. In cooperation with the Charité University Medicine Berlin, a research project for skin cancer detection was completed successfully [1]. In addition, this method was applied to a series of non-biological samples, e.g. plastic particles or printing ink (Fig. 1) [2].



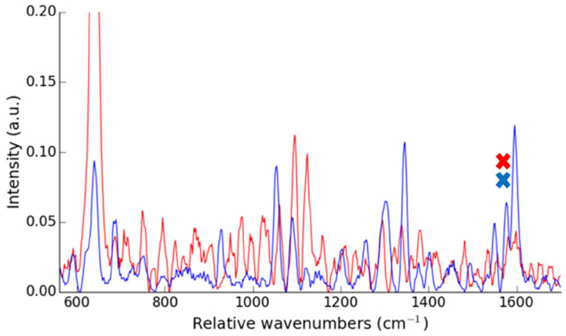


**Figure 1.** Part of the letter “E” printed on a EUR 10 bill. Upper left: camera picture. Upper right: pseudo color Raman image of the intensity at 1576 cm$^{-1}$, which corresponds to the distribution of the printing ink of the “E”. Below: Corresponding Raman spectra at positions ✖ and ✖. The background was removed by applying shifted excitation differential Raman spectroscopy (SERDS). Excitation at 784.5 nm and 785.5 nm. The spectra of the entire sample were recorded within 2 × 10 s without any scanning procedure. Figure reprinted from [2].

## Acknowledgements

This work has been financially supported by German Federal Ministry of Education and Research (BMBF) VIP program, “Multiplex-Raman-Spektroskopie” (MRS), Grant No. 03V0843, and the Zwanzig20 program, grant no. 03ZZ0423.

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# In or out the laboratory: A direct comparison of micro- and portable Raman spectroscopy on the analysis of Patagonian rock art (Argentina)

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**Keywords:** micro-Raman spectroscopy; mobile Raman systems; pigments; degradation; rock art paintings

Rock art studies consist of the collective efforts of various disciplines to analyse, document and interpret one of the earliest human (artistic) creations. From the analytical point of view, Raman spectroscopy - a well-established vibrational spectroscopic technique - is extensively used for the physicochemical characterization of pigments, substrata and degradation products found in prehistoric rock art paintings.

Both, micro-Raman spectroscopy and mobile Raman spectroscopy, have been applied on a variety of rock art paintings located around the world. In the case of rock art paintings found in the Argentinian part of Patagonia, paintings from rock shelters and caves were extensively discussed in literature, together with the applicability of Raman spectroscopy for the study of these outstanding works of art [1-3].

Here, a comparison between the results retrieved from rock art paintings with micro-Raman spectroscopy and with mobile Raman spectroscopy is considered. The case study is based on samples/paintings located in the Piedra Parada Valley of the Chubut province in the arid environment of the steppes. Data collected with Raman microscopy from a 1996 and a 2016 sampling campaign are compared with the results from an extensive *in situ* Raman spectroscopy campaign (2016).

The outcome of this research has three main targets: (a) to identify and document the colourful pigmented layers-white, red, yellow, green, black-of shelters from Chubut province (b) characterize possible weathering compounds and (c) compare the Raman approaches as a direct result of working in and out the laboratory, without jeopardising the artefact. For the latter, *state-of-the-art* Raman spectrometers can be proved powerful tools towards the non-invasive analysis of rock art paintings.

## Acknowledgements

Anastasia Rousaki thanks the Research Foundation–Flanders (FWO-Vlaanderen) for her postdoctoral fellowship, number 12X1919N and the travel grant for a short stay abroad, project K204416N. The authors are greatly acknowledge for their financial support the Ghent University, through the concerted research actions programme (GOA), Consejo Nacional de Investigaciones Científicas y Tecnicas (PIP 365). Emilio Eugenio (IMHICIHU, CONICET) and Lisandro Lopez (UBA) are also acknowledged.

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# Session 5

# Presentations by sponsors

# Renishaw InVia Raman microscopy

From Basics to Applications

Dr. Marc Richter

Renishaw GmbH, Germany

Raman spectroscopy, a non-destructive, label-free vibration spectroscopy technique, enables the analysis of samples in a very brought variety of research areas. Starting from Nanotechnology (single carbon wall nano tubes) to biological research (single cell analysis), it also is involved in electrochemistry research (battery efficiency research) and health care (diseases and/or cancer detection). Depended on the research topic specific system modifications can be performed.

This presentation will present the latest developments in Raman spectroscopy. Including innovations to allow imaging over rough or undulating surfaces by using its LiveTrack™ technology. Several examples will be presented demonstrating the ability to obtain high quality Raman images with minimum sample preparation. This method eliminates the need section or polish potentially valuable samples expanding the use of Raman imaging in the field of historic artefacts like the Terracotta Warriors and Horses of the First Qin Emperor.

The Terracotta Warriors and Horses of the First Qin Emperor

# HORIBA Jobin Yvon an archaeological company? Celebration of 200 Years History

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**Keywords:** Raman instrumentation, painting analysis

In 2019 HORIBA Jobin Yvon celebrates its 200th anniversary. The presentation gives an compact overview of the company's history beginning in 1819. In doing so, a strong focus will be placed on the history of Raman instrumentation provided by the company since the introduction of the first microscope based Raman instrument in 1976.

In the further course of the presentation some recent results of artefact analysis done at the Victoria and Albert Museum in London are discussed. These results were kindly provided by Dr. Lucia Burgio working with an XploRA Raman microscope on the Leman Album [1] and a Barniz de Pasto cabinet [2].

**Figure 1:** The Leman Album (E.1861-1991) © Victoria and Albert Museum, London

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# Session 6

# Chemometrics in Raman spectroscopy and Material characterization

# Fading in the spectroscopic determination of the age of ballpoint inks

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**Keywords:**, ink dating, chemometric, fading, Raman, UV-Vis reflectance spectroscopy

Differentiation and dating is one of the current challenges of forensic studies. The method of determination of the age when the ink was deposited on the paper became the most frequently discussed issue referring to fraudulent documents analysis. There are several analytical methods used in the identification of ink and the processes involved in their ageing on paper including Raman spectroscopy, ATR, gas chromatography of residual solvents, UV-VIs absorption, chromatographic methods (TLC, HPLC) [1,2,3,4]. Nevertheless the main methods used up to day based mainly on the analysis of ink volatile components. Constantly those methods are developed but still there are several limitations like the unfeasibility for dating documents older than two to five years and the need of sampling or even destruction of the questioned document after the analysis.

The aim of the study was to compare the non-invasive methods of determination of the age of the ballpoints inks. There were compared three methods applying the Raman spectroscopy[5], UV-VIS reflectance spectroscopy[6] and analysis of ΔE based on the spectrophotometric data (7) proposed by authors. There was analysed the group of the blue inks from various commercially available brands. The naturally aged handwriting samples were stored for seven year at the room temperature at the stable humidity at the different lightening conditions: without direct expose to the light, in the direct exposure to the light, UV lamp and to the sunlight. The Raman spectra library of naturally aged handwriting samples were collected at two laser excitation 514nm and 685nm lines (Figure 1).

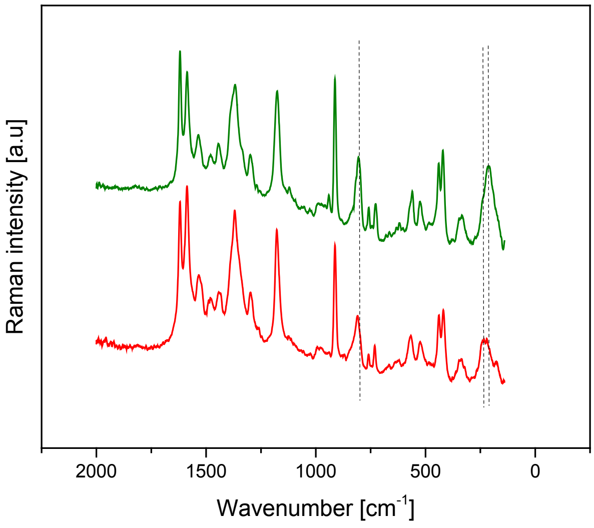

**Figure 1.** Raman spectra of the naturally aged samples of blue ballpoints inks (laser excitation line 514nm)

Then samples were subjected to the UV-Vis analysis performed by the means of the 2D polymorphic scanner designed at Wroclaw University of Science and Technology. The reflectance spectra were gathered in the range between 400 and 1000 nm.

The chemometric methods are often applied the forensic studies and has proved their effectiveness in the discrimination of the various ink (Figure 2).

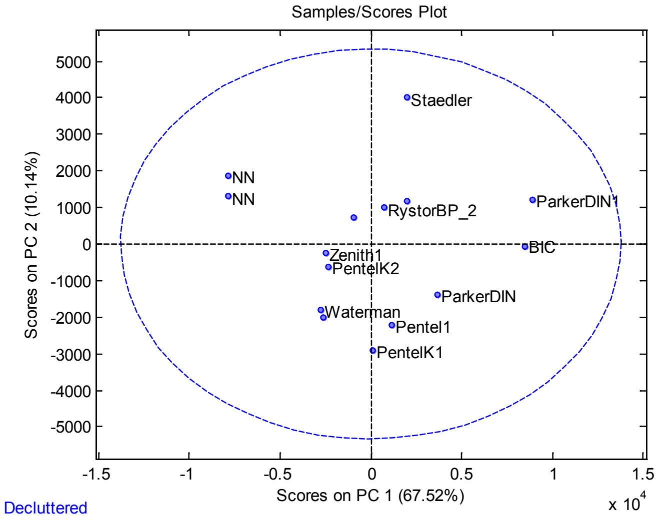

**Figure 2.** Principal component analysis score plots for ink samples with 95 % confidence interval based on Raman spectra.

In the presenred study the chemometric treatments were used in the analysis of the gathered spectral data. Principal component analysis (PCA) and others chemometic tools are required due to discreet spectral changes and large diversity of analysed objects.

In the presented study were evaluate the effectiveness of the invasive methods recently proposed by Gorshkova et. al and Ortiz-Herrero et.al applied in determining of the age of the ballpoint inks and it wasanalysed the influence of fading on the applicability those methods. Moreover authors proposed the usage of ∆E in analysis of the ink ageing processes.

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# New Insights into Paper. Chemical Paper Analysis by Raman Microscopy

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**Keywords:** paper, chemical composition, authentication

The knowledge of the detailed chemical composition of paper can be important and useful for different purposes. It can give information on historic paper making practices and can assist paper conservators to evaluate the preservation state of old papers and to find suitable measures for paper conservation or restoration. Furthermore, the chemical analysis of paper can help to date paper or even to reveal forgeries of works of art or documents.

The complex composition of paper still today presents a great challenge to chemical analysis of paper, especially when the used methods have to be non-destructive and paper components are only present in low concentrations. Spectroscopic methods like infrared (IR) and Raman spectroscopy offer a strong potential for a non-destructive, comprehensive and specific chemical characterization of paper [1]. Especially, Raman microscopy gives new possibilities to chemical paper analysis [1-3]. Raman measurements have a high chemical specificity and the use of an excitation laser and an optical microscope provides for a very high spatial resolution of less than 1 µm. By using the Raman imaging technique, the chemical paper structure, that means the presence and distribution of different paper components on the surface or along the cross-section, can be 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 detected and identified.

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 [4]. There are many publications dealing with the analysis of color pigments and printing or writing inks on paper but not with the paper itself [5].

The objective of our research at PTS is to use consistently Raman microscopy to detect and identify different components in paper and to analyse the chemical structure of paper. The presentation will demonstrate the application of Raman microscopy to paper analysis with results from measurements on different old papers from the 15th and 19th century.

The Raman measurements were done with a Raman Microscope WITec alpha 300M+ with a 532 nm laser. The laser power at the sample was 5 to 10 mW. The spectra were acquired with an integration time of 500 ms. The step size of the mapping measurements was 1 µm. The paper cross-sections were prepared by a simple cut with a razor blade. Data analysis was accomplished by an in-house developed spectral imaging software based on MATLAB (The MathWorks Inc.).

Figure 1 shows Raman images from the cross-section of a book paper from 1886. Beside the fiber structure one observes the distribution of the clay particles and the rosin. In this case no other paper components or trace particles could be detected.

As the paper contains 18 % chemical pulp (sulphite), 10 % cotton, 60 % straw fibers it should be possible to detect and to identify different fibers. The right Raman image shows those fibers that could be identified.

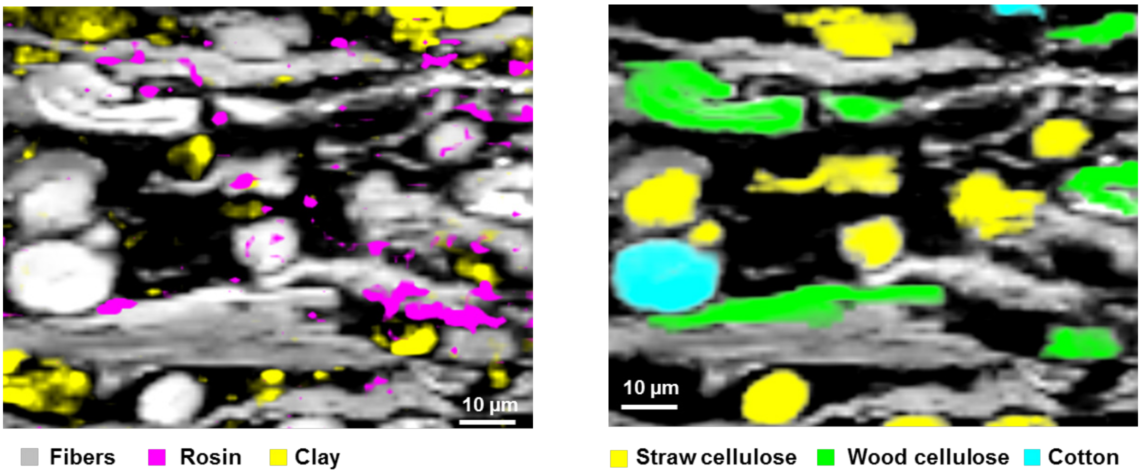

Fig. 1 Raman images of the paper cross-section of a book paper from 1886

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

This work has been financially supported by the German Federal Ministry of Economics and Technology BMWi. We would like to thank especially Gangolf Ulbricht, Werkstatt für Papier (Berlin, Germany), for providing the old paper samples.

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# Determining the archaeometric and chemometric characteristics of the old documents. Paper and writing support

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**Keywords:** cultural artefacts, conservation, paper analysis, ink analysis, micro-RAMAN spectrometry

In order to valorise museum artifacts, it is necessary to investigate them, multilateral and in depth through archaeometric and chemometric studies. The present paper presents the analysis and comparative data on the chemical composition of three old documents from the "Poni - Cernătescu" Museum from Iaşi. The documents presented are unique in content and have particular relevance to the history of chemistry education in Romania. The documents represents the theses of chemistry and physics of some students of chemist Petru Poni.

The following objectives were pursued:

- Recovery of unhealthy artifacts with poor conservation status through preservation-restoration;
- Determining the patrimonial value;
- Valorisation of artefacts displayed through new museum presentation systems and thesauring through studies and research;
- Development of museum pedagogy projects;
- Preservation - restoration interventions;
- Monitoring of the state of conservation at display and storage.

Optical microscopy, scanning electron microscopy coupled with X-ray spectroscopy, FT-IR and Raman were used in the study to determine the composition of papers and the type of ink used in text writing. Micro-FT-IR analysis shows that the paper contains calcium carbonate (1428 $cm^{-1}$ absorbance), calcium sulphate (1621 $cm^{-1}$), starch (1000 cm and 894 $cm^{-1}$) [1] and a characteristic acidic degradation in the 1000-1200 $cm^{-1}$.

Another band, often associated with acidic degradation is shown at 3340 $cm^{-1}$ in the OH region, and was possibly due to a strong intermolecular hydrogen bonding [2]. Cellulose Raman bands have their counterparts in the FTIR spectrum except for the 1600-1650 $cm^{-1}$.

In conclusion, this work was conducted to provide a study on deteriorated old documents utilizing non-destructive techniques. From the analysis of the types of damage and degradation of the paper and ink support [3], the document conservation status was established in order to be able to choose the most appropriate restoration treatment for historical artifacts.

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# Identification of synthetic organic pigments in *Gebrüder Schmidt* printing inks by Raman spectroscopy – A case study

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**Keywords:** synthetic organic pigments, printing inks, Gebrüder Schmidt, Raman spectroscopy

The printing ink company *Gebrüder Schmidt* GmbH was founded by the brothers Ernst and Rudolf Schmidt in 1878, in Bockenheim, near Frankfurt am Main. In the following years the company developed highly respected products and won a golden medal for its printing inks at the 1900 Paris Exposition. During the 1930s *Gebrüder Schmidt* had factories in ten European countries and its products were used worldwide in the printing sector [1].

The analysed *Gebrüder Schmidt* catalogue (Figure 1) is part of the *Rathgen-Forschungslabor* library and was likely printed between 1910 and the 1930s. It contains 22 plates with nine colours each. The objective of the presented work was to identify the synthetic organic pigments used for the *Gebrüder Schmidt* printing inks to aid technological research and conservation.

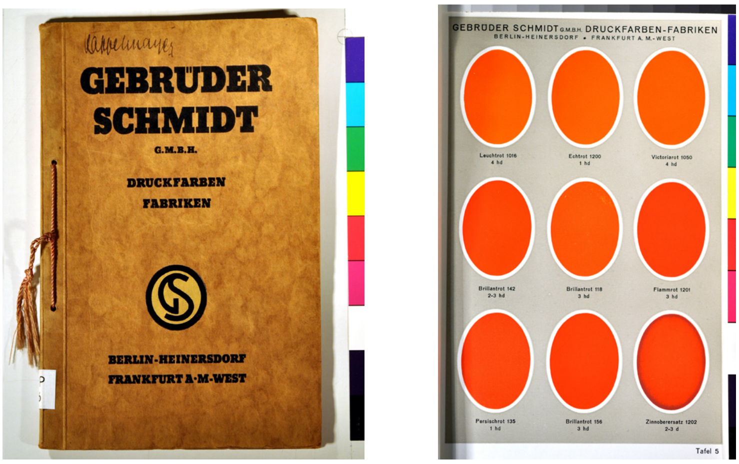

**Figure 1 a** Gebrüder Schmidt catalogue cover (left), **b** plate no. 5 (right)

More than 300 synthetic organic pigments have been produced since the latter part of the 19th century. Their identification is particularly important in conservation, because some of them, especially the earlier pigments, have been found to exhibit poor light and solvent resistance. It is often difficult to identify synthetic organic pigments, since some of them differ in structure only by the position of substituents on an aromatic ring [2]. However, Raman spectroscopy has been a successfully applied for synthetic organic pigment identification [3].

Colour patches in the *Gebrüder Schmidt* catalogue, which suggested organic pigments based on colour and name, were selected for analyses. Raman analyses were carried out directly on the catalogue, using a *Horiba Scientific* µ-Raman spectrometer with *Xplora* Raman microscope, equipped with a laser operating at 785 nm. The laser beam was focused with a 50x objective lens, laser intensity varying from 1 to 100%. Raman radiation was dispersed with a 1200 lines/mm grating. Average spectra from 5 to 20 measurements (20 to 60 seconds measuring time) were collected in the range of 100 to 2000 $cm^{-1}$. The background (paper and barite priming) was subtracted from the obtained spectra, and the result compared with a *LabSpec* database and spectra in the *Rathgen-Forschungslabor* reference library. Raman analyses allowed the identification of the majority of the synthetic organic pigments used. In some instances, not all necessary pigment bands were clearly visible due to fluorescence, which made it impossible to distinguish pigments from a similar chemical group using the Raman library search tool of the software. In these cases, manual comparison of spectra was necessary, although very time-consuming. Due to the existence of many yellow, orange and red synthetic organic pigments, which show very similar spectra, their recognition was particularly challenging.

Several red pigments were identified in the printing ink; this includes PR3, PR4, PR8, PR12, PR49:1, PR53, PR54, PR60 and PR81. The red colour sample "Zinnoberersatz 1202" (literally translated: surrogate for vermilion) of plate 5 (Fig. 1b, lower right ellipse) blackened on the rim. The phenomenon was observed also for the colour sample 9 on plate 4 and the colour sample 1 on plate 7. All three printing ink samples are composed of an organic pigment mixed with the orange inorganic pigment red lead, $Pb_3O_4$. Optical observation suggested the degradation product to be dark brown plattnerite, $PbO_2$, which is a weak Raman scatterer and easily undergoes laser induced degradation to red and yellow lead pigments [4, 5]. Raman analyses on the degraded areas indeed detected only red lead and massicot, the yellow pigment β-PbO. The blackening, which only occurred along the white frame, may have been catalyzed by the white pigment and air as the pigment is present underneath the red ink where the colour seems stable. The yellow and orange pigments showed very weak bands in comparison to the other colours. Hence the suggested pigments PY1, PY3, PY6 and PO5 should be confirmed using other additional techniques. Most of the pigments have been mixed with $BaSO_4$ in different concentrations to obtain several different hues.

The *Gebrüder Schmidt* printing inks contain many synthetic organic pigments. It is assumed that several prints of that time contain these inks and hence pigments. This will be important information for their preservation and any conservation treatment, especially in terms of light policy and solvents used during conservation treatments. Raman spectroscopy can be a useful tool for the identification of these pigments in the inks as proven above.

## Acknowledgements

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# The colours of the Power plant in *Levada de Tomar*

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**Keywords:** Industrial Heritage, coatings, µRaman

The early 20th-century powerplant in *Levada de Tomar* (Portugal) is a representative Industrial Heritage site of the electricity production for public lighting and industry [1]. The powerplant comprises three groups of generators (Figure 1) that produced electricity using hydro and diesel as primary energy sources. These generators fabricated and operated during different periods are composed by several elements, as turbines and alternators, made of metal alloys and wood partially coated with blue, red, orange, yellow and black paints.

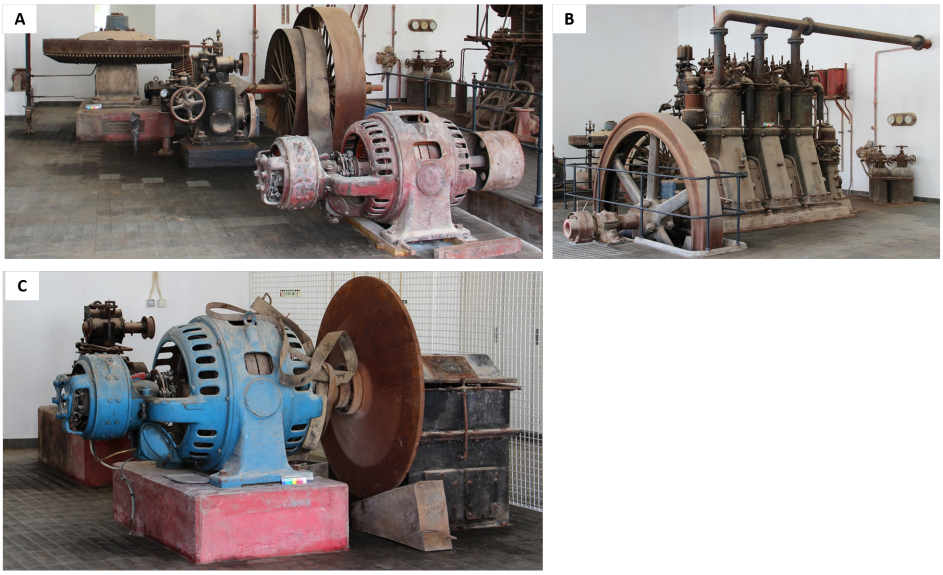

**Figure 1.** The three groups of electricity generators at *Levada de Tomar* powerplant. **(A)** Hydraulic generator with a Francis turbine (1924), **(B)** Winterthur diesel engine (1927) and **(C)** hydraulic generator with a Mayer turbine (1944).

In this work, by analysing the paint components (pigments, binders and fillers), we aim to infer on the generators' usage and undergone changes. To attain this objective samples of different paints were analysed by µRaman for the identification of pigments and fillers and by FTIR for the characterisation of binders. To disclose the presence of multi-layered coatings, a stratigraphic study was carried out by optical microscopy and SEM-EDS.

The results showed the use of distinct coatings for the three generators' groups. Coatings of the generator dated from 1924, are mainly composed of inorganic pigments, such as Prussian blue (blue coating), and lead chromate (orange coating). On the contrary, the coatings of the generator dated from 1944, are organic pigment-based; cu- phthalocyanine (blue coating) and the monoazo PR3 (red pigment). The use of distinct paints may be related to the periods of fabrication and usage, for example, the copper phthalocyanine is only used since 1935 [2].

Differences in the coating scheme were also observed. The black coating of the 1924 generator group elements comprises four layers: a carbon black layer under which lies an ochre layer of goethite and barite among two white anatase-based layers (Figure 2). The other two generators are also coated with black paint, but only comprising one carbon black layer.

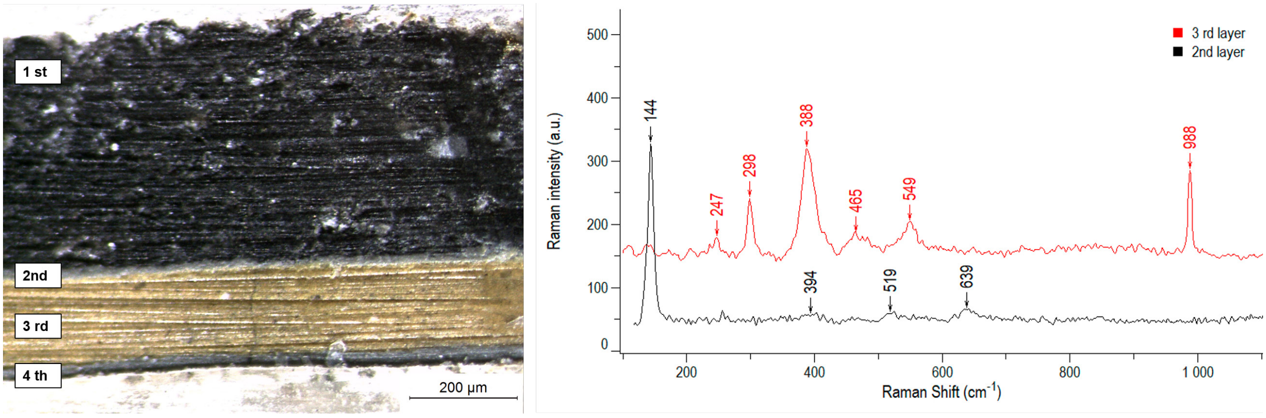

**Figure 2.** Micrograph of a stratigraphic sample taken from the 1924 hydraulic generator and Raman spectra of the pigments identified in the 2$^{nd}$ (anatase) and in the 3$^{rd}$ (goethite and barite) layer [3-4].

Some parts of the generators' group were re-coated with distinct colours, as the case the Mayer alternator of the 1944 generator group. This alternator shows a red haematite coating; however, the stratigraphic study revealed underneath the presence of a copper phthalocyanine blue layer followed by a carbon black one.

The results attainted in this work will contribute to increase the knowledge on the Industry and Technology history, a field where the science-based material study is still to be fully developed and implemented.

## Acknowledgements

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# Session 7

# Material characterization and Conservation issues

# An unlikely Modigliani?

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** Address and Institution where and when the research was carried out*

**Keywords:** painting, Raman, Modigliani, forgery

It is now well-stablished that scientific evidences are necessary when authenticity issues are under questioning, because they give support to the subjective evaluation of artwork experts. There is now a substantial number of publications reporting on painting forgeries and it is also known that Amedeo Modigliani is one of the most targeted artists; to avoid the commercialization and exhibition of fake paintings a thorough documentation together with the chemical characterization of the materials used by the artist is mandatory. Style evaluation, however, still plays a major role in the authentication procedure. In this work, an interesting question is raised: regarding authenticity is the artist style argument stronger than documentation and scientific evidences?

A small (18x25 cm) painting (oil on cardboard, Fig. 1) supposedly painted by Amedeo Modigliani was analyzed by Raman microscopy, X-ray fluorescence spectroscopy (XRF) and imaged by UV, white light, infrared and X-ray. It is not clearly signed or dated, but an extensive and trustable documentation exists and link Modigliani to the Brazilian artist José Wasth Rodrigues (1891-1957) [1]. Briefly, in 1910 Wasth Rodrigues was prized by the government of São Paulo State (Brazil) with a grant to study art in Paris and had classes at the Académie Julien and École National des Baux-Arts. In 1914 he returned to Brazil but during the years in Paris he met and stablished a friendship with Modigliani. Apparently, they met again in the early months of 1918 (before Modigliani moved to south of France) when the Brazilian traveled to Paris with Monteiro Lobato (a very important Brazilian writer) in connection with the launching of the book *Urupês* (which cover was illustrated by Wasth Rodrigues). It seems that it was during this short visit that Wasth Rodrigues gave a brown coat and bluish scarf to Modigliani and, in return, received some drawings and paintings. In the painting “Seated man leaning on a table” (1918) a man which resembles very much Wasth Rodrigues is wearing a coat and a scarf also very similar to the ones that Modigliani was wearing in his “Self-portrait” (1919); the heavy coat also suggests that the latter was painted in the wintertime. Several years later, the painting here studied was given by Wasth Rodrigues to a friend, Ruy Affonso (Brazilian poet, actor and director) who, shortly before his death (2003), handled it over to Alex R. do Prado. At that time, the painting authorship was unknown and the details given above were collected along the last 12 years.

Raman Microscopy measurements (633 nm and 785 nm, inVia Reflex) were carried out directly on the painting and lead white, barium white (or lithopone), zinc white, basic lead chromate (chromium orange), zinc yellow ($ZnCrO_4$), Pb chromate, vermillion, Prussian blue and ultramarine were all detected in the painted surface; iron oxide (hematite) and carbon black were also found in some areas. Green areas consist in a mixture of Prussian blue and lead chromate ($PbCrO_4$). XRF (Moxtek Ag anode and Amptek Si-PIN detector) detected Fe (brown areas); Hg (red); Pb and Zn (white); Fe (blue); Fe, Cr and Pb (green); Ba, Cr and Sr (yellow).

The pigments identified in this work were also found in a recent investigation on the Modigliani's "Self-portrait", which belongs to the Contemporary Art Museum of the University of São Paulo (MAC-USP) and are also in agreement with the data recently published on Modigliani's late portraits [2]. Imaging revealed that although a clear signature is not observed "M", "i", "g" and "l" letters can be observed (in orange) at the bottom of the painting. UV images show no evidence of any intervention, indicating its originality; conventional visible, UV and IR images showed graphisms and symbols which were not identifiable on the painted area. X-ray and digital 3D images revealed numbers, letters, astrological and apparently cabala symbols, which were intentionally inserted. Modigliani was very proud of his Jewish origin [3] and also was frequently seen reciting Alighieri's Divine Comedy in Parisian cafes, therefore, the symbols found in the painting cannot be considered unexpected, if his authorship is accepted.

**Figure 1.** Painting supposedly painted by A. Modigliani (right) and image captured by Reflectance Transformation Imaging (RTI) from the bottom left area of the painting (left).

Although the painting authorship cannot be unambiguously assigned, the investigation here reported provides sound evidences that (1) the artist's palette identified by Raman microscopy and supported by XRF results is in full agreement with recently reported data on Modigliani's late portrait; (2) it is at least plausible that the marine scene was in fact painted by Amedeo Modigliani possibly during one of his visits to Livorno; and (3) José Wasth Rodrigues received the painting as a gift and brought it to Brazil in 1914 or 1918; in return, Rodrigues gave to Modigliani his brown coat and scarf, which the painter was using when produced his "Self-portrait" (1919).

*This work is dedicated to the memory of Prof. Robin Clark*

## Acknowledgements

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# The conservation of 18th century gun-powder horn with amber decoration: a top-down approach.

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**Keywords:** amber, resin, hyperspectral imaging, depth profiling Raman spectroscopy, XRF

The object of our study was a gun-powder horn from the Princes Czartoryski collection owned by the National Museum in Krakow. It is dated to 1784 and belonged to Stanislaw August Poniatowski, king of Poland. The object is made of ox horn with a wooden closure, decorated with amber medallions and buttons.

The conservation works required to confirm presence of amber and identify conservation materials previously applied to the object. Based on preliminary research, the question was if the medallions and buttons are made of amber or other natural resin, or if the amber decorations were covered with a protective layer.

To answer these questions, various spectroscopic techniques were employed to collect both macro- and microscopic information (Fig. 1). Moreover, because of sampling limitation the study focused on techniques that enable *in situ* measurements. Additionally, because of the dimensions of the gun-powder horn (25.5 cm x 6.5 cm), only certain techniques could be applied, where the size of the object allows to carry the measurements.

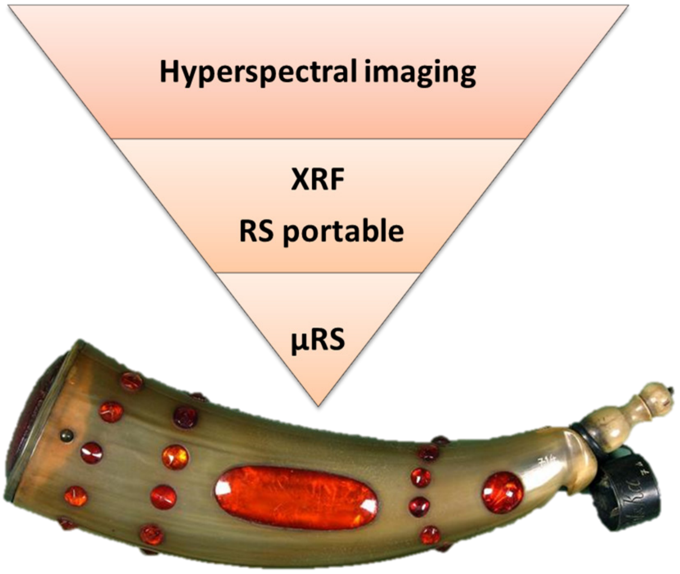

**Figure 1** The scheme of spectroscopic analysis together with a photo of the Stanislaw August Poniatowski's gun-powder horn from the collection of National Museum in Krakow. (Photo: National Museum in Krakow archives)

The "macro" technique employed was a hyperspectral imaging (SWIR 965-2500nm, Specim, Oulu FIN). This method, supported by chemometric analysis, allows to quickly scan and roughly compare all elements of the analysed object. X-ray fluorescence spectrometry (XRF) (ARTAX 800, Bruker, Berlin, DE), a semi-micro technique, was applied for elemental analysis of medallions, buttons and its metal mounts.

The analysis with portable Raman spectrometry (DeltaNu, Wyoming, US) enabled to obtain averaged Raman spectra with good quality, but its spatial resolution was insufficient for microanalysis. Therefore, a benchtop Raman spectrometer (InVia Raman, Renishaw, Wotton-under-Edge, UK) equipped with steerable arm was employed to account for this limitation. This equipment allowed to conduct measurements with a resolution below microns as well as depth profiling. Both Raman spectrometers are equipped with lasers with 785 nm wavelength.

The data acquired from various techniques indicate that amber was the material used for gun-powder horn decoration. Additionally, the depth-profiling using micro-Raman spectroscopy enabled to identify the protective layer as a colophony.

# Raman Spectroscopy in the Restoration of an *Our Lady of Czestochowa* Icon

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**Keywords:** conservation, Raman spectroscopy, icons

### Introduction

Icons as works of art are highly complex in their technological structure that comprises canvas stretchers—usually made of wood—multiple layers of distemper paints, gold leaves, punched-dot patterns and, frequently, metal plates. In my project, I studied an icon with faded gold leaves and lavish ornamentation in the form of structural combing, in addition to painted stars, a distinctive feature of popular Our Lady of Czestochowa depictions.

### Subject facts

Title: *Matka Boska Częstochowska* (Our Lady of Częstochowa)
Time of origin: 20th century
Technique: icon, distemper
Canvas stretcher: wooden board
Dimensions: 25x17,5x1,5 cm

### Examination types

A full range of tests, including UV and IR scans, canvas stretcher identification, XRF and Raman spectroscopy to identify pigments and other components of the paint layers. The UV and IR tests were performed by Roman Stasiuk.

### Identifying the type of wood

The icon was examined with a stereoscopic microscope (Nikon SMZ 1000) to determine the anatomy and distribution of different sections of wood within a fan depicted in the icon. The surface of sample's cross-section was evened out with a scalpel and examined with a stereoscopic microscope (Prolab MSZ). Then, thin slices were extracted from tangential and radial sections to obtain aqueous preparations designed for viewing in passing light (Nikon E200 biological microscope).

Sample no. 1

A cross-section revealed structures of diffuse-porous hardwood. Uniform wood rays were visible in a radial section with no spiral beads found in longitudinal walls of the vessel elements. Perforation of transverse walls of the vessel elements was of the ladder type. A tangential section revealed single-row rays, including both seemingly wide and seemingly tall wood rays.

Conclusion: The studied wood is of the alder type (Alnus).
The above examination was performed by Elżbieta Jeżewska

### XRF spectrometry

XRF spectrometry was used to scan *Our Lady of Częstochowa's* complexion: a cheek at x-16; Y-9. The following pigments were identified: lead white, cinnabar, iron earth pigments, admixtures of zinc white as well as what probably was bone black. The detected high amounts of copper could come from additions to the siccative or elements painted on a brass leaf. They could also signify the presence of copper blue.

### Pigment identification employing Raman spectroscopy

The microscopic Raman technique is a perfect analytical method, offering a sensitive, non-destructive, selective and *in-situ* tool for testing pigments. This type of spectroscopy was used here to restore the icon and identify the pigments.

### Summary

Raman spectroscopy proved to be most useful in the analysis of pigments used in the studied icon.

The method enhanced the researchers’ knowledge of pigments used by the icon painter in the different color layers, most notably revealing burnt sienna and cardinal purple.

Raman spectroscopy in the pigment analysis was performed by Aleksandra Wesołowska from the Inter-University Institute of Conservation and Restoration of Works of Art.

The study employed a dispersive spectrometer with a inVia Qontor confocal Raman microscope by Renishaw, fitted with two excitation lasers at the wavelengths of 532 nm and 785 nm.

# Session 8

# Material characterization and degradation processes

# Micro-Raman and X-ray fluorescence spectroscopy applied to the characterization of glazes from Portuguese *azulejos*.

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**Keywords:** Tiles, Glaze, μ-Raman, XRF.

Decorative tiles, or as they are called in Portuguese: *azulejos*, have been used in the decoration of buildings, in Portugal, since the 15th century [1]. Nevertheless, it was not until the 16th century that local production started. Tiles are made of a ceramic body covered with a glaze, which is the support for the decorative painting. In this investigation, we seek to understand the differences in Portuguese glaze production over time. For this purpose, the material composition of white glazes from the 17th to the 20th century have been obtained using a non-destructive methodology consisting of X-ray fluorescence spectrometry (XRF) and micro-Raman (μ-Raman) spectroscopy analysis. XRF shows that all glazes have predominantly Si and Pb in their composition. In all the samples analysed in this study, regardless the age of the tiles, we found bands correspondent to the Si–O–Si bending vibration in the regions between 330-380 $cm^{-1}$ [2], and bands corresponding to Si–O Raman bending mode centred at 450-480 $cm^{-1}$ [3]. Lead oxide was the most important flux used for lower-temperature glazes and increased surface reflexion in historical tiles. Tin, an opacifying agent added to the glazes, has also been identified by XRF in all the samples but the ones presenting zirconium. A Raman band at 630 $cm^{-1}$, characteristic of cassiterite ($SnO_2$), was also identified in these samples [1]. Tin-oxide is the most common opacifying utilized in the production of glazes until the 18th century. From 1750 onwards, lead arsenate compounds gradually began to replace it. In fact, arsenic was also identified in a twentieth-century sample by XRF and its presence is attributed to lead arsenate compounds with a Raman band at 830 $cm^{-1}$ [3].

## Acknowledgements

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# Investigating glass beads and the funerary rituals of ancient Vaccaei culture (s. IV-II BC) by Raman Spectroscopy

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**Keywords:** archaeological glass, polymerization index, pigments, thermal alteration

Glass pieces, particularly beads and lacrymatory, were highly appreciated goods in the Protohistory of the Iberian Peninsula. The specialized production of these glass pieces seems non-compatible with local workshops, and therefore, they are proof of commercial relationships with other cultures with the technical capability to produce such pieces. However, detailed studies of glass beads of archaeological relevance are scarce. Among other reasons, these samples usually appeared without a clear context, making impossible to establish direct relationships with their chronology and region of origin.

Nevertheless, the archaeological site of Pintia (Padilla de Duero, Valladolid, Spain) is a relevant exception to this situation. From the beginning of the archaeological work, it was possible to recover hundreds of glass beads, reaching about six hundreds pieces by 2018, which makes Pintia the most important archaeological site in terms of glass beads in the interior of the Iberian Peninsula. The typology of the beads is generally ellipsoidal, smooth or gilded, while their color is usually dark blue, although pearly, yellow and green beads have also been found. Moreover, a great number of these pieces have been found in closed contexts, in particular in well-preserved graves from the necropolis of “Las Ruedas”, emplaced nearby the remaining of the city-state of Pintia. The large number of well-preserved graves found in the necropolis, together with the diverse trousseaus and viatic offerings found in them, suggest the relevance and complexity of the funerary rituals in the ancient Vaccaei culture.

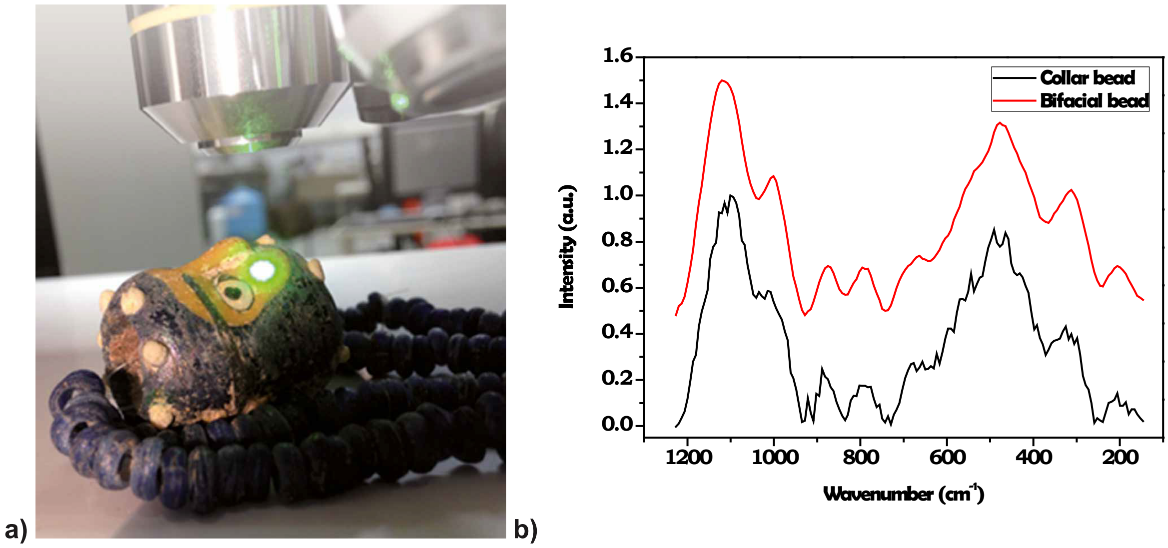

**Figure 1.** Bifacial cylindrical bead from s. II BC (Pintia, Valladolid, Spain) subjected to micro-Raman analysis (a). Raman spectra of the bifacil cylindrical bead and of the beads from the accompanying collar.

This work employs Micro-Raman Spectroscopy to investigate glass beads of particular relevance found in Pintia. This technique allowed us to correlate the dynamic vibrational Raman analysis of the samples with a simplified model of the Raman spectra of the collective tension modes $\upsilon$(Si-O) of the Si-O-Si network [1], as well as with the type of archaeological glass sample and manufacture process [2]. Moreover, Raman spectroscopy is a well-established technique for the identification of pigments in art, cultural heritage, and archaeological samples [3]. These results were complemented with an Energy-dispersive X-ray spectroscopy (EDS) study, whose results provided information about the relationship between vitrifying oxides ($SiO_2$, $Al_2O_3$), fluxes ($Na_2O$, $K_2O$), and stabilizers (CaO, MgO, MnO, PbO, $TiO_2$, $Fe_2O_3$, etc.) and the properties of the glass.

First, a complex and unique sample, a polychromic cylindrical bead showing two opposed human faces found in a grave of s. II BC was carefully analysed (Figure 1). Special attention was place on the different pigments employed in this sample. Secondly, common blue glass beads found on graves from s. IV and II BC were compared to determine if they have a common origin or production, or if it changed along time. In particular, glass beads from s. II BC were found accompanying the bifacial cylindrical bead as a necklace. Finally, some graves present evidence of a cremation ritual, being possible to found altered glass beads as well as equivalent well-preserved glass beads in a grave from s. IV BC. These samples were comparatively studied to analyse the alteration of the beads, to ensure that this was consistent with the suspected cremation funerary rituals.

The Raman spectroscopy study carried out in this work provides evidence about the diverse pigments employed in these glass beads (e.g., $Sb_2O_3$, FeS, MnO, $Cu^{+2}$, $Fe^{+2}$, $Pb_3(SbO_4)_2$. Moreover, diverse manufacture procedures or origins can be identified. In particular, the bifacial cylindrical bead shows a manufacture typical from Syria or Egypt, being clearly distinct from the beads of the accompanying necklace (e.g., according to their polymerization index ($I_P$) the bifacial bead was produced in a furnace able to reach only 600º C, while the beads from the collar were produced in a furnace reaching 1100-1200º C. Finally, the thermal alteration found in some beads from s. IV BC was found to be consistent with the suspected cremation funerary rituals of the ancient Vaccaei culture.

## Acknowledgements

The authors acknowledge the TEMPOS Vega Sicilia group (Valladolid, Spain) for the patronage of the "Centro de Estudios Vacceos Federico Wattenberg".

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# Raman Identification, Compositional Characteristics and Degree of Deterioration in Ancient Komana Glass Bracelets

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**Keywords:** ancient glass, composition, weathering, μ-Raman

This paper aims to present analyses of a group of medieval glass bracelets, coming from Hamamtepe, Komana, a multi-layered archaeological settlement, located in the Gümenek village of Tokat, central Black Sea region of Turkey. Excavations were initiated by D.Burcu Erciyas in 2009, and have continued to date in different sections of Hamamtepe. The glass bracelets analysed in this paper were recovered in HTP01, the central area of the mound, between 2009-2017. Glass for everyday use, such as bottles and bowls; handles and stems belonging to lighting elements; and bracelets, rings, beads for personal adornment are among the finds recovered at Komana. In stylistic grounds the bracelets share common fetures with bracelets excavated at a number of other middle Byzantine sites in Anatolia, and they present all the formal varieties and colours documented at these sites. This study on the bracelets will shed further light on their technological characteristics and build possible links with other centers in Anatolia.

In this study, twenty-four bracelet pieces representing Komana glass bracelets were analyzed by using stereo microscope, XRF and μ-Raman spectroscopy to investigate their structural and compositional characteristics[1]. The stereo microscopic investigations showed that most samples were in good state of preservation with no iridescence and some had either thin or thick iridescence. XRF results of those glass bracelet samples representing three different states of weathering are given in table 1. μ-Raman spectroscopy is very useful to describe the glass structure since relative intensities of Si-O stretching and bending modes in Raman spectra are strongly affected by the glass composition and the process temperatures of glass production[2,3]. Raman signatures of the samples were obtained with a Bruker Senterra Raman Microscope Spectrometer using Opus 7.2 analysis software, operating at 532 nm, with a laser power of 10 mW, at integration time 150 s with 2 spectra accumulations.

Combined interpretation of Raman signatures and compositional characteristics by XRF were made to identify the glass types and their weathering behaviour (Table 1, Figure 1). The sample having no iridescence (477) had Raman signature with Si-O stretching peaks at 1081 cm-1, 990 cm-1, 945 cm-1 and bending peaks at 579 cm-1, 497 cm-1. That sample had the highest CaO percentage being 8.82. It was classified as Type 1 “Ca glass”, which is a Ca-rich, Na-containing silicate. The sample having thin iridescence (206) had the main Si-O stretching peaks at 1095 cm-1, 948 cm-1 and bending peaks at 585 cm-1, 488 cm-1. That sample had the second highest CaO content in the composition being 4.36%. The doublet peak at 990 cm-1 was hardly recognizable and for this reason, the sample (206) was classified as Type 2 “Na+Ca glass” which is a Na-rich, Ca-based silicate. The third sample (313-a) had the thickest iridescence among the three sample. Its main Si-O stretching peaks were at 1084 cm-1, 958 cm-1 and the bending peak was at 603 cm-1. The sample had the least CaO content (3.49%) among the three samples and it was also classified as Type 2 “Na+Ca glass” which is a Na-rich, Ca-based silicate.

The results showed that fragments of glass bracelets belong to two types of glass structures: Type 1 glasses being Ca-rich, Na-containing silicates are the most durable type of glass structure and show no iridescence on the surface. Type 2 glasses are Na-rich, Ca-based silicates. Their surfaces are weathered with different rates of iridescence. XRF results confirm that Type 1 glasses have higher CaO content in comparison to the Type 2 glasses and the samples with thick iridescence has the lowest CaO content. The grouping done by Raman signatures is in line with the XRF results of the samples and their weathering states.

| **Sample ID** | **Color** | **Iridescence** | **XRF Results*** | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | **P** | **Al2O3** | **SiO2** | **K2O** | **CaO** | **TiO2** | **Cr2O3** | **MnO** | **Fe3O4** |
| 477 | Bd | None | **-** | 9,04 | 54,87 | 8,82 | 8,82 | 0,08 | - | 0,03 | 1,37 |
| 206 | Tm/W | Thin | 0,72 | 4,05 | 71,60 | 7,27 | 4,36 | 0,22 | 0,02 | 0,02 | 1,96 |
| 313A | Gm | Thick | 0,58 | 10,19 | 66,11 | 9,61 | 3,490 | 0,20 | 0,01 | 0,41 | 2,58 |
| **Colours:** Bd: dark blue, Gm: green medium, W: white, Tm: Turquoise medium | | | | | | | | | | | |

**Table 1.** Chemical Composition (wt%) of glass samples representing three different states of weathering. *Sodium (Na) could not be detected by XRF.

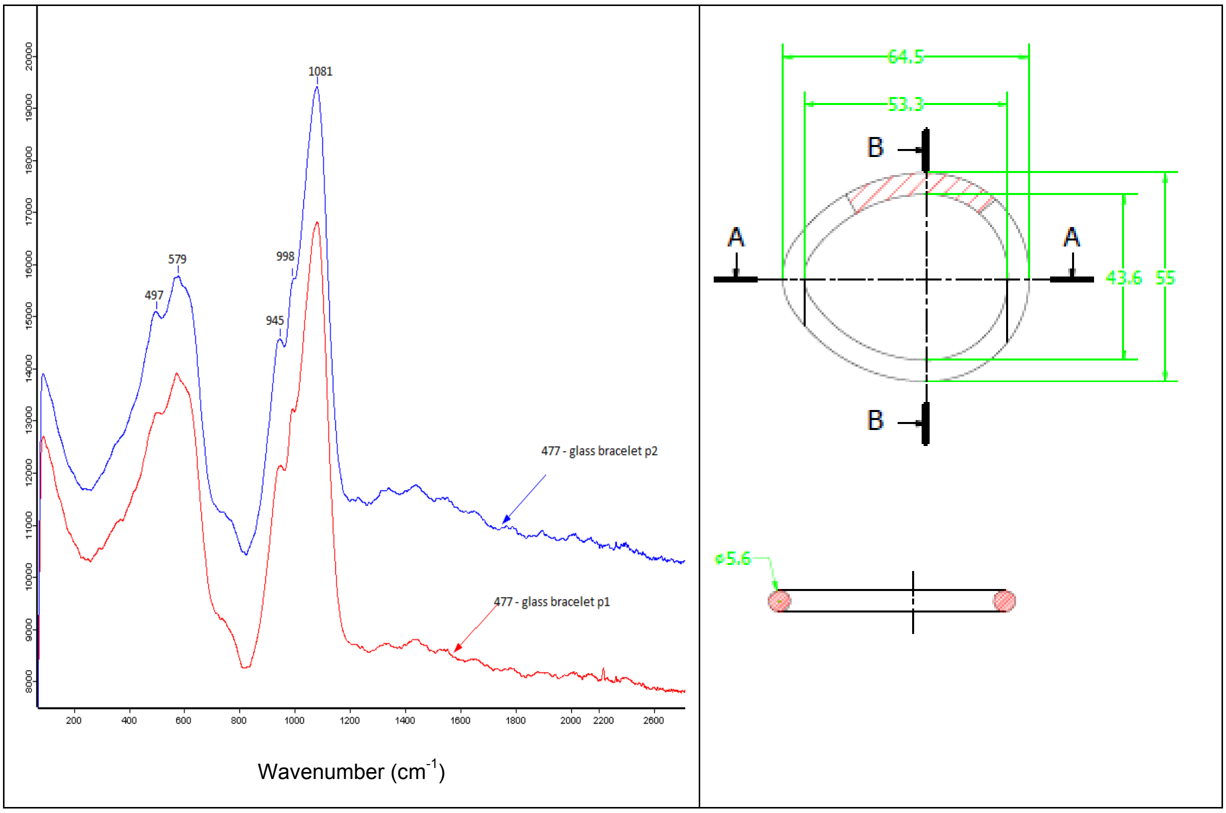

**Figure 1.** Raman Spectra of glass sample (477) with no iridescence: Type 1: Ca glass.

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# Raman investigation for the understanding of a blackening phenomenon on late Gothic wall paintings

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**Keywords:** wall paintings, pigment degradation, plattnerite, sulphation.

The present work concerns the study of painting fragments taken from late Gothic wall paintings preserved inside the Saint Stephen's chapel in Montani (Italy) in order to characterize the alteration products that cause the blackening of paintings. According to restorers the blackening phenomenon was caused by plattnerite (β-$PbO_2$) present as degradation product of white lead. For this reason, some delimited areas were treated with preliminary cleaning tests carried out with the method of reconverting of white lead without a prior analytical exploration.

As attested by previous studies, plattnerite has a very weak Raman scattering, and it can degrade if the excitation laser power is not kept sufficiently low. Thus, we decided to perform Raman measurements first on plattnerite standards, both on mineral plattnerite and on powdered synthetic plattnerite (with excitation lines 633 and 532 nm), with the aim to choose the suitable analysis parameters and to avoid any thermal degradation on the real mural painting samples. All the Raman features at 159 (m), 380 (s), 515 (vs), 540 (sh) and 653 (m) $cm^{-1}$ were reported for the first time belonging to the β form of lead dioxide (Figure 1).

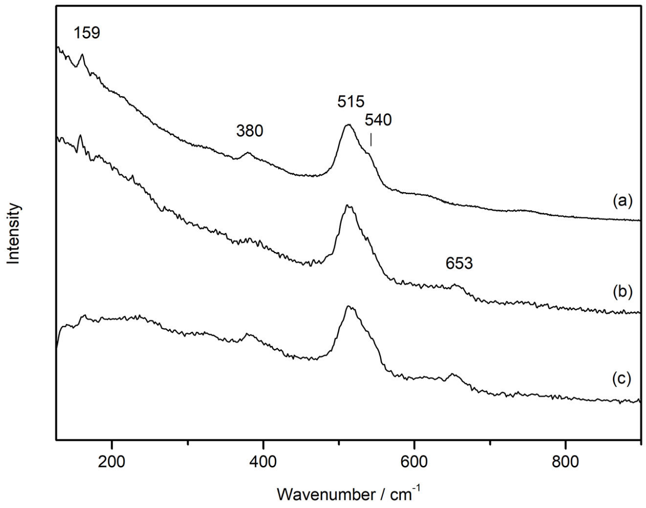

**Figure 1.** Unpolarised Raman spectrum of mineral plattnerite (a) and powdered synthetic plattnerite analysed with 633 nm (b) and 532 nm (c).

Raman spectra obtained at low laser excitation power (≈ 1.0 mW) evidenced the presence of plattnerite on all blackened samples and, in minor amount, of anglesite as alteration products of lead-based pigments. The aging process occurs in the presence of a basic substrate, humidity and sunlight (dry and wet cycles) and was favoured by the presence of acidic pollutants ($SO_x$) in the atmosphere, which stagnate in the area where the chapel is located, due to the particular orographic characteristic of the valley.

Red lead was clearly identified on the samples belonging to red painted areas originally. On the other hand, we have no evidence that the darkening of wall paintings could be attributed to the use of white lead because its Raman spectrum has never been collected nor on the blackened samples neither on those taken from cleaned areas. All spectra collected in brownish samples showed additional features at 165 and 228 $cm^{-1}$ which did not appear neither in the Raman spectra of pure plattnerite, nor of mineral plattnerite (Figure 2). They have not been reported, according to the existing bibliography, to any known phase of the lead oxides family. The constant presence of lead tin yellow pigments (type I and II) on all the analysed blackened samples suggested that these unassigned features, always visible together with the main plattnerite band, could prove the presence of tin and lead based compounds as secondary products not yet mentioned in the literature. However, further laboratory tests will be necessary to clarify a possible involvement of the yellow lead and tin pigments in the degradation process.

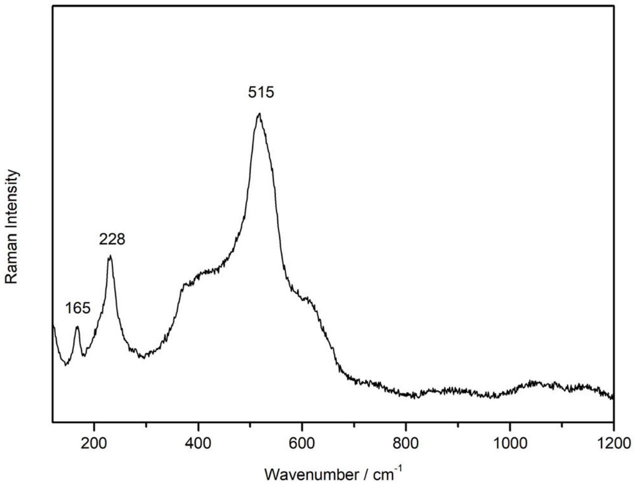

**Figure 2.** Spectrum of black alteration product presents on the wall painting.

The spectroscopic results obtained allowed to identify another degradation process other than the initially expected one. Indeed, the blackening process of haematite was also demonstrated by using Raman spectroscopy, and the presence of magnetite caused, together with the plattnerite, the chromatic change of the painted surfaces. Among the sulphate compounds identified in the samples, coquimbite was also identified as a haematite decay product, which confirmed that a strong sulphation process has been produced.

This work represents an example of the importance of the use of non-destructive diagnostic techniques with the aim to identify the secondary products and to give indications to restorers and conservators on the suitable method to be used. In addition, the study has shown phenomena of indirect degradation caused by the environmental and by the morphological conditions of the territory in which the buildings are located. This suggests that it would be necessary to study in a more detailed way also scenarios that apparently to be not damaged because they are placed in environments with a low level of anthropogenic pollutants.

## Acknowledgements

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# Session 9

# Material characterization, Development of Raman techniques, SERS

# Characterization of the degree of crystallinity in zinc soaps with variable-temperature Raman spectroscopy

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**Keywords:** zinc soaps, metal soap degradation, variable-temperature Raman spectroscopy

Metal soaps, formed by the reaction between saturated fatty acids and metallic ions such as zinc or lead, can lead to irreversible damage in paint films. This is a widespread problem in artworks, as over 70% of paintings in museum collections are affected by metal soap-related degradation phenomena. While recent work has begun to investigate the mechanisms of metal soap degradation in bio-based films, there is still a limited understanding of the structural and chemical nature of metal soap domains, especially at early stages of formation.[1] Suggestions have also been made that it is when metal soaps crystallize that damage occurs in painting layers , at surfaces and interfaces.[2] The ultimate goal of this work is to characterize early stage metal soap formation using tip-enhanced Raman spectroscopy (TERS). In order to achieve this, we characterize the relationship between crystallinity and vibrational signature in Raman spectra of synthesized metal soaps (Zn palmitate, Zn stearate) by variable-temperature (VT) Raman experiments.[3] The degree of alkyl chain disorder is assessed by the $\nu_{as}(CH_2)/\nu_s(CH_2)$ peak intensity ratio and the position of the $\nu_s(CH_2)$ mode.[4] VT-Raman spectra indicate that zinc soaps are crystalline solids at room temperature and disordered solids at temperatures between ~40°C up to the melting point (~120°C), a temperature at which the Raman spectra is clearly indicative of the liquid/molten metal soap. The experimental results indicate the sensitivity of Raman spectroscopy to chain disorder in Zn soaps. Current work is underway to characterize Zn-oil model paint films by atomic force microscopy to understand the structure and spatial distribution of Zn soap domains within a thin section of a paint film. The chemical information from VT-Raman and structural information are combined in the TERS experiment, where the structure and crystallinity of soap domains in cured model Zn-oil films is correlated to the acquired TER spectrum. TERS has the potential to significantly advance the understanding of how chemical reactivity at the nanometer scale can impact the macroscopic qualities of a system. This work will also contribute to the advancement of nanoscale spectroscopy and the probing of heterogeneous, non-resonant systems with TERS.

### Acknowledgements

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# SERS-procedure in the heritage science by utilising photoreduced substrates based on HPC and silver nanoparticles

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**Keywords:** surface-enhanced Raman spectoscopy, photoreduction, silver nanoparticles, organic colourants, paint layer analysis

Surface-enhanced Raman spectroscopy (SERS), a powerful spectroscopic technique for molecular identification at low detection limits, is frequently used in heritage science for the detection of different organic colourants, including traditional organic pigments.[1,2] This work was devoted to the optimisation of SERS-procedure for the detection of organic colourants in paint layers by utilising HPC (hydroxyproply cellulose)-based photoreduced Ag-colloids as SERS substrates. Additionally, the research focused on testing of different pretreatments steps or approaches of substrates application to the samples, such as direct application of the substrate to the place of interest, soaking/icubating the samples in the substrate for a longer period of time, and hydrolysing the sample with the vapours of hydrofluoric acid (HF).

As already established in our previous research [3], properties of the HPC-based photoreduced substrates could be tailored according to the method of preparation which subsequently optimises the method of analysis. The parameters affecting the characteristics of the substrates depend on the energy of incident UV-light, weight ratio between silver ions and HPC, and time of irradiation. Substrates' characteristics were evaluated by different techniques (*e.g.* UV-Vis and infrared spectroscopy, measurments of viscosity, SERS, electron microscopy and atomic force microscopy). It was found out that beside the size, shape and distribution of the silver nanoparticles other characteristics, such as viscosity and pH-value, could be adjusted.

In this research, we used a HPC-based photoreduced Ag-colloid, irradiated at lower UV energy (dominant wavelength of irradiation at 365 nm), for the detection of traditional organic colourants, such as madder lake, cochineal lake and lac dye (also present as mixtures), within paints prepared with two different binding vehicles (protenacious and lipid binder). The substrate has hydrophobic and hydrophilic regions, and higher viscoscity due to lower degradation rates of the HPC-matrix in comparison to irradiation at higher energies. Viscous SERS substrate showed the potential for the direct detection of the organic colourants since the colourants constituting the egg tempera colour layers were detectable immediately after the application of the substrate on the surface of the paint layer. On the other hand, for the analysis of colourants bound in linseed oil a pretreatment step was required (soaking/incubating the samples in the substrate for a longer period of time or hydrolysing with vapours of hydrofluoric acid). As the analyses by means of SERS are (minimaly) invasive, we also tested the potential of non-invasive reflection FTIR-spectroscopy analyses. Furthermore, by exposing the cross-section of the sample, taken from a polychrome work of art, to the vapours of HF, and by SERS-detection of the cochineal lake pigment in a paint layer of this cross-section (Figure 1), we also showed that such SERS substrates could be used for specific detection of the spatial distribution of colourants in real cultural heritage samples.

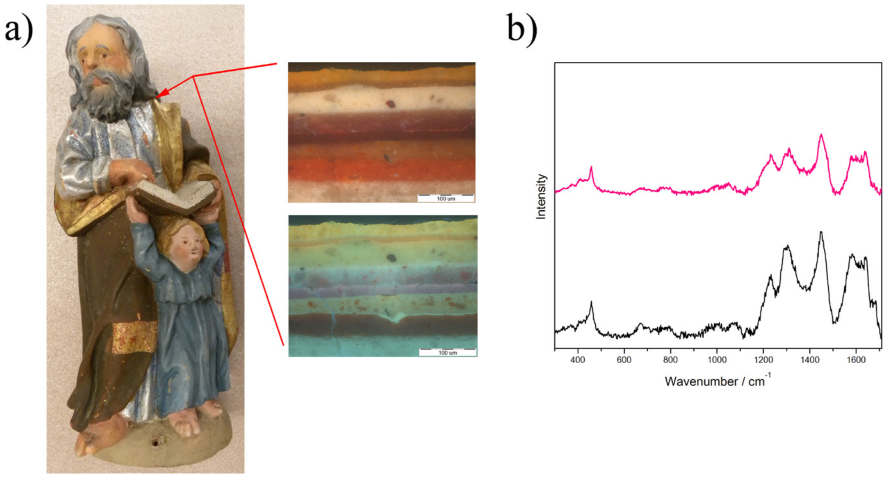

**Figure 1.** a) Marked location of sample removal from the polychrome work of art (Posavje Museum Brežice, Slovenia), and the optical micrographs (in visible and UV light) of the cross-section of the sample. b) SERS spectrum obtained on the cross-section of the sample (upper spectrum), identifying cochineal lake pigment, and comparison to the SERS spectrum of cochineal lake pigment in linseed oil reference material (lower spectrum). $\lambda_0$ = 514nm, SERS substrate: HPC-based photoreduced Ag-colloid.

## Acknowledgements

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# Multipurpose SERS substrates for nanodestructive detection of small molecules in collections

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**Keywords:** SERS, detection dyestuff, woodblock prints, plastic degradation, nanodestructive sampling, LEGO©

This work presents the results obtained with 3D aluminum coated Surface Enhanced Raman Scattering (SERS) substrates on a variety of materials commonly found in cultural heritage, design and contemporary art collections. Additionally, it is demonstrated that the substrates provide reliable data to address conservation science research questions (e.g. detection of early degradation products), as well as technical art history questions (e.g. the identification of dyes). Preventing the decay of artworks is a sensible issue in museums, requiring minimal sampling but reliable diagnostic information. In this respect, a dry and gentle contact method has been optimized, whereby a minimally invasive micro-extraction is performed by gentle adhesion of a silicone strip on the analytical surface. The removed material is subsequently transferred on the SERS substrate with a solvent that selectively extracts different components from complex mixtures for Raman analysis. The method is nanodestructive, considering the size of the fragments being deposited on the substrates, mostly not visible to the naked eye. In fact, small molecules (below 1000 dalton), either derived from the degradation processes taking place on the surface of plastic artworks, or as dyes used to print Japanese woodblocks (Figure 1) and LEGO© bricks are detected with the 3D aluminum coated SERS substrates fabricated for the aim of this research.

The strip sampler is tested with gas chromatography (GC) to evaluate the release of siloxanes, and concurrently pyramidal and cylindrical nanostructures are replicated using fluorinanted polymers by Nano Imprint Soft Lithography (NIL), and coated with an aluminum film by Physical Vapor Deposition (PVD). Rough and continuous metal structures enhance the Raman scattering, in the range of $10^7$–$10^9$ for compounds at concentrations between $1 \times 10^{-6}$ and $1 \times 10^{-15}$ M [1]. Two benchtop Raman spectrometers are used for extended analytical work: an InVia Renishaw and a Witec 3D Confocal Microscope. In addition, different wavelengths (e.g. 514 nm, 785 nm, 488 nm) of the Raman excitation laser are tested to validate the results and accomplish reproducibility. In figure 2, results of inks from commercial felt-tip pens are presented [2]. In this manner, new advances expand the available knowledge reported by the authors on polymers degradation in recent works. [3,4].

Overall, the multipurpose SERS devices optimized and tested in this work allow to achieve different research goals, including the development of the nanodestructive sampling methodology for non-invasive and *in situ* investigations of collections materials.

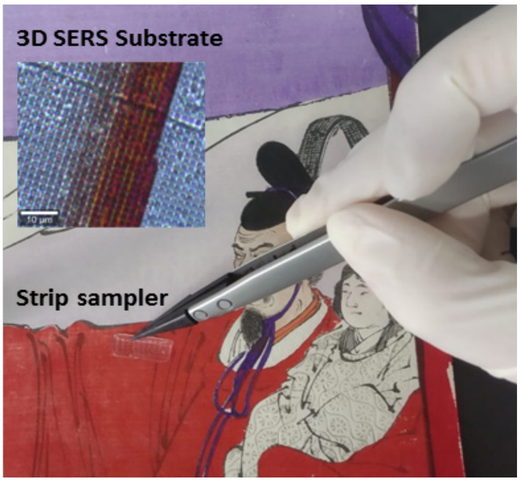

Figure 1. Japanese woodblock print and silicone strip sampler on re red dye in insert on SERS substrate on the top left.

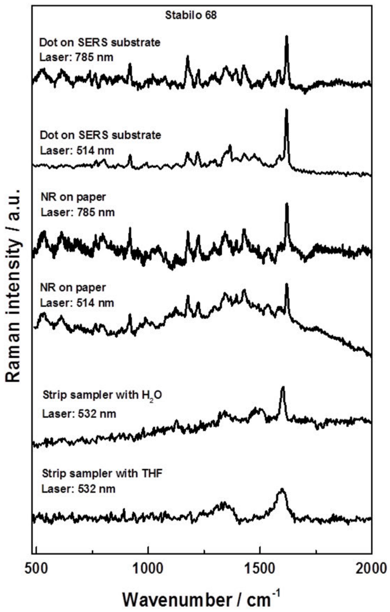

**Figure 2.** Compared Raman spectra on green Stabilo 68 felt-tip pen.

## Acknowledgements

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# FT-Raman, SERS and DFT analysis of safflower red dyed Japanese paper

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**Keywords:** Raman, SERS, DFT, paper, safflower, dyes

Safflower red is a traditional natural dye with a brilliant red hue. It is extracted from the petals of Carthamus tinctorius L. These petals contain a yellow and a red dye. Safflower yellow, also known as hydroxysafflor yellow A (CI Natural Yellow 5), is water soluble and very light fugitive and it was only rarely used as a dye or colorant. The red dye is mainly composed of carthamin (CI Natural Red 26, CI 75140). Despite its poor lightfastness, safflower red was greatly appreciated in Asia as a dye and a colorant for its bright and attractive red color. Safflower was particularly important in *nishiki-e* multicolour Japanese woodblock printing, were it represented the most highly prized red before being supplanted by cochineal in 1869 [1].

In this work, the analysis of washi paper dyed with safflower red was carried out by FT-Raman and SERS spectroscopies. Non-invasive and microanalytical techniques are particularly important for the study of woodblock prints, since the dyes are usually present at very thin layers absorbed by paper fibers. Our goals were to obtain the ordinary Raman spectrum of safflower red, assign its bands, and determine the best experimental conditions for the SERS detection of safflower red in Japanese paper. For this reason, diverse conditions, such as different pH values (neutral and acid), and previous hydrolysis of the dye with HF were studied. In order to get a better knowledge of the effect of the pH in safflower, a SERS study of safflower extract was also carried out.

The FT-Raman spectrum of safflower red was carried out after ethanol extraction from the paper. SERS spectra were obtained from both the alcoholic extract and directly on the dyed paper. Thus, small pieces of fibres were taken from the edges of the paper. A drop of Ag nanoparticles was put on one fibre together with the aggregating agent ($KNO_3$ or $HNO_3$). The SERS analysis were collected at 488 nm before drying of the Ag colloid. DFT calculations were also carried out in order to assign the experimental SERS bands to the vibrational normal modes of the dye. The B3LYP/6-31G** was employed to calculate the geometry of safflower red and the Raman spectrum, by means of the Gaussian Software [2].

The FT-Raman spectrum of safflower red shows bands at 1623, 1602, 1586, 1457, 1441, 1297, 1208 and 1172 $cm^{-1}$. The SERS spectra of the safflower extract on Ag nanoparticles aggregated with $KNO_3$ (neutral pH) and $KNO_3/HNO_3$ (acid pH) show several shifts and changes in the relative intensities of the bands. These changes suggest a deprotonation of one of the OH groups of safflower, which leads to an electronic delocalization on the dye molecule. The SERS spectra of the dyed paper with and without HF pre-treatment show similar Raman enhancement (figure 1). However, the SERS spectra after the addition of $HNO_3$ (figure 1) shows a much lower intensity. Thus, it can be concluded that the best experimental condition for the detection of safflower on paper is the aggregation with $KNO_3$. The main bands observed in the SERS spectrum are located at 1623, 1603, 1579, 1489, 1423, 1401, 1295, 1244, 1163, 955 and 776 $cm^{-1}$.

The Raman spectrum obtained from the DFT calculations fits well the experimental spectra. The visualization of the vibrations leads to the assignment of the observed Raman bands to the vibrational normal modes of the red dye. The interaction mechanism of the safflower molecule on the Ag can be concluded from the differences observed between the FT-Raman and SERS spectra of the safflower extract. Several bands are enhanced due to the presence of Ag NPs, such as those observed at 1623, 1583, 1406, 1164, 958, 865, 776, 746 and 733 $cm^{-1}$.

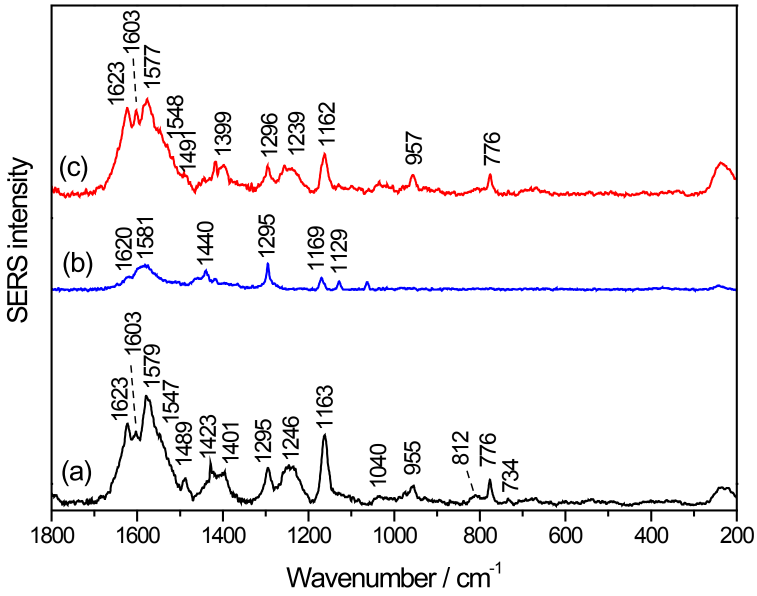

**Figure 1.** SERS spectra of washi paper dyed with safflower red dye on Ag nanoparticles in different experimental conditions: a) neutral pH: b) acidic pH, and c) after hydrolisis with HF. All the spectra were baseline corrected.

## Acknowledgements

This work has been financially supported by CSIC (project i-Link1148) and Comunidad de Madrid/EU (project TOP Heritage-CM).

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# Session 10

# Material characterization and degradation processes

# Spectroscopic investigation of Cappadocia proto-Byzantin paintings

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**Keywords:** Cappadocia, rupestrian churches, painting analysis, micro-Raman spectroscopy, Fourier tranform infrared spectroscopy, SEM-EDS

The rupestrian churches in the turkeysh region of Cappadocia have been included by UNESCO in the World Heritage List due to their extraordinary uniqueness [1].
Given the relevance of this complex, since 2006, the Italian Ministry of Education, University and Research funded an archaeometric study within the project *"Rupestrian art and habitat in Cappadocia (Turkey) and in central and southern Italy. Rock, excavated architecture, painting: between knowledge, preservation and enhancement"*. Since the beginning of the project, more than fifty churches have been investigated to gather a deep knowledge of the materials used and to study the degradation phenomena [2-3].

The present contribution focuses the attention on the oldest Cappadocian paintings, the so-called "proto-Byzantin paintings". These materials have never been investigated before and represent a starting point of paramount importance to understand the evolution of both materials and execution techniques during the ages. In fact, in the wide panorama of the rupestrian settlements, the oldest churches deserve a particular attention due to the interesting painting techniques, highlighted during the various campaings, which seems to be made by *secco* method on a gypsum ground layer, often representing pre-iconoclastic patterns.

Specifically the first investigated church was St. John the Baptist at Çavuşin whose architectural structure is dated back to 5th-6th century (Fig. 1). The painting apparatus, as in many Cappadocia churches, contains different subsequent phases ranging from to 6th to 10th century. The wall paintings in the church of St. John the Baptist are characterized by the presence of superimposed or adjacent layers ascribable to different historical periods, as it occurs in many of the Cappadocia churches.

Preliminary visual in situ investigations have been performed to select the most promising sampling areas. Some of the samples have been prepared as cross section to access their stratigraphy. A multi-technique approach, based on micro-Raman and FT-IR spectroscopy and SEM-EDS investigations was used to study pigments, mortar binders, stones and degradation products.

In particular, the cross sections of the micro samples from the first pictorial phase, highlight the presence of two mortars: the first one rich of limonitic aggregates and the second one (ground layer for the painting) made of gypsum with the addition of organics, probably proteins; the surface of the painting is very irregular and covered by a black soot layer (Fig. 2A). On the other hand, the second decorative phase is characterized by a completely white ground layer, without any aggregate. In this phase the painting layer is thin and partially penetrated in the ground (Fig. 2B) ). This last phase finds exact comparisons with the paintings of Uzumlu, St. Basilio (2nd phase), and Karsibucak. The correct interpretation of the different phases is far from being easy because they are not pure painted mortars but instead can be assumed as *a secco* layers applied over thin whitewashings, sometimes without any decoration at all. Moreover, the reading of the layers is complicated by the bad state of preservation and by the fragmentary character of the paintings. Pigments have been successfully identified and the presence of gypsum and its anidrous form, anhydrite, oxalates and organic materials have been highlighted on the surface, thus suggesting a biological degradation.

Our study allowed to better understand the technique and the materials of the wall paintings, to find analogies and differences between the pictorial phases within the same church and among churches of the same period and give important information to adress a specific conservation/restoration treatment.

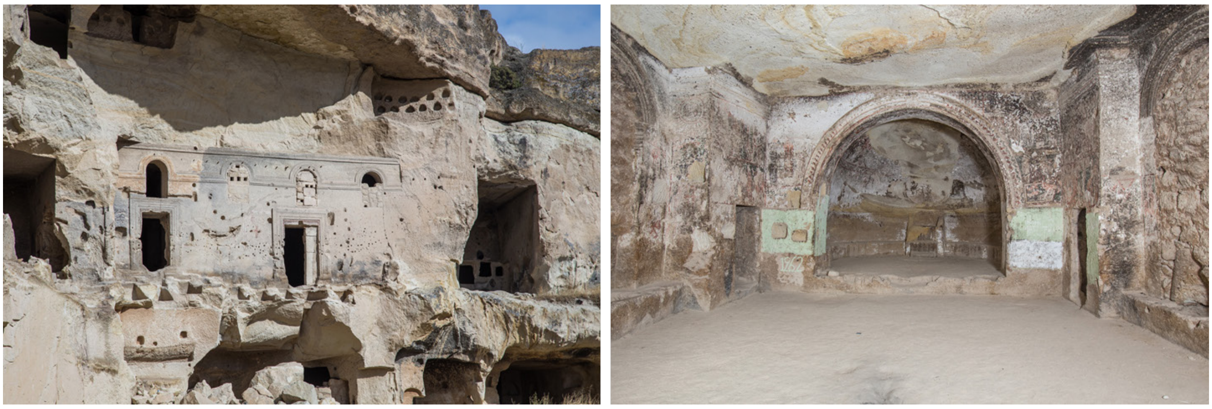

**Figure 1.** Photos of St. John the Baptist church at Çavuşin, external and internal views (Photos by Gaetano Alfano).

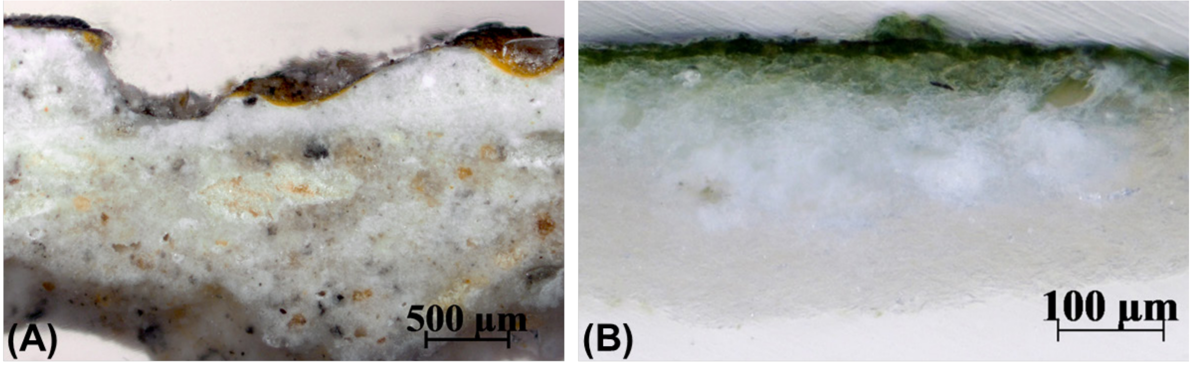

**Figure 2**. Microphotographs of sample cross-sections from the first (A) and second (B) phases, under optical micrscope.

## Acknowledgements

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# Micro-Raman Spectroscopy and Complementary Analytical Techniques for Material Characterization of Archaeological Mural Paintings at El Alto del Aguacate, Tierradentro Cauca, Colombia

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**Keywords:** pigments, mural paintings, micro-raman spectroscopy, materials.

The National Archaeological Park of Tierradentro, located in the northern region of the central Andes, was declared World Cultural Heritage Site by UNESCO in 1995, mainly due to the presence of underground tombs (hypogea) dating from 500-900 A.D according to radio carbon dates and archaeological information[1][2]; its volcanic tuff rock walls are profusely decorated with sculptures and mural paintings in different colors.

The site Alto del Aguacate, has been the least studied of the sites in Tierradentro as a consequence of its remoteness, difficult access, high altitude and lack of electricity; restrictions associated with difficulties in the transportation of equipment and materials to perform analyses on site. Some of the studies carried out throughout the decades consist of archaeological excavations [3], preventive conservation projects [4], and prior archaeometric studies, performed at other sites within the archaeological zone of Tierradentro [5]; these works gave the first approximation to the materials used in the elaboration of the mural paintings.

Although there are some similarities in the mural paintings from the various sites, It is important to highlight the technological and stylistic differences found at El Alto del Aguacate, with use of red and yellow hues unique of this site, along with the specific conservation issues and variations in the soil. These differences were decisive to determine the main objective of this study, which aims to assess wheter the paintings of El Alto del Aguacate were elaborated using the same materials and techniques found in other sites.

Four *hypogea* distributed across the site (A-0, AR-50, AR-44 and AR-38) Figure 1, presenting a variety of colors and techniques, were selected to take micro-stratigraphic and powder samples of the paintings for chemical and mineralogical characterization of the materials, especially the paint, through confocal micro-Raman spectroscopy and complementary techniques including optical microscopy, scanning electron microscopy coupled with energy dispersive x-ray spectrometry (SEM-EDS), x-ray diffraction (XRD), and fourier transform infrared spectroscopy (FT-IR).

**Figure 1**: Details of paintings in *hypogea* A-0 (top), AR-50, AR-44 and AR-38 (bottom).

The results show that the black paint correponds mainly to carbon black. The red paints pigment used was characterized as red ochre, hematite ($Fe_2O_3$) mixed with clays, and the light yellow paint have several bands correponding to yellow ochres, with presence of goethite and white clays. Minerals containing calcium, and white clays such as caolinite were used for the white paints and preparation layers, in some cases mixed with other pigments to modify the color.

In conclusion, it was possible to accurately determine the compositional nature of each pigment through the analysis of the spectra obtained by means of confocal micro-Raman; using SEM-EDS, XRD and FT-IR to verify and complement the results with elementary and mineralogical composition, same as organic compounds identification. Even though, there are coincidences in the main materials found in this study with the ones from prior research projects, some interesting variations between the four different hypogea studied, allowed to raise hypotesis about the variability in the mix of pigments and additives used to modify the characteristics of the paint.

The information about the materials can be used to generate hypothesis about the techniques applied to the elaboration process, determine possible chemical transformations, approach the interaction of the paint with the soil and its components, same as with deterioration materials like biological colonization products, saline efflorescence and other mineral crystallizations, which can be analyzed using different techniques to determine its nature and impact on the conservation of the mural paintings and hypogea structures, contributing to the assessment of conservation diagnosis and future restoration processes with compatible materials and techniques.

## Acknowledgements

This work was developed in the framework of the master´s thesis Technology and Conservation of the Mural Paintings at the Hypogea of El Alto del Aguacate, Tierradentro, Cauca, financially supported and supervised by the Instituto Colombiano de Antropología e Historía ICANH through the Research Development Incentive ICANH 2019. The authors would like to thank Corporación GIPRI-Colombia, Conservator María Paula Álvarez Echeverri, MEng. James Rosero Romo and Dr. Natalia Acevedo Gómez for their contributions to the project.

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# Session 11

# Material characterization, commercial pigments

# Analysis of pigments by Raman spectroscopy

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**Keywords:** pigment analysis, Raman instrumentation

From the beginning of the application of Raman spectroscopy to the study of Cultural Heritage, pigments have been one of the most investigated class of materials. Raman spectroscopy fits perfectly with such kind of analysis: spatial resolution, ability to discriminate similar substances, possibility to investigate small particles on all the possible substrates without any preparation, speed and non-invasivity.

Some drawbacks are however present, as fluorescence, very often present in the analysis of art or archaeological objects, and the high difference in the cross-section of various materials, making difficult the identification of all the components of mixtures.

In this work we will give a panoramic view of the main results and the typical problems encountered when analysing pigments on different substrates (walls, paper, ceramics, glasses, textiles, etc.), with special attention to hard-to-detect and rare pigments.

The identification of a substance as intentional pigment is often crucial in the study of an artwork. The problem of alteration of pigments, including environmental alteration and, in particular, laser-induced alteration, is presented. Identification of restoration and synthetic products is also discussed.

The choice of a correct experimental setup is fundamental for the complete determination of a palette. The different possibilities offered by mobile and fixed Raman apparatuses is illustrated. Different materials often require different excitation lines: the use of different wavelengths influences fluorescence, resonance, space and spectral resolution, spectral range and scattering efficiency so they should carefully chosen. The last developments in the instrumentation and techniques (including SORS and micro-SORS) useful for pigment analysis are shown.

# Early 20th century commercial pigments from a manufacturer's sample collection analyzed with Raman spectroscopy

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**Keywords:** pigment, commercial sample, Arzberger

## Background and objectives

The object under investigation in this study is a historical sample case from the town museum at Grimma (Germany). The leather case contains 397 small glass vials filled with pigment powder of all hues. All vials carry hand-written paper labels, only consisting of cryptic letters and numbers. Some indications suggest that the case was earlier in the possession of Wilhelm Ostwald (1853 - 1932), Nobel prize winner and colour researcher in his late years. By comparison with a similar case in Ostwald's heritage, it could be shown that the case was produced by the pigment factory „Arzberger, Schöpff und Co." in Eisenach (Germany). A specific feature of this collection is the arrangement of some specimens according to their field of application or composition. As this collection of commercial samples represents a snap-shot of the pigments available on the market at the time of their production, the aim of this investigation was to gain an overview of the pigments and their mixtures with a focus on synthetic organic pigments (SOP). Around one quarter of these specimens (109 items) were investigated with Raman-spectroscopy, in some cases supported by Fourier-transform infrared (FTIR) spectroscopy and portable X-ray fluorescence (XRF).

## Methods

Prior to spectroscopic analysis, the powder samples were investigated directly under an incident light microscope or distributed in immersion oil and viewed under transmitted polarised light (PLM) microscope.

Raman experiments were performed using a dispersive Horiba Jobin Yvon XPlora Raman microscope with excitation wavelengths of 532 nm and 785 nm. Output laser power was individually adjusted to the Raman response of the different samples. To quench the intensity of the fluorescent background, powder samples were photo-bleached prior to acquisition of the spectra, using the same wavelength as for the measurement. Further techniques to suppress fluorescence (e.g. preparation in sodium bromide pellets, SERS, preparation on TLC plates [1]) were not successful, however. The resulting Raman spectra were interpreted by matching against different pigment databases [2]. The identified synthetic organic dyes and pigments are designated according to the Colour Index [3].

Additional FTIR analysis was performed under a Bruker Hyperion FTIR microscope connected to a Bruker Tensor 27 spectrometer. Samples were prepared on a diamond anvil cell and measured in transmission mode.

For X-Ray Fluorescence analyses, a portable XRF spectrometer Thermo Niton XL3 air was used. Samples were prepared in polymer cups and measured in a protective chamber

## Results

The following inorganic pigments were identified: iron oxyhydroxides (ledidocrocite, goethite), strontium chromate (PY32), chrome yellow (PY34), zinc yellow (PY36) cadmium yellow

(PY37), Naples yellow (PY41), chrome orange (PO21 / PO45), iron oxide red (hematite), molybdate red (PR104), red lead (PR105), vermillion (PR106), „zinc green" (= Prussian blue + zinc yellow), „chrome green" (= chrome yellow + Prussian blue), Prussian blue (PB27), emerald green (PG21s), synthetic ultramarine (PB29), lead white (PW1), zinc white (PW4), lithopone (PW5), and carbon black (PBk7). Detected fillers are: calcite, barium sulfate, gypsum, calcium sulfate (anhydrite), possibly zeolites. Zinc sulfate possibly is a degradation product.

A broad range of synthetic SOPs were identified: Azo dyes (PY 1, PR3, PR49-1, PR 51, PR53, PR60); triarylmethane dyes (PV3, PV39, PB62, PB24 or PG 1), one xanthylium dye (PV 1), and one indamine pigment (PG9). Most of the SOPs were mixed with barium sulfate as filler. Several samples showed distinct fading on the upper side of the glass vessels which probably was caused by prolonged exposure to light during exhibition. Several light-sensitive SOPs were detected in those samples (PR 51, PV1, PV3, PV39, PB62, PB24 / PG 1). Sensible inorganic pigments showed darkening (PO21, PR105).

As already visible under the optical microscope, a number of hues were pigment mixtures: different inorganic pigments (e.g. chrome yellow + hematite, "chrome green" + carbon black, or "chrome green" + zinc yellow), mixtures of SOPs (e.g. PV3 + PV39 + PB62) or even mixtures of inorganic pigments with SOPs (e.g. PY1 + chrome yellow, or PG1 + ultramarine, or PR53 + barium sulfate + gypsum + chrome yellow, or PG1 + Prussian blue, or PG9 + ultramarine).

## Conclusions

The commercial pigment sample collection can be dated into the time after 1920, as indicated by the presence of PR51 [3]. Thus, the results give an overview of commercial pigments available in the time after 1920. A big number of specimens contain chromate pigments. Barium sulfate proved to be the predominant filler. Remarkably, Emerald green was still found in one of the samples, although the use of this toxic pigment had already been prohibited in Germany in the year 1882.

Among the spectroscopic techniques used for this investigation, Raman microscopy proved the most versatile and powerful technique for the identification of pigments. Especially a number of synthetic organic pigments (SOP) could be detected. Nevertheless, some measurements suffered from strong fluorescence which could not be overcome by common methods of fluorescence suppression. FTIR spectroscopy proved helpful for identification of inorganic fillers (eg. barium sulfate, silicates). The presence of inorganic pigments and fillers could be confirmed by portable XRF as well.

## Acknowledgement

The authors wish to thank Tim Bauer, Simon Enders, Erik Friedrich, and Jan Haberstroh for collecting several of Raman spectra.

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# Characterization of powdered pigments for pictorial retouching by Raman spectroscopy

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**Keywords:** pigment characterization; *Kremer Pigmente*

A set of 27 commercially available pigments by *Kremer Pigmente* (Figure 1), including traditional and synthetic compounds, has been characterized on the chemical-mineralogical point of view by using different analytical technique such as Raman, FT-IR, DRIFT Reflectance spectroscopy and NIR. Here we present results obtained by Raman spectroscopy on these materials currently widely employed for pictorial retouch purposes of both ancient and contemporary works of art. For this reason, the necessity of a deeper comprehension of their composition is fundamental in order to better understand their long term behavior once applied. As a consequence, the presented investigation focused on the use of Raman spectroscopy to determine the constituents of the pigments powders in order to ensure a precise knowledge of materials applicable for painting retouching.

The studied pigment set is classified by the company into 4 categories: dyes and colors deriving by plants, pigments of own production and historical pigments, modern pigments and natural earths. Spectra were interpreted in order to identify the existing phases and results were compared with data sheets available by Kremer Pigmente: many inconsistencies were observed (especially concerning the pigments CAS numbers), e.g. spectra of Raw Umber (40612) and Burnt Umber (40700) resulted difficultly interpretable because of several inconsistencies between the CAS number of phases declared by the manufacturer and Raman analyses. At the same time, some compounds were not declared in the official data: many mineral diluting phases were, in fact, added into pigment formulations and Raman spectroscopy permitted their fast identification in various pigments, especiallythose belonging to the natural earth group. In other cases the commercial manufacturer increasingly introduced constituents into the composition of a pigment in order to obtain a specific desired shade. This is the case of the three Bristol Yellows (pale- 43101-, medium-43111, reddish- 43131), wherethe main component is Pigment Yellow 139 (Isoindoline Yellow) followed by clinobisvanite ($BiVO_4$) and Pigment Orange 73, whose amounts were increasingly added to change from pale Bristol Yellow to a reddish one.

The study allowed evidencing problems related to the analysis of organic materials such as Madder lake, whose colouring agent could not be recognized; only the spectrum related to an additional phase could be recorded. At the same way also the acquisition of vibrational spectra on natural earths resulted particularly difficult operating with a 785 nm source because of the high fluorescence background exhibited. A similar behaviour was found for Azurite MP (10207) and Malachite MP (10300), both displaying only the main peak of quartz over an high fluorescence background.

Raman spectroscopy is indubtably a valid method for the characterization of many powdered pigments allowing the identification of additional phases often undeclared by producers or suppliers, and employed as diluting materials or to modify the hue or other pigment properties. Sometimes these components can represent undesired or, in the worst case, unknown variables for conservators applying them during restoration processes since unexpected final results can be achieved, even years after their application. Despite this, here some limits due to the use of portable instrumentation and to the employed wavelength did not permitted the complete study of all selected materials since phenomena such as fluorescence or luminescence limited the observation of Raman modes. This applied, for example, to earths or dyes. For this reason, a deeper characterization is foreseen and further results concerning the study of the same set of pigments through different spectroscopic techniques such as Reflectance and FTIR spectroscopy will be provided in future papers currently in preparation.

The final aim of this project is the creation of an easily accessible database, reporting the characteristic features of each phase in every analyzed pigment in order to obtain a useful tool for the study of original and retouched artworks, as well as for conservators needing complete data on the materials they are going to introduce on a work of art.

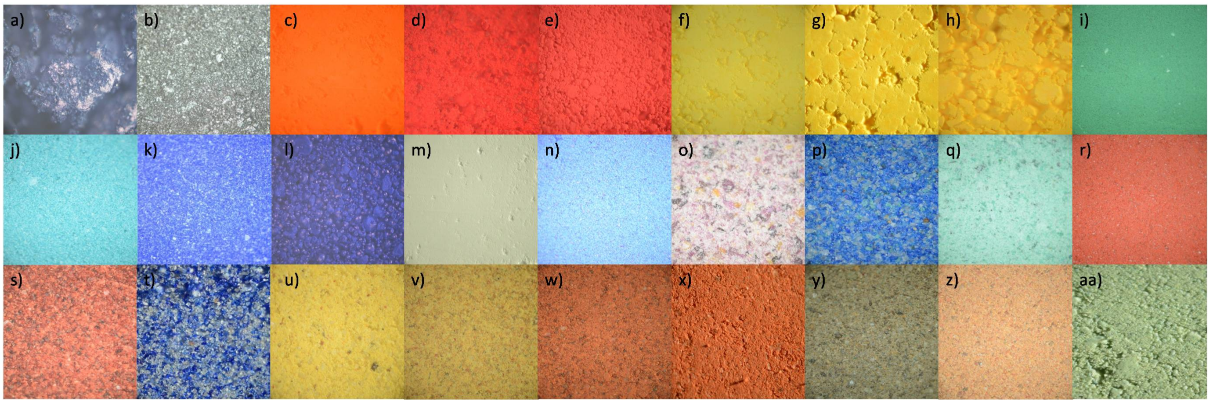

**Figure 1.** Optical Microscopy images of the 27 powder pigments. a) Indigo, 36000; b) Peach Black, 12010; c) Irgazine Orange, 23178; d) Irgazine Ruby, 23182; e)Quindo Pink D, 23402; f) Pale Bristol Yellow, 43101; g) Medium Bristol Yellow, 43111; h) Reddish Bristol Yellow, 43131;i) Cobalt Green, 44100; j) Bluish Cobalt Green A, 44151; k) Ultramarine Blue, 45000; l) Prussian Blue LUX, 45202; m) Zinc White, 46300; n) Dark Cobalt Blue, 45700; o) Vesuvianite, 104500; p) Azurite MP, 10207; q) Natural Malachite MP, 10300; r) Cinnabar, 10624; s) Madder Lake made of roots, 372142; t) Lapis Lazuli from Cile, 1056038; u) Italian Light Gold Ochre, 40220; v) Raw Sienna, 40400; w) Dark Burnt Sienna, 40430; x)Venetian Red, 40510; y) Greenish Raw Umber, 40612;, z) Reddish Burnt Umber, 40700; aa) Bohemian green earth, 40810.

## Acknowledgements

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## Session 12

# Material characterization and degradation processes

# New evidence for the intentional use of calomel as a white pigment

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**Keywords:** micro-Raman spectroscopy, calomel, mercury white, illuminated manuscripts, portrait miniatures

This presentation will report the results of the in-situ application of micro-Raman spectroscopy to the analysis of two historic painted objects: a 15th-century illuminated manuscript and a late 16th-century portrait miniature. Both objects were unexpectedly found to contain calomel (Hg2Cl2), used as a white pigment. Calomel was a widespread and popular medicine until it fell out of use at the end of the 19th century due to its toxicity and a material called 'mercury white' is referred to in 16th-century technical literature on painting. However, although calomel has been recognised in the past as a degradation product of cinnabar in both wall and easel paintings [1-3], its deliberate use as a pigment on a cultural heritage object has only been documented recently, in white areas painted on a 17th-century Peruvian cabinet [4]. The present study describes the first-ever verified use of calomel as a white pigment on European works of art, both of which pre-date its documented use in South America.

The so-called 'Fitzwilliam Missal' (Fitzwilliam Museum, MS 34) was most probably made in York around 1470 and is illuminated in typical 15th-century English style. Dark offsets are clearly visible on many pages (Figure 1) and usually correspond to areas painted in white on the facing page. They attest both a degradation process that must have affected some of the pigments, and the fact that the manuscript has been disbound and the pages re-ordered at least twice in the past.

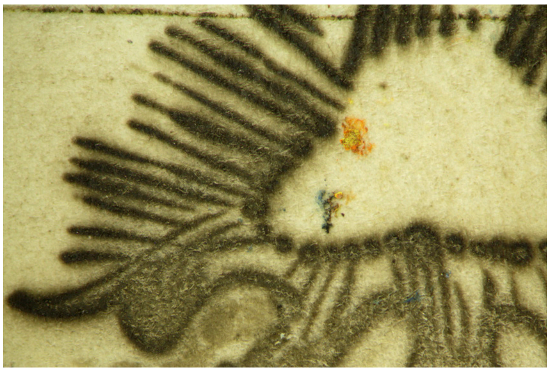

**Figure 1.** Dark offset on a page of the Fitzwilliam Missal (MS 34), facing a white painted area on the opposite page.

A portrait of a fashionably attired unknown lady (Fitzwilliam Museum, 3868) has long been considered a 'typical' miniature by Isaac Oliver, one of the most renowned 'limners' (miniature painters) working in London in the late 16th and early 17th century. Interestingly, however, UV imaging and XRF analyses revealed that large part of the white collar and lace in her costume contains barium white and must therefore have been heavily overpainted at some point in the 19th century. The barium white appears to be covering dull grey (original) paint, which must have been the reason for the extensive intervention.

Two portable Raman spectrometers were used during this work, both of them equipped with optical fibers and microscope objectives. One was a portable i-Raman Plus spectrometer (B&W TEK Inc., Newark, USA) provided with a 785 nm excitation laser line. The second was a custom-built spectrometer with a 633 nm excitation line. In both cases, long-working distance objectives were used and the laser power was kept below 1 mW at the sample, to prevent pigment photodecomposition. Typical acquisition times were between 5-20 seconds. Figure 2 shows the comparison between a Raman spectrum of commercial $Hg_2Cl_2$ and one of the spectra collected on a white area on the Fitzwilliam Missal, which corresponds to the same compound.

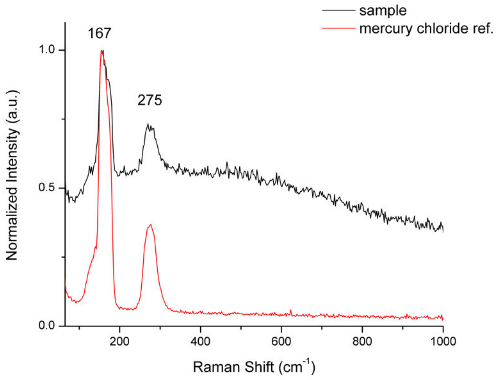

**Figure 2.** Raman spectra of white area in the Fitzwilliam Missal (MS 34, fol. 134r) and reference commercial $Hg_2Cl_2$.

The presentation will discuss the analytical protocol used and then focus on the significance of these findings in the context of late medieval/early Modern England, where both artworks were produced.

## Acknowledgements

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# Tubes of paint used by Vieira da Silva (1908-1992): Application of Raman spectroscopy and complementary techniques

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**Keywords**: paint tubes, tempera, pigments, nano-analysis, contemporary art, Raman spectroscopy

Maria Helena Vieira da Silva (1908-1992) is one of the most significant Portuguese painters of the 20th century, who left an enormous amount of works in a great variety of supports and painting materials. One of those materials was tempera, which she used on almost 1/5 of her whole production, from 1946 onwards [1].

One of the main producers of the tempera paints used by Vieira da Silva was 'Sennelier', a French company that is active producing materials for artists since 1887 [1]. With the increase in chemical and industrial innovations, new and very different formulations of synthetic pigments and dyes started to be commercialized [2-3]. These new formulations (which usually include additives, such as extenders, fillers, byproducts of reaction synthesis, etc.) present increased difficulties for conservation scientists and restorers dealing with their conservation, especially when it comes to identifying and characterizing the paints, understanding their composition and the way they may have deteriorate over time [4].

The aim of this work is to create a database of the tempera paints Vieira da Silva used over more than forty years. For that purpose, a series of paint tubes of the brand "Sennelier" is studied for the very first time with complementary micro-analytical techniques.

One of the most relevant techniques employed in this study is Raman spectroscopy because it enables the simultaneous identification and characterization of organic and inorganic materials present in the samples. In particular, the inorganic part of the samples reveals information on the phase of the materials and in some case, the conditions in which these materials were stored or used (temperature and stress) by studying the peak shifts as well as variations in their intensity and width. One issue usually associated to these samples is the small amount of material which results in very low intensity signals. In this work, we overcome this constraint by combining state-of-the-art micro- and nano-Raman techniques by employing first resonance enhancement for the different constituent materials. This is achieved by utilizing various laser sources and tuning the excitation wavelength from the ultraviolet (325 nm) to deep red (785 nm) spectral range. Secondly weak signals are further enhanced by employing Surface Enhanced Raman Scattering (SERS). For this purpose, a solution of colloidal silver nano-particles is added to the powder samples.

The results obtained by Raman spectroscopy are compared with those gathered by means of complementary micro-analytical techniques: Scanning Electron Microscopy coupled with Energy Dispersive X-Ray Spectroscopy (SEM-EDS), Fourier-Transform Infrared Spectroscopy (FT-IR) and X-ray Diffraction (XRD).

Regarding the binding medium, the results obtained reveal, at least, the presence of egg (glair and/or yolk), vegetable oil (such as canola oil), resins, and other proteinaceous substances. Concerning the paint composition, the results reveal, in some cases, mixtures of unexpected colouring matters, with significant discrepancies between the content of the tubes and the information supplied on the label.

The overall results, at molecular and elemental composition levels, allow a better elucidation of the chemical composition of the tempera paints used by Vieira da Silva, thus providing valuable information regarding their conservation and a new tool for further authentication of her paintings.

This pioneering work introduces a scientific approach that will not only improve the knowledge regarding painting materials used by Vieira da Silva, but also contribute to a new perspective about her work and life.

**Figure 1.** Some paint tubes (among others) of the Sennelier brand used by Vieira da Silva. ©ALeGac

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# A closer look at red in Portuguese historical plastics: a Raman microscopy study

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**Keywords:** historical plastic objects, colouring technology, colourant identification, synthetic organic pigments, Raman microscopy

The history of the Portuguese plastics industry is based chiefly on documentary sources, leaving aside the analysis of historical plastic objects which are of growing cultural significance. To fill this gap, a research project, *The Triumph of Bakelite - Contributions for a History of Plastics in Portugal* was launched to track the history of the Portuguese plastic Industry [1]. Accordingly, several hundred plastic objects from both private collections and industry have been selected for historical, technological and material studies.

Although the polymer identification in a plastic object has been frequently addressed in conservation studies, the identification of colourants is more challenging and less common, even though colour changes (such as fading, yellowing and darkening) have been found in cultural objects. Due to the small concentration of colourants (0.5%-5%) within plastic formulations [2] as well as the complexity of polymer systems under study (composite formulation), the characterization of colourants poses methodological and analytical challenges.

In this study, optical microscopy, µ-Energy Dispersive-X-ray fluorescence Spectroscopy (µ-EDXRF), Fourier Transform Infrared Spectroscopy with Attenuated Total Reflectance (FTIR-ATR), Fibre optic Reflectance Spectroscopy (FORS) and Raman spectroscopy are explored for the study of red historical plastic objects from a Portuguese private collection, dating from the 1940s to 1980s. The collection was selected due to its representativeness of the birth of the national thermoplastic processing industry and because it shows red historical objects made of different polymer matrixes (polyethylene (PE), polypropylene (PP) and polystyrene (PS)) as well as different colour stabilities. Within the selected multi-analytical approach, Raman microscopy provided the most valuable information for colourant identification (for both inorganic and organic pigments), even in the presence of complex systems such as plastics.

From the assessment of approximately 40 objects, mainly β-naphthol pigments such as PR 48, PR 49 and PR 53 in mixture with PW 6 (titanium $TiO_2$, dioxide) and PR 104 (molybdated lead chromate, $Pb(Cr,Mo,S)O_4$) along with PR 108:1 (cadmium sulfo-selenide CdS/CdSe lithopone) have been unequivocally identified as colouring agents using Raman microscopy. For the first time, β-naphthol red pigments have been identified in Portuguese historical plastic objects (Figure 1). Also, β-naphthol reds were detected in objects showing colour fading. In the red caps shown in Figure 2, although they show completely different colour stabilities, PR 53 was identified in both cases. One is made of PS and the colour is well preserved, while the other is made of PE and the colour faded drastically. Thus, this study provides new insights into the plastic technology, and offers reliable data for the study of the long-term stability of this family of colourants in plastics. Although the colourfastness of this class of synthetic colourants is unclear, preliminary considerations on their stability in different plastic formulations are also discussed in this study. The potential, efficacy and limitations of the multi-analytical approach is discussed, along with some technical and practical aspects of the use of Raman microscopy for colourants identification. This work also intends to give an overview of the colourants found in Portuguese historical objects.

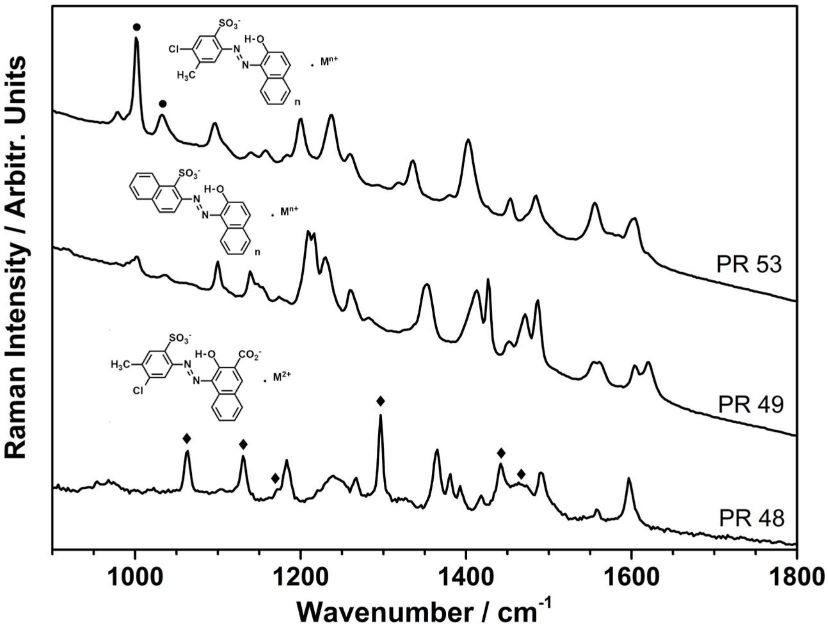

**Figure 1.** Raman spectra (acquired at 100x using the 785 nm laser line) of β-naphthol pigments PR 48, PR 49 and PR 53 identified in the red historical plastic objects. The contribution of PE (♦) and PS (•) are often present in spectra.

**Figure 2.** Example of two plastic recipients with red caps made of PS (left) and PE (right) showing different colour stabilities. In both caps PR 53 was identified as the red colouring agent.

## Acknowledgements

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# Poster

# Assessing the performance of space-derived spectroscopic and diffractometric portable systems in the characterization of Cultural Heritage materials: “La Santisima Trinidad” church (Spain) as case of study

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**Keywords:** portable XRD, portable Raman, mural paintings, space-exploration technology

The commercial spreading of portable spectroscopic systems (e.g. Raman, FTIR, XRF and LIBS) over the past two decades helped to consolidate the scientific study of Cultural Heritage materials as a routine work to be performed prior to any conservation treatment [1.2].

Indeed, the main advantage provided by portable systems, consisting in the ability to perform in-situ elemental and molecular analysis, allows to perform the mineralogical and geochemical screening of original and degradation materials of artworks, thus limiting the number of samples to be collected for complementary laboratory studies (e.g. XRD).

Although portable analytical tools are nowadays routinely employed in the field of art and archaeology, the technological advances derived from space-exploration missions, especially in terms of miniaturization and automated control of analytical instruments, are bringing new technical solutions that can help to further increase the scientific outcome deriving from the in-situ study of Cultural Heritage materials.

In this context, the present work aims to compare the analytical results provided by conventional spectroscopic and diffractometric instruments with those obtained from analytical systems derived from space-exploration technology.

For this purpose, offering a wide palette of pigments and degradation products, the mural paintings preserved in the church of La Santísima Trinidad of Segovia (Spain, Figure 1)) were chosen as an ideal case of study.

On one side, the diffractometric results obtained from a laboratory X-Ray Diffractometer (Philips PW1720) were compared to those provided by the first portable XRD instrument in the market (Terra, Olympus), which make use of the technology employed by the CheMin instrument on board the Curiosity/NASA rover [3].

On the other side, the spectroscopic molecular results obtained from the use of commercial Raman systems (both portable and benchtop) were compared to those provided by the RAD1 (RAman Demonstrator) spectrometer. Developed by the Erica research group (University of Valladolid, Spain), the RAD1 is a field-portable prototype of the Raman Laser Spectrometer (RLS) instrument that will be soon deployed on Mars as part of the ExoMars/ESA rover payload [4].

According to the results provided by conventional instruments, cinnabar, minium, hematite, goethite, litarge, coal, phthalocyanine blue, shellac and azurite were used to paint and restore the artwork, while nitrates (nitratine and nitro), hydrated magnesium sulfate (epsomite and hexahydrite) and calcium sulfate (gypsum) were detected as main alteration products.

Under a qualitative point of view, spectroscopic and diffractometric data obtained through space-derived analytical systems were in agreement with commercial instruments results. The main advantage provided by the use of theTerra XRD system consists in the in-situ characterization of samples below 50mg of weight, thus enabling for the first time the mineralogical screening analysis of immovable artworks.

On the other hand, the series of space-derived algorithms employed by the RAD1 system to automatically obtain high quality spectra (i.e. signal to noise ratio optimization and integration time/number of accumulations selection) [5] helps to obtain a higher numer of spectra compared to the manual procedures offered by commercial instruments, maximizing the amount of data that can be obtained throughout the campaign of analysis.

**Figure 1.** a) Location of one of the pigmented columns analyzed in this study. b) Greenish coloration of the column

## Acknowledgements

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# Identification of the painting materials described and used in the “Berliner Musterbuch”, a XVth century treaties for book illumination

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**Keywords:** pigments characterisation, manuscript analysis

The so called “Berliner Musterbuch” from around 1450-60, belonging to the Kupferstichkabinett Berlin (Museum of Prints and Drawings), is a manuscript on parchment, which presents a rare documentation of instructions for the decoration of illuminated books. Step by step the treaties describes, how to prepare colours and how to draw and paint decorations for initials and borders in illuminated manuscripts or early printed books. Painting materials such as inorganic pigments and organic colorants are described. The scribe also contains explanatory samples, which illustrate the instructions with step by step models and exemplifies each colour. With the aim to explore if the drawing and colour materials mentioned in the text are indeed the same used in the drawings, different analytical techniques were used. The Raman analyses, crucial for the identification of the inorganic pigments and its mixtures, as well as XRF and FORS results are presented in this poster. It was possible to conclude that the pigments used were mostly the ones mentioned in the book and new insights in historic nomenclature of pigments and binders were gained.

# Non-invasive spectroscopic study of mural paintings of a hermitage church from the XV$^{th}$ century

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**Keywords:** mural painting, portable X-ray fluorescence, non-invasive, portable Raman spectroscopy

The hermitage of La Consolacion (Figure 1) is a small church located in the village of Torredonjimeno in Jaén province (Andalusia, Spain). The origin of the hermitage is dated back to the VII$^{th}$ century when a primitive construction could have existed as can be deduced from the archeological pieces found inside it. The church was severely remodeled in the XVII$^{th}$ century but parts of the original gothic structure were respected.

**Figure 1.** Facade of the hermitage church of Consolation of Torredonjimeno (Jaén, Spain).

This study is focused on the remains of wall paintings that conservators have discovered during recent restoration works lurking behind layers of whitewash added over centuries in the gothic sacristy dated to the XV$^{th}$ century [1]. Applying limewash coatings was a common practice during the XVI and XVII$^{th}$ century employed as a prophylactic method against several epidemics. The uncovered mural paintings (Figure 2) represent the scene of the Annunciation and the figures of two saints. Furthermore, it is possible to appreciate an additional woman figure, which is believed to be the wife of Diego López de Pacheco, who was responsible for the construction of this section of the church.

The study has been carried out *in situ* in a completely non-invasive way. The first characterization was done using an energy dispersive X-ray fluorescence (EDXRF) handheld analyzer. This study provided chemical elemental information. The research is being completed with a portable Raman microspectrometer using a 785 nm laser for excitation.  If necessary, a selection of microsamples will be analyzed in the laboratory by means of confocal Raman microspectroscopy with excitation at both 514 and 785 nm and other complementary techniques.

**Figure 2.** Mural painting remains studied of the hermitage of Consolación of Torredonjimeno (Jaén).

Typical pigments of the XVth century have been identified. In the red areas, iron in the form of hematite was used. The total absence of silicon discards the use of clay-based red ochre pigments. Azurite, the most widely used blue pigment in European paintings of this period, was identified in the Virgin´s mantle. The blue color is relatively well preserved despite the instability of this pigment, probably thanks to the protection of the coating. Copper was also presented in green decorations but the pigment has still not been unambiguously identified. Gold remains have been identified in the halo of the Virgin. Copper and iron were also found in these remains of gilding, but their role in these decorations is still not clear. The paintings were executed over a preparation layer of lead white, which causes an intense signal of lead in all XRF spectra. The purpose of this white lead primer layer was to achieve a homogeneous surface and to give the paintings more luminosity due to the high refraction index of this pigment.

Finally, we have also studied other polychrome scarce remains located in the front cover of the stone facade of the hermitage church. This part of the hermitage belongs to the restoration and extension carried out during the XVII$^{th}$ century. The painting remains consist of some small red coloured areas. Iron oxide pigments were used to achieve the colour. These findings allow us to hypothesize that originally the whole facade of the hermitage church was painted in red colour. The macroscopical examination appreciated a white layer above the polychrome, probably applied during some posterior period, to hide the original aspect of the facade.

## Acknowledgments

This work has been financially supported by the *Diputación Provincial de Jaén (*Institute of Giennenses Studies).

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# In-situ Raman spectroscopy vs. laboratory analysis for the pigments characterization of the Ariadne´s House (Pompeii, Italy).

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**Keywords:** Pompeii, pigments, wax, Raman Spectroscopy, in-situ analysis.

The House of Ariadne, also known as the House of the Coloured Capitals, located in the Regio VII of the Archaeological Park of Pompeii, was one of the largest residential buildings of the ancient city, covering over 1700 m$^2$ (Figure 1-left). The structure was built at the beginning of the 2nd century BCE. At the time of the Mount Vesuvius eruption (79 CE), the building consisted of a large Tuscan atrium and two peristyles surrounded by more than 40 rooms on the ground floor. Most of the rooms were decorated with frescoes of the third and fourth style, painted in the decades proceeding to the volcanic eruption [1].

The aim of this work was to characterize the molecular and elemental composition of the pigments used in House of Ariadne in order to detemine the mixtures of pigments used and their state of conservation. For this purpose, in-situ Raman spectrosocopy was selected to avoid sampling due to the poor state of preservation of the house (Figure 1-middle). After the in-situ analysis, a guided sampling based on the results of the in-situ measurements was carried out in order to prevent from the unnecessary damage, since the conservation of the house was a priority. In this case, micro-sampling of some areas was required because in the first in-situ analyses the fluorescence emitted by the wax layer of the walls masked the signal coming from the pigments.

In this work, portable Raman spectroscopy and hand-held energy dispersive X-ray fluorescence spectrometry (HH-ED-XRF), as complementary technique, were used. On the one hand, the in-situ Raman analyses were carried out with a portable InnoRam spectrometer (B&W Tek INC, Newark, USA) equipped with a 785 nm diode excitation laser. The spectrometer worked in a spectral range from 65 to 2500 cm$^{-1}$. The maximum laser power of the system is 300 mW at the excitation source. For the analyzed samples, the laser power was adjusted up to 1% of the total power to avoid the pigment thermal decomposition. Spectra acquisition was done with the software BWSpec™ 3.26 (Newark, USA). The spectra were recorded with an integration time varying from 0.5 to 10 s, and with a number of accumulations ranging from 10 to 50. At the laboratory the same instrument was used, but the fiber optic was connected to a microscope [2]. On the other hand, the HH-ED-XRF XMET5100 (Oxford Instruments, UK) equipped with a Rh tube working at a maximum voltage and current of 45 kV and 50 mA respectively, and 9 mm spot collimation was used for the elemental characterization of the pigments. The instrument includes: *i)* a Peltier cooled silicon drift detector (SDD) of high resolution that is able to provide an energetic resolution of 150 eV (FWHM value of the Mn $K_\alpha$ line at −20 °C) and *ii)* a PDA to control the conditions of the measurement, the spectrometer and also to save the spectral and semiquantitative information.

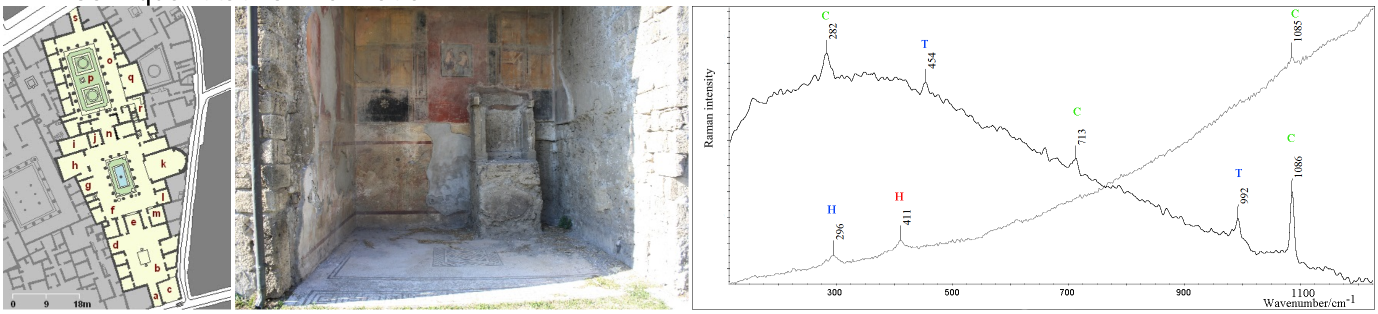

**Figure 1.** Plan of the House of Ariadne (left). The room *d* (middle) and Raman spectra taken on a efflorescence (room *g*) and red color (room *h*) (right). H: hematite, T: thenardite, and C: calcite.

The walls and the mural paintings exposed to the rain were the worst preseved with evident loss of painting and plaster observed at the naked eye. In the walls of the rooms with roofs (g,d and m), in areas without pictorial layers, calcite ($CaCO_3$; Raman bands at 1085s, 712w and 280m $cm^{-1}$), albite ($NaAlSi_3O_8$; Raman bands at 508s and 478m $cm^{-1}$) and quartz ($SiO_2$; Raman band at 464s $cm^{-1}$) were identified as original components of the mortars and from the sand grains. Almost all of the spectra collected on efflorescences were epsomite ($MgSO_4·7H_2O$, main band at 985 $cm^{-1}$), syngenite ($K_2Ca(SO_4)_2·H_2O$, band at 982 $cm^{-1}$), gypsum ($CaSO_4·2H_2O$; main Raman peak at 1008 $cm^{-1}$) and thenardite ($Na_2SO_4$, band observed at 994 $cm^{-1}$). The presence of these sulfates evidences the atmospheric impact of the modern pollution by the fixation of the acid gases (as $SO_2$) and the degradation of the original compounds.

Regarding pigments, red ochre (hematite, $Fe_2O_3$; Raman bands at 295 and 410 $cm^{-1}$) and yellow ochre (goethite, FeOOH; Raman band at ~390 $cm^{-1}$) were identified in-situ in different red and yellow areas of the wall paintings. However, it was not possible to identify the composition of the blue pigment by in-situ Raman spectroscopy because of the fluorescence produced by the wax layer (identified by IR spectroscopy). By means of HH-ED-XRF it was determined the presence of Cu and Si. Raman spectrosocopy measurements performed in the laboratory, allowed to identify Egyptian blue ($CaCuSi_4O_{10}$), a synthetic pigment prepared by melting the copper-rich ingredient with lime and desert sand manufactured since ancient Egyptian civilizations [4], which came in agreement with the elemental results.

## Acknowledgements.

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# A Raman Spectroscopic Study of Zircons in the Gemological Collection of Abraham Gottlob Werner

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**Keywords:** zircon, Raman spectroscopy, gemological collection

Abraham Gottlob Werner was the first scientist, who systematized geology to be a science subject, he provided an extremely important theoretical foundation for the modern nomenclature and classification of minerals, this was also crucial to the research and development of gemology[1–3]. In his unique geological collection, the most special is his gemological collection, including 1368 groups of samples for 22 kinds of minerals. But the gemological collection of Werner is not visible and available for general public.

Zircon is a common accessory mineral of sediments and it has a widespread geological significance. On account of its high quality of optical properties and chemical durability it has been used as a gemstone for a long time. The crystallographic unit cell of zircon is tetragonal containing 4 formula units of $ZrSiO_4$ and its space group is $D_{4h}^{19}$. In general, every method of structural analysis, such as nuclear magnetic resonance spectroscopy, X-ray absorption or powder diffractometry, can be applied to investigate the degree of metamictization in a zircon sample. As a nondestructive testing, Raman spectroscopy can well characterize the metamictization of gem-quality or historic zircon. Frequency shift and band broadening rely on the degree of metamictization. The degree of lattice decay can be estimated utilizing the half-width (FWHM) of the $\nu_3$ ($SiO_4$) Raman band at about 1000cm$^{-1}$, even in a highly metamict zircon with an extremely disordered lattice[4–8].

According to the catalog in 1823 of Werner, No. 039-173 samples are classified to zircon. One number represents a piece or a group of samples. Most of them are grain (46.7%) and crystal (39.3%), 10 groups of zircon samples were cut in different forms, 6 pieces crystal with mother rocks and 1 wood crystal model are also in these numbers. No. 094 and No. 151 are lost.

This study deals with the application of Raman spectroscopy analysis for estimating the degree of metamictization in zircons in the gemological collection of Werner, and discuss the influence of metamictization to the gemological properties of zircon.

Raman spectra of samples were determined by A LabRam800 HR (Horiba Jobin Yvon) microprobe (Institute of theoretical physics, Technische Universität Bergakademie Freiberg). The 532 nm line of a frequency-doubled diode-pumped HeNe laser was used. For laser focusing, an Olympus microscope with a 50× objective (0.5 numerical aperture) was employed. The laser power at the sample surface was 20mW. Scattered laser light was suppressed by an edge filter (Jobin Yvon, cut off at about 150 cm$^{-1}$). The resolution of the system was better than 2cm$^{-1}$. External calibration was reached using the Raman line of Si (520.6 cm$^{-1}$).

Half of the zircon samples in the gemological collection are intermediate, more than 40% of the samples are well crystallized, different degree of metamictization were observed in about only 7% of samples. The Raman spectra of zircons with different levels of metamictization are distinguishing (Fig. 1). With decreasing degree of lattice ordering, the bands of internal (intra-tetrahedral) as well as of external (inter-tetrahedral) vibrations become less intense and less sharp. In addition, as zircons become increasingly metamict, the vibrational frequencies are clearly lowered. The origin, gemological properties and parameters of $\nu_3$ ($SiO_4$) Raman band of some zircon samples are listed in Table 1. Combining the data of all zircon samples in the gemological collection, well crystallized zircons show brown color with red tone regularly, light green tone with gray and yellow appears in intermediate zircons, and green is the main color of metamict zircons. Density increases with the decreasing crystallinity.

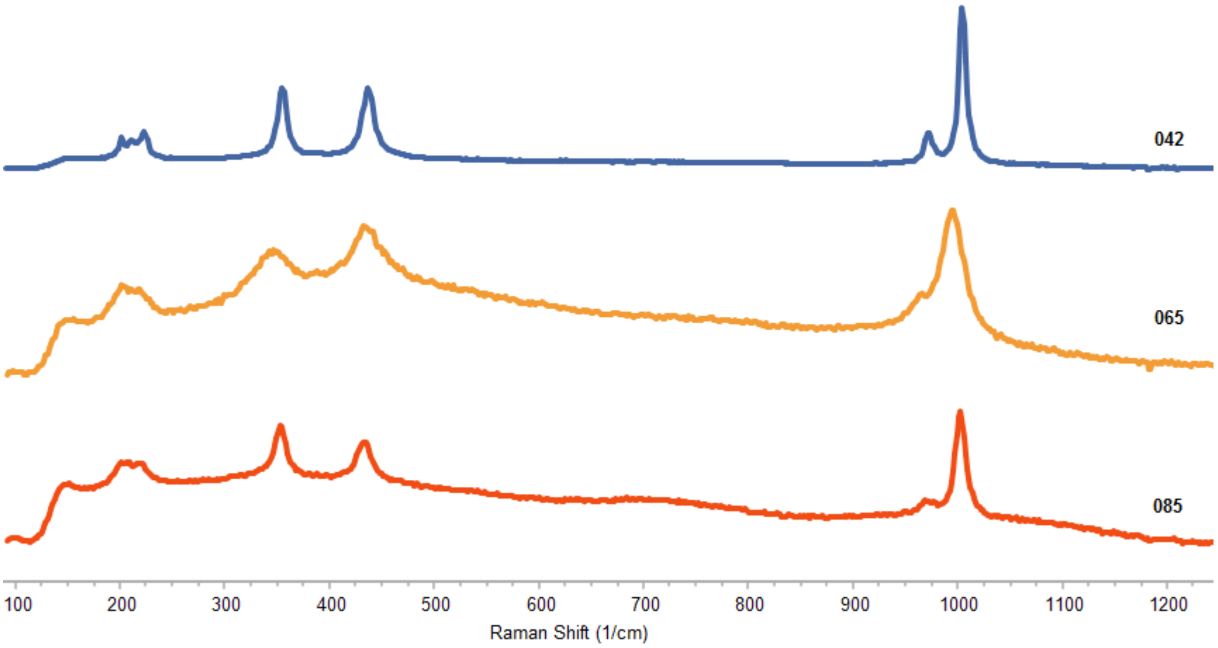

**Figure 1.** Raman spectra of zircon samples representing different degrees of metamictization.

**Table 1.** The description, parameters of $v_3$ ($SiO_4$) Raman band and crystallinity of zircon samples

| No. | Origin | Color | Transparency | Density ($g/cm^3$) | Band $v_3$ ($SiO_4$) ($cm^{-1}$) Raman shift ($cm^{-1}$) | Band $v_3$ ($SiO_4$) ($cm^{-1}$) FWHM ($cm^{-1}$) | Structural state |
|---|---|---|---|---|---|---|---|
| 042 | Sri Lanka | orange-brown | translucent-opaque | 4.852 | 1005 | 9.1 | well crystallized |
| 065 | Sri Lanka | gray-green | translucent-opaque | 4.261 | 995 | 39.3 | highly metamict |
| 085 | Sri Lanka | gray | translucent-opaque | 4.577 | 1002 | 15.3 | intermediate |

This work focuses on the Raman spectra of zircon samples in the gemological collection of Abraham Gottlob Werner. More than 90% zircon samples are well crystallized or at intermediate level of metamictization. The process of metamictization of zircon greatly influences not only its Raman spectrum but also the gemological properties.

## Acknowledgements

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# Plattnerite – Scrutinyite in a Central Asian wall painting of a Buddhist cave temple of the northern Silk Road

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Keywords: plattnerite, scrutinyite, silk road, mural paintings

The Turfan Collection of the Museum of Asian Art (*Museum für Asiatische Kunst*) in Berlin holds a vast number of Central Asian wall paintings, sculptures, architectural fragments, textiles, and other archaeological artifacts from Buddhist cave temples of the Kucha region in northwestern China. Located at the northern Silk Road, this area flourished between the 5th and 10th century AD. The extensive amount of various pigments used for the interior decoration clearly underline the importance of these cave complexes as cultural centers. The majority of the collection was brought to Berlin between 1902 and 1914 during four German expeditions lead by Grünwedel and Le Coq. Details of the mural paintings were documented by Grünwedel with high precision before being detached from the walls and ceilings of the caves [1]. Back in Europe, the fragments of the paintings were reattached together and hence have been exposed to several conservative treatments, such as consolidation with a polyvinyl acetate dispersion (trade name Caparol®) in the 1970s [2]. Additional fragments from residual murals of some of the same caves have been retrieved during an expedition recently. Both of these samples, exposed to different preservative environments, were studied for comparison. For this work, pigments in fragments from the cave no. 8 in Kizil, named “Cave of the 16 Sword Bearer” (”Höhle der 16 Schwertträger”) for the mural depictions of sixteen Tocharian donors, were investigated using optical microscopy and Raman spectroscopy.

Special emphasis was given to areas with brown appearing paint layers, which mainly comprise of bigger, black plattnerite (beta-$PbO_2$, tetragonal) grains surrounded by a finer, orange minium ($Pb_3O_4$) matrix. Raman analyses of plattnerite grains [Fig. 1] revealed the presence of unusual bands related to scrutinyite (alpha-$PbO_2$, orthorhombic) along with the common plattnerite spectrum [consistent peaks with scrutinyite reference spectrum at 166 and 225 $cm^{-1}$; and further possible peaks at 119 and 84 $cm^{-1}$]. Intensities of the scrutinyite bands vary in relation to plattnerite intensities; however, no specific trend is apparent.

Similar plattnerite-scrutinyite associations had been found previously by Raman spectroscopy in a medieval wall painting in the chapel of Vipperow/Germany [3] and by XRD on Buddhism murals of Afghanistan as well [4], rendering these findings not as a rare uniquity, but possibly representing a more common constellation yet to be considered. However, the conditions for the transformation of plattnerite to scrutinyite are not fully understood so far. As a matter of fact, given its scarce utilization in European murals, plattnerite itself has been mostly regarded as a discoloration product of minium and thus received less attention as a genuine pigment. The presence of the even more rare plattnerite-scrutinyite configuration may shed light on the original painting techniques, that is to say, i) the usage of primary plattnerite-scrutinyite compounds as occurring in natural mines; ii) secondary alteration to plattnerite-scrutinyite during embedment in mural paintings; iii) incidental plattnerite-scrutinyite formation consequent to the synthesis of lead pigments The latter is of major interest, as it considers the production of fine minium from lead ores or perhaps even directly from primary plattnerite [5].

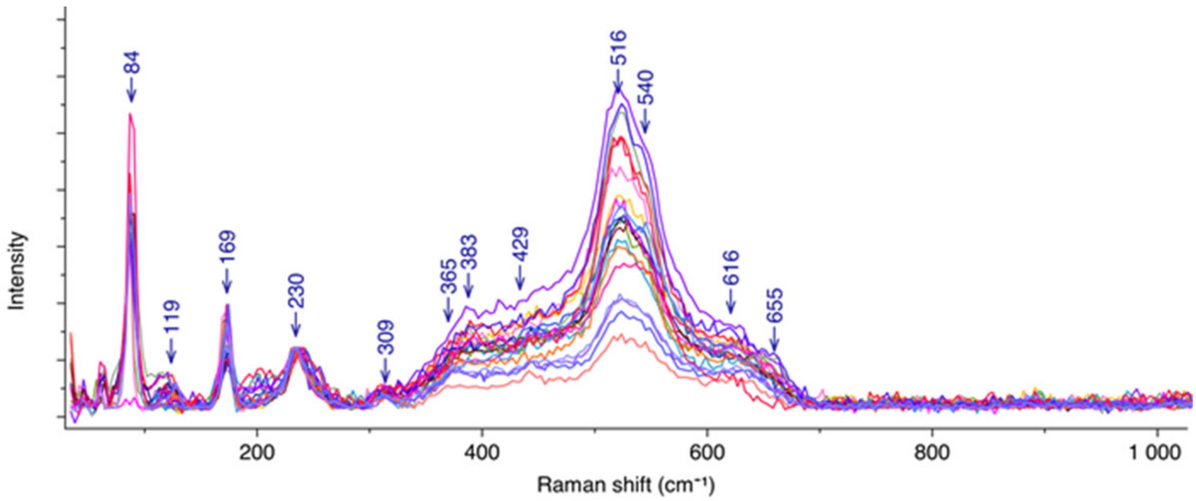

Figure 1: Raman spectra of black grains in the brown paint layer from „Cave of the 16 Sword Bearer“. Plattnerite shows a main peak at 516 cm$^{-1}$ (with a shoulder at 540 cm$^{-1}$); confirmed main peaks of scrutinyite at 169 and 230 cm$^{-1}$ with not yet confirmed peaks at 84, 119 and 309 cm$^{-1}$. Futher bands of plattnerite and scrutinyite overlap between 350 and 670 cm$^{-1}$.

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# Raman Spectroscopy in the Study of the Wall Paintings in the Church of St Nicholas in Sofia (the Russian Church)

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**Keywords:** wall paintings, pigments, binders

The church of St Nicholas in Sofia (known as the Russian church), was built in 1911. It was decorated with wall paintings in 1912-1914 by the Russian artist Vasily Perminov and his team. The second stage of wall paintings decoration dates from 1945-1946, when the south chapel was reconstructed after the bombardment during the World War II. This part of the church was painted by another Russian artist, Michail Maletski. In 1954 the crypt of the church was embellished with wall paintings by Nikolay Shelehov, also Russian artist. The fourth and final stage of the wall paintings dates from 1996, when the antechamber of the crypt was decorated.

The technique of the wall paintings of the different periods and artists vary and for the purposes of their conservation an extended study is carried out. Twenty samples of all three periods of the wall paintings were taken to be analysed by micro-Raman spectroscopy. The samples are taken from: 1. Scene of *Congregation of Russian Saints* in the western apse; 2. Inscription to the figure of *Archangel Michael* in the southern stairway; 3. The Scene of *Virgin Orant* in the crypt of the church (Figure 1A); 4. The scene of *Mourning of the Jesus Christ* in the crypt (Figure 1B). This analytical technique was substantial part of the analysis of the palette of the artists. FT-IR, XRF and micro chemical analysis were performed as complimentary to the Raman spectroscopy.

**Figure 1.** (A) The scene of *Virgin Orant*; (B) The scene of *Mourning of the Jesus Christ*, in the crypt of the Russian church in Sofia.

The analysis allowed the identification of chrome green, titan white (Figure 2A), vermilion, hematite, ultramarine, green earths, carbon black, barium white, and alizarin as pigments.

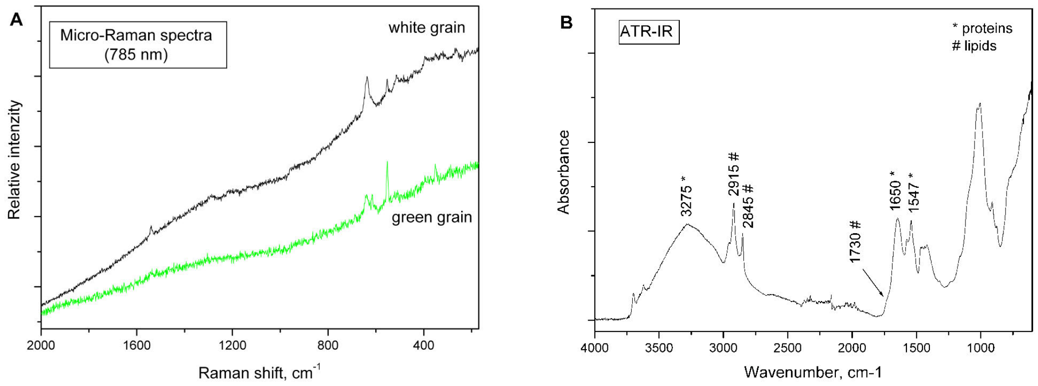

**Figure 2.** (A) Micro-Raman spectra depicting chrome green (in green) and titan white (in black) in a sample from the *Virgin Orant* green garments; (B) ATR-IR spectrum showing the presence of egg binder in a sample from the *Mourning of the Jesus Christ* in the crypt.

The organic material used as binder was studied by ATR-FTIR spectroscopy. The characteristic bands for lipidic and proteinaceous materials detected in the spectra (Figure 2B) indicated the use of egg.

Raman spectroscopy analysis of the Russian artists' wall paintings in Sofia is performed for the first time. The results provide important data for the artists' technique, valuable in formulating the conservation strategy. This research can be regarded as a pilot study. A more extended research on the palette of wall paintings by Russian artists in Bulgaria is planned.

## Acknowledgements

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Equipment of INFRAMAT (Research Infrastructure from National roadmap of Bulgaria), supported by Contract D01-155/28.08.2018 with Bulgarian Ministry of Education and Science is used in a part of the present investigations.

# The Exonarthex Mural Paintings of the Church "The Nativity of the Virgin" of Rila monastery: Analysis of Pigments, Binders, and Degradation Processes

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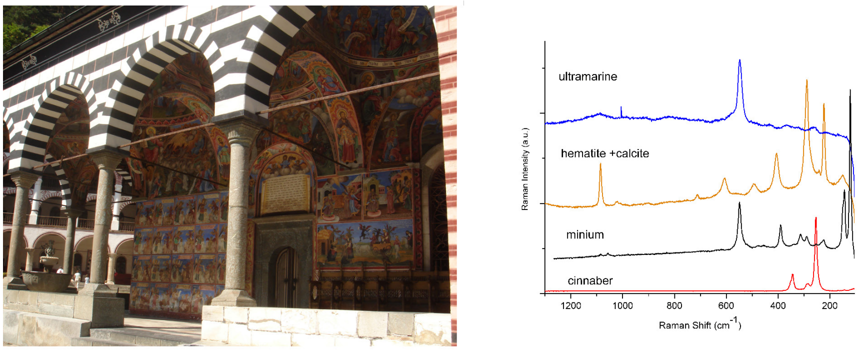
**Keywords:** Rila monatery, mural paintings, pigments, binders, degradation

Nowadays the work of the Bulgarian National Revival zographs (religious artists) is well studied from artistic point of view [1]. However, there are only limited number of analytical studies on the painting materials that they have used. Aiming to expand the knowledge in this area, recently we have focussed our efforts on studying the technological characteristics of the mural paintings in the church "The Nativity of the Virgin" (the main monastery church) of Rila monastery by complementary spectral and physico-chemical methods.

The mural paintings in the altar area of the church were painted by Ivan Obrazopisov and Kostadin Valyov in 1841–1842 year. The murals in the two chapels were executed in the same period: 1840–1841 year, by Dimitar Zograph and Kostadin Valyov (chapel “Assumption of St John of Rila”, 1840) and Dimitar Zograph and his son Stanislav Dospevski (“St Nikolay”, 1841). The murals of the main nave were painted later by Dimitar Zograph and his brother Zahari Zograph (1842–1844). The final stage of the church painting comprised the murals in the outer church galery - the exonarthex. They were made by Dimitar Zograph and his son in the period 1843–1847 year.

In the framework of our survey concerning the mural painting materials and technology used by the zographs in the different parts of the church, up to now we have examined samples from the altar and nave murals [2,3]. The present study reports on the pigments, binders and degradation drocesses found in the mural paintings of the exonarthex (Figure 1A).



(A) (B)

**Figure 1.** (A) Exonarthex of the church "The Nativity of the Virgin" of Rila monastery; (B) Red and blue pigments identified by micro-Raman spectroscopy in the exonarthex mural paintings.

Spectroscopic (micro-Raman and ATR-IR) analysis combined with SEM and XRD allowed the identification of red ochre, cinnabar and minium as red pigments (Figure 1B). Smalt which was consistently used for execution of the blue background in other parts of the church, was not present as blue pigment in the exonarthex. Instead, ultramarine was detected in the blue paint samples (Figure 1B). Several green shades were examined and showed the presence of green earths and verdigris. The preservation state of the red paint layer presents serious concerns - a white alteration product is observed in some areas, and blackening of the pigment in other. Having in mind the susceptibility of the red lead pigment to transformations such as white $PbCO_3$ or black $PbO_2$ or PbS, an important part of the study was examination of the red paint samples by micro-Raman measurements for identification of the alterations.

ATR-FTIR analysis of the samples revealed that in all cases strong absorptions for metal oxalates are present in the spectra suggesting severe binder degradation. Further identification of the organic binder was attempted by microsamples extraction, spectroscopic studies and enzyme-linked immunosorbent assay (ELISA).

The information provided by the study is of great importance for reconstruction of the colour palette and technologies used by the zographs as well as for assesment of the murals preservation state and the necessary treatment.

## Acknowledgements

This work has been financially supported by the National Science Fund of Bulgaria, Contract КП-06-ОПР 05/5.
Equipment of INFRAMAT (Research Infrastructure from National roadmap of Bulgaria), supported by Contract D01-155/28.08.2018 with Bulgarian Ministry of Education and Science is used in a part of the present investigations.

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# "The great painter Salzedo", master of Peninsular Mannerism: Analysis by Raman spectroscopy and associated spectroscopic techniques

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**Keywords:** Characterization, products of degradation, painting conservation, Raman spectroscopy, analytical techniques, conservation of cultural heritage

The small museum collection of the Holy House of Mercy of Lourinhã constitutes one of the most remarkable and almost unknown from the general public groups of the country, in terms of museums of this extensive institutional assistance and charity network.

The artistic interest of this pictorial group to Peninsular Mannerism, together with the advanced state of degradation of some paintings, have been the major causes for the genesis of this study.

The valences of this ancient painting collection extend, in continuity, to the presence of four large tables that belonged to the old altarpiece of the main chapel of Saint Jerome Monastery of Vale Benfeito and came to this Holy House after the expiry of the order in 1834. The paintings represent “The profession of Saint Paula”, “Trial of Saint Catherine, “Saint Jerome in the wilderness” and the “Immaculate Conception”. They are due to a Sevillian artist who served the Queen Catherine of Austria as a painter of her court, named Lourenço de Salzedo (c. 1530-1577). This altarpiece, *circa* 1570, has been painted at the same epoch that Salzedo painted the altarpiece of the main chapel of the Jerónimos Monastery, in Lisbon, both commissioned by the same Queen. These are the best paintings in Portugal of Italianate Mannerism, attesting to the pictorial culture learned in Rome, where the artist worked, along with Girolamo Siciolante of Sermoneta and Giorgio Vasari, before coming to settle down in Lisbon[1-3].

Cross-sections from the paintings were examined by optical microscopy and analysed by micro-Raman spectroscopy (μ-Raman) to identify the core materials in the painting, complemented to other techniques such as micro-X-ray Diffraction (μ-XRD), Energy Dispersive X-ray Fluorescence spectroscopy (EDXRF), scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) and micro-Fourier Transform Infrared spectroscopy (μ-FTIR).

The comparison of these results to those of the altarpiece of the main chapel of the Jerónimos monastery, will bring new data on the barely studied work of the "The great painter Salzedo", highlighting the altarpiece conservation and restoration decision, by identifying painting layers technique, pigments, binders, ground layers raw materials and their products of degradation.

## Acknowledgements

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The authors acknowledge Fundação para a Ciência e Tecnologia for financial support, Post-doc grant SFRH/BPD/103315/2014 through program QREN-POPH-typology 4.1., co-participated by the Social European Fund (FSE) and MCTES National Fund;,Laboratório José de Figueiredo (LJF-DGPC), Ana Machado and Luís Piorro. Also wish to acknowledge Santa Casa da Misericórdia da Lourinhã for allowing this study.

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# Application of µ-Raman Spectroscopy to investigate production techniques in medieval pottery

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**Keywords:** µ-Raman Spectroscopy, medieval potteries, provenance, technology, firing conition

The study of manufacturing technologies in archaeological potteries[1] is a very challenging aspect in providing valuable information about complex sociocultural questions on past societies. In this respect, the understanding of furnace technology and manufacture routines is a key factor in archaeological studies.

In this contribute, µ-Raman Spectroscopy has been used in order to explore the potential of such non-destructive approach in supporting the classical minero-petrographic characterization of ancient ceramics[2] and exploring the production technologies of artefacts, in regard to furnace conditions and microtextural reactions during firing [3].

In detail, a combined approach including preliminary petrographic analysis and µ-Raman Spectroscopy has been applied to medieval pottery (colature) found in Volterra (Tuscany, Italy) dating from IV to V century with the aim of evaluating the occurrence of peculiar mineral assemblages and the distribution of newly formed minerals as imprint of moulding methods, raw materials and firing temperatures/environment.

By using profiling and mappings tools correlation among (i) inhomogeneity occurring within the sample bulk and differences in temperature or atmosphere, (ii) compositional ranges reflecting the different use/provenance of clayey sediments and (iii) red decorative slips features, are discussed in the framework of the investigated ceramic production.

Moreover, even if the experimental approach has been used in laboratory on small ceramic fragments sampled from the excavated shards, the possibility to extend the method for fast, non-invasive and non-destructive ceramic classification and fabric discrimination in situ is discussed, highlighting potential and limits.

**Acknowledgements**
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# The importance of Raman spectroscopy in the investigation of glazed pottery: Medieval southern Italy examples.

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**Keywords:** glaze, glass, medieval pottery, pigments.

A multi-technique investigation carried out on Medieval Campanian glazed pottery by means of Inductively Coupled Plasma–Mass Spectrometry (ICP-MS), Optical and Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (OM and SEM-EDS) and Raman Spectroscopy, highlighted the usefulness of the latter to give answers to somearchaeological questions. Even though less used for the study of this kind of archaeological findings, it can provide important information concerning the production technology and raw materials constituting the glaze, i.e. the glass matrix and the pigments.

The studied samples come from the Castles of Montella and Ariano Irpino (Avellino, southern Italy), fortified villages inhabited between the end of the 8th and the beginning of the 16th century. It was observed that pottery from Montella is part of a wider production, which was evenly distributed to a great extent in the Campania hinterland,including manufacturing centres such as Ariano Irpino [1].

The findings from Montella belong to three classes of medieval lead-tin-glazed ceramics: *protomajolica* (second half of the 13th century - early 14th century), transitional glazed products (14th – 16th centuries) and white enamel with blue motives pottery (beginning of the 16th century); one of the objectives of this study was to prove that these three classes were the result of technological evolutions in the field of glazed ceramic production.

Findings fromAriano Irpino include monochrome white enamel and white enamel with blue motives, classes of ceramics generically attested starting from the beginning of the 15th century.

Concerning the Montella site, the Raman results supported both the archaeological hypothesis and the results obtained with the other techniques, highlighting an intermediate content of cassiterite ($SnO_2$) for the transitional glazed objects with respect to the other classes; futhermore, thanks to the Raman spectra glass types differentiation and their polymerization index, this technique added valuable information concerning the use of recycled glass in glazes making o, due to the identification of soda-lime glass relics in otherwise lead-based glazes [2].

Raman results on Ariano Irpino samples were particularly interesting concerning the origin of the pigment employed to give the blue color to the enamels. The finding of an arsenate phase on euhedral crystals present only in the blue areas, and not in the white ones, suggested the hypothesis that As is not linked to the presence of an opacifying matter, but it could be rather connected to the phase added to provide the blue color.

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# Characterization of ancient ceramics from San Kamphaeng Kilns, northern of Thailand

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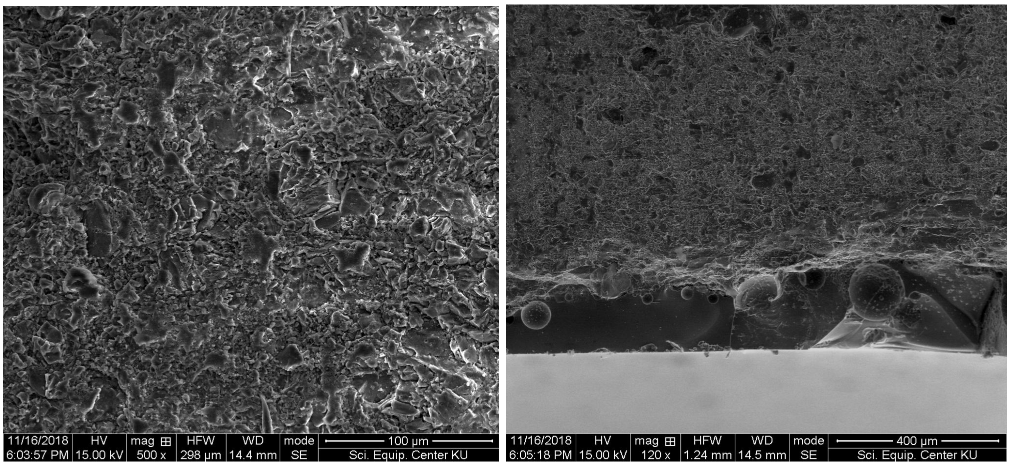
**Keywords:** San Kamphaeng Kiln, ancient Thai ceramics, Raman spectroscopy, synchrotron radiation

Archaeological studies for ceramics focus on some topics such as dating, provenance and technology seem to be an important information about the development of ceramics manufacturing throughout history. In this work is aimed to investigate structure and composition of ancient ceramics from San Kamphaeng Kilns, northern of Thailand. They are ten sheds from different kilns. The studies are preformed with Raman spectroscopy. Micro X-ray fluorescent spectroscopy and X-ray tomographic microscopy based on synchrotron radiation are also carried out to characterize the elemental composition and distribution, and internal configuration. The clay minerals are idenified and confirmed to each other.



(a) The clay body (b) the glaze

**Figure 1. The micrograph of ancient ceramics from San Mamphaeng Kilns**

## Acknowledgements

This work has been financially supported partly by the Kasetsart University (Department of Earth Science at Faculty of Science) and the Center of Excellence in Materials Science and Technology at Chiang Mai University.

# Characterization of ancient red ruby glass

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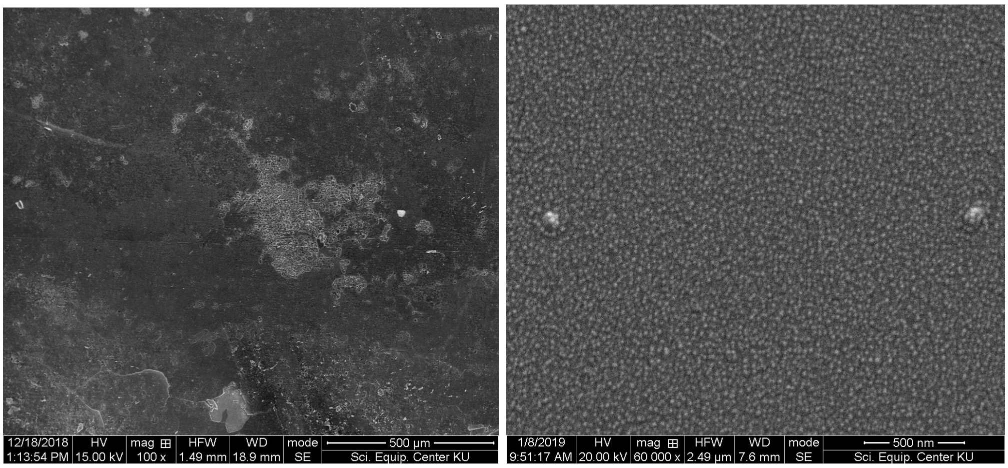
**Keywords:** red ruby glass, ancient Thai glass, Raman spectroscopy, synchrotron radiation

Red ruby glasses have been used for old-style decorations in Thailand such as ancient Thai glass, enamel and glass bead. In this work, their composition and structure are determined using Raman spectroscopy and scanning electron microscope coupled with energy dispersive X-ray fluorescence spectrometer (SEM-EDS). X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) based on synchrotron radiation is also carried out to study the oxidation states. The results showed that the ancient red ruby glasses were mostly lead-silica based glassed. It was also found that the presence of chromophore was copper nanoparticles. The details were discussed.



(a) 100x (b) 60,000x

**Figure 1. The micrograph of ancient red ruby glass**

## Acknowledgements

This work has been financially supported partly by the Kasetsart University (Department of Earth Science at Faculty of Science) and the Center of Excellence in Materials Science and Technology at Chiang Mai University.

# Dyed Silk in the Prussian Palaces - HPLC and SERS Investigations

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**Keywords:** dyestuff identification, 18th-century silk

A large number of original silk textiles from the second half of the 18th century has been preserved in the collection of the Prussian Palaces and Gardens Foundation. In the last years, the collection has been studied in detail for the first time by a team of art historians, restorers and scientists, culminating in the preparation of a collection catalogue [1].

"Rotes Tressenzimmer" (red braid room) of the prince's lower chambers in the New Palace, Potsdam Sanssouci with original wall covering (Brothers Baudouin and sons, Berlin, 1766-68). The red damask was dyed with cochineal. Photo: W. Pfauder SPSG.

One of the main aims of this investigation was to characterise the dyeing materials used in the Prussian silk fabrication. The results provided a deep insight into the praxis of Prussian silk dyeing that developed rapidly during the reign of Frederick II (1740 - 1786). The Prussian palette of dyestuff was compared with the one recommended in the written historical sources of that time. The results of this examination were also used to answer questions about dating, provenance, state of preservation and colour changes of the silks.

Dyestuff analysis of 36 objects (damasks, colourful patterned fabrics and brocades) from this collection was carried out using High-Performance Liquid Chromatography (HPLC) and Surface-enhanced Raman spectroscopy **(**SERS**)** among other methods. This presentation also compares the results of HPLC and SERS measurements in order to emphasize the advantages and disadvantages of both methods.

The Prussian palette of dyeing materials corresponds largely with the written 18th-century historical sources. The Prussian dyers did not use all materials mentioned in contemporary literature, but rather those that were found to be most suitable.
Cochineal, redwood, safflower, orchil, indigo, logwood, weld and dyer's broom were identified in the Prussian silks; these dyeing materials were often used in "fine-tuned" and quite complex mixtures. This can be seen as proof of the Prussian silk dyer's craftsmanship. The use of redwood, safflower and orchil – all containing colourants with poor light fastness – was necessary in order to create all the colours fashionable at that time.

Both methods – HPLC and SERS – were able to identify the major components of most dyeing materials mentioned above (see also table below). However, HPLC turned out to be more effective in the identification of mixtures and minor components. For example, mixtures of cochineal and gallnuts or redwood and logwood as well as different anthraquinonoid components in Cochineal – useful for the determination of the origin of the dye insects – could only be identified using HPLC.

| | *Dyeing materials identified using* ***HPLC*** | *Dyeing materials identified using* ***SERS*** |
|---|---|---|
| ***Blue shades*** | - indigo or woad | - indigo or woad (conventional Raman) |
| ***Red shades*** | - cochineal + gallnuts<br>- redwood<br>- safflower<br>- mixtures of red- and logwood + indigo | - cochineal<br>- redwood |
| ***Violet shades*** | - orchil | - orchil |
| ***Yellow shades*** | - weld | - weld |
| ***Green shades*** | - indigo + weld<br>- indigo + dyer's broom | - indigo + weld |

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# Towards the Feasibility of Characterizing Resins of the Paraloid Family by Raman Spectroscopy

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**Keywords:** resins; Raman spectroscopy; 1064 nm laser; portable spectrometer; paraloid

Raman spectroscopy is a key technique for the characterization of a variety of inorganic and organic materials in works of art. Raman analysis can be conducted relatively fast (depending on the scattering capabilitites of the material under study), on treated or untreated samples while the information retrieved is localized on a micrometer-sized spot. Although the technique is well-established, certain challenges can be faced when perfoming Raman analysis on organic materials. One of the most common drawbacks of measuring organic materials is the fluorescence introduced in the spectrum that masks the Raman signal.

Surface-enhanced Raman spectroscopy (SERS) has been proposed as an alternative approach to traditional Raman microscopy for the analysis of organic components, e.g. dyes. Thus, the Raman signal of some organic constituents can be enhanced by several orders of magnitute by introducing a melticulous sample preparation that includes metal nanostructures. On the other hand, someone can take advantage of the wide variation of lasers coupled to Raman spectrometers and choose one in the near-infrared (NIR) region of the electromagnetic spectrum. The latter can be helpful to suppress fluorescence without using an extensive sample preparation.

In this work, different types of resins from the Paraloid family were chosen and investigated with a 1064 nm dispersive Raman system. The aim of the study is twofold: to prove the applicability of the NIR lasers to identify organic art materials and to differentiate and characterize several types of paraloid using *state-of-the-art* Raman instruments.

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# Portable Raman: the new hammer for architects restoring 20th Century Built Heritage elements made of reinforced concrete

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**Keywords:** Portable Raman, Built Heritage, Reinforced concrete, 20th century

The practice of architects when inspecting a building for diagnosis is the *visu* analysis (at the naked eye) and the tactil response of a hammer when knocking a wall of a column, without paying attention to scientific methologies. In this work we propose the use of portable Raman as the *modern hammer* of architects to perform such inspections on protected buildings of the 20th century where reinforced concrete was used for structures and portland type cement for mortars and binders in the walls.

Two different buildings of that type, in the province of Biscay(North of Spain), were selected for this study: (a) the Galerias de Punta Begoña of Getxo (1918), qualified as monument, affected by a direct marine and industrial environment and (b) the Library of the University of the Basque Country UPV/EHU, Campus of Leioa (1968), affected by the diffuse urban-industrial atmosphere of Bilbao.

Our approach is to first search for the avaliable documentation on the building because in those times all works on buildings were well documented. The analysis of such documentation allows to know where to analyse in order to confirm the constructive method. On the other hand, Raman measurements by the BWTEK innoRam portable spectrometers were performed (532 and 785 nm laser wavelengths) in order to take decisions based on the results obtained. Figure 1 shows such the approach for the Galerias de Punta Begoña building, where the unexpected presence of aragonite (diagnostic band at 205 $cm^{-1}$) was confirmed, indicative of the use of sand beach (nowadays forbiden due to the corrosion problems enhanced by chloride) in the binder/aggregate of mortars.

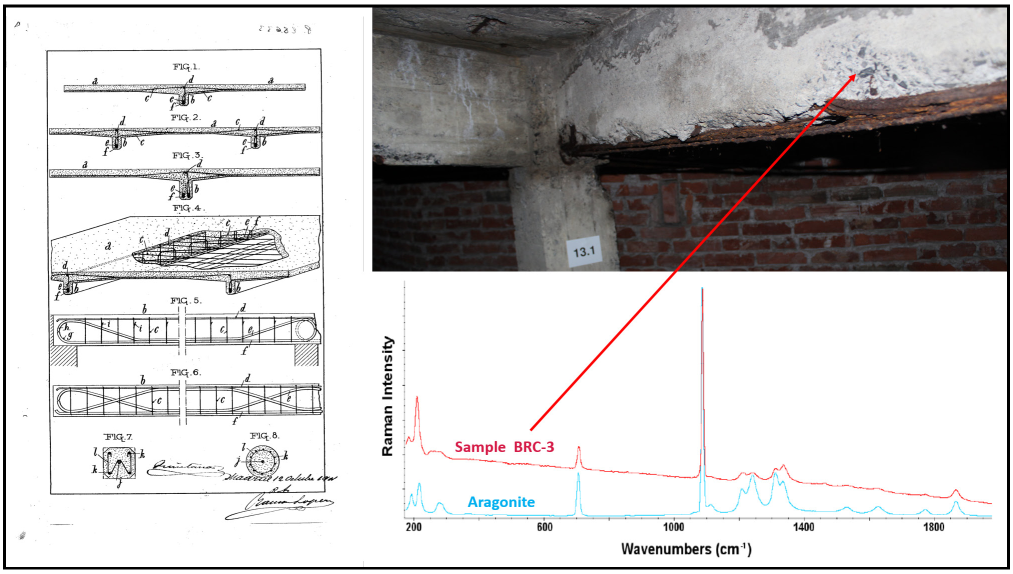

**Figure 1.** Detail of the patent from Blanc (1901) used to construct Galerias de Punta Begoña (left). Photograph of the analysed site and In-situ Raman spectrum of the binder in the reinforced concrete.

Other abundant mineral phases were: (a) **original**: alite ($3CaO\cdot SiO_2$, 838 $cm^{-1}$), belite ($2CaO\cdot SiO_2$ 861 $cm^{-1}$), calcite (282 and 1085 $cm^{-1}$), gypsum ($CaSO_4\cdot 2H_2O$, 1008 $cm^{-1}$), quartz ($SiO_2$, 467 $cm^{-1}$), aragonite ($CaCO_3$, 205 and 1084 $cm^{-1}$), and (b) **degradation**: nitratine ($NaNO_3$,1067 $cm^{-1}$), nitrocalcite/niter ($NaNO_3$,/$KNO_3$1050-1051 $cm^{-1}$), hematite ($Fe_2O_3$, 292 $cm^{-1}$), $\gamma$-anhidrite ($CaSO_4$,1025 $cm^{-1}$), bassanite ($CaSO_4\cdot 1/2H_2O$,1015 $cm^{-1}$) and whewellite ($CaC_2O_4\cdot H_2O$, 1463 $cm^{-1}$). The latter is usually associated to the presence of microorganisms. However, in this case, microorganisms were absent and the calcium oxalate came from the reaction of oxalic acid, coming from organic exhausts of ship engines and transported by the marine aerosol, with the calcium compounds present in the facade of the building.

Besides, salt occurrence in concrete materials is related to polluted environments but it is also subjected to infiltration of waters. This is the case of the efflorescences found descending on a brick wall erected under a beam of reinforced concrete, located just below the garden shown in the upper image in Figure 2 (Library of the UPV/EHU, Campus of Leioa). The presence of infiltration waters and their source is quite evident when, for example, construction elements are in contact with soils or gardens (both buildings have gardens in the upper parts). Waters can go down larger distances into the construction (through pore net or cracks) and the degradation effects can be observed far away.

The identification of high amounts of niter (715, 1049, 1342 and 1357 $cm^{-1}$) in the upper floor suggests the infiltration of amonium nitrate charged waters as the origin of nitrates in the efflorescence formed on the brick wall (marked in spectrum b). The percolation of waters into the beam of reinforced concrete and the subsecuent degradation of its materials was also evidenced thanks to the identification of thenardite ($Na_2SO_4$, 452, 464, 619, 632, 644, 992, 1100, 1130 and 1151 $cm^{-1}$), syngenite ($K_2Ca(SO_4)_2\cdot H_2O$, 427, 441, 474, 492, 608, 620, 632, 641, 660, 980, 1004, 1140 and 1167 $cm^{-1}$), gypsum (414, 493, 618, 669, 1007 and 1137 $cm^{-1}$), aphthitalite ($K_3Na(SO_4)_2$, 452, 620, 992, 1083 and 1201 $cm^{-1}$), hematite (222, 294, 406, 607 and 1318 $cm^{-1}$) and anatase (143 $cm^{-1}$) in efflorescences.

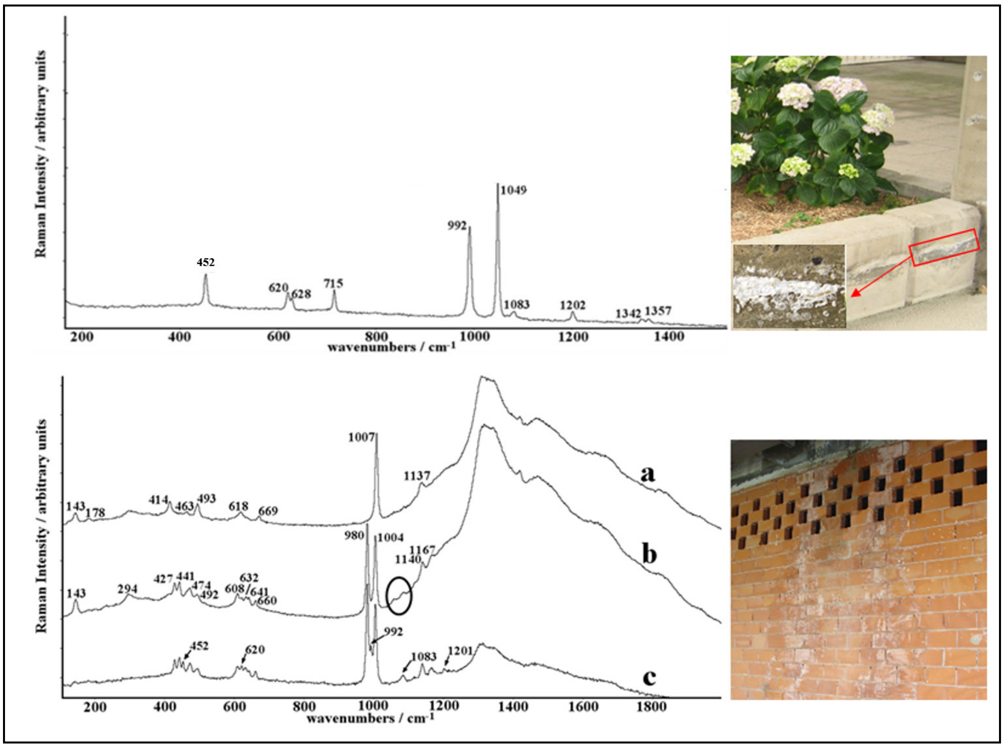

**Figure 2.** Efflorescences with syngenite and niter (concrete wall) and a) gypsum and anatase, b) syngenite, hematite, anatase, calcite and niter, c) syngenite, aphthitalite and thenardite (brick wall).

## Acknowledgements

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# Analyzing compositional differences of medieval *émail champlevé* by means of Raman spectroscopy

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**Keywords:** *émail champlevé*, glass, analysis, medieval enamels

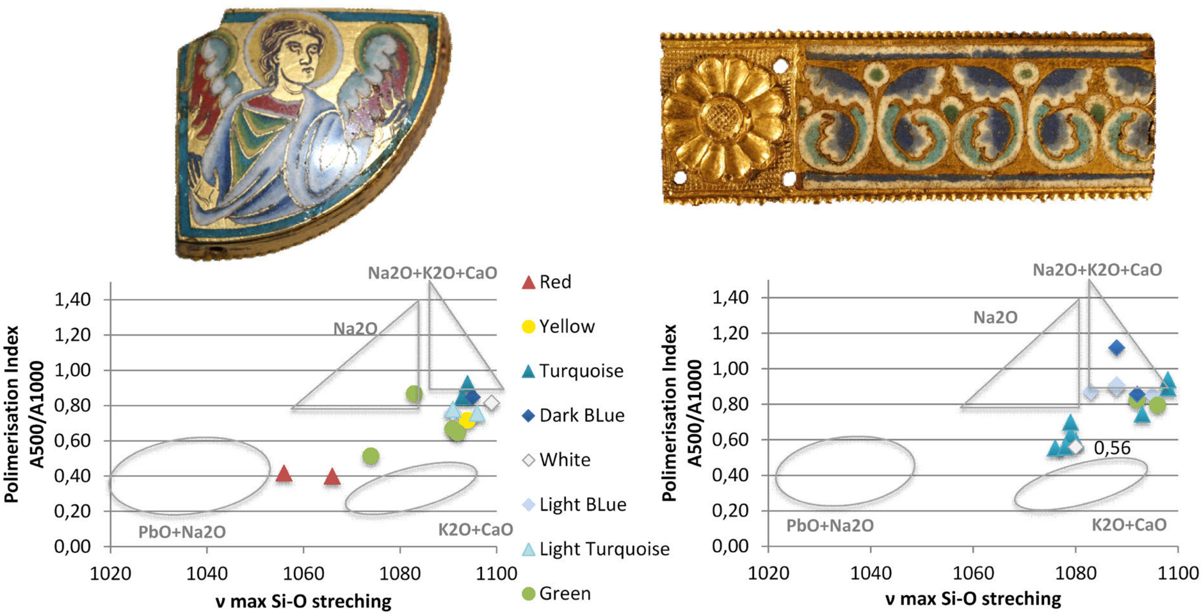
Most of the medieval *émaux champlevé* are made from strongly coloured and opacifyed soda lime silicate glass. In general, two glass types are employed (mineral soda or plant ash soda), which are mainly characterized by their differences in oxides of magnesium and potassium, but can also vary in the opacifier (tin of antimony) and lead [1]. Red enamels can be of a different composition with high potassium content.

Raman spectra obtained from vitreous silicate-based materials show a spectral fingerprint related to composition and thermal history of the glass. Information on the glass type can be obtained by comparing spectral components. Spectra of typical glass families and their spectral components have been described in literature [e.g.2,3,4]. The decomposition of a spectrum into its components followed the model proposed by Robinet [3]. The wavelength of the bending and stretching regions, $\delta_{max}$ and $\upsilon_{max}$ and the area of the corresponding band areas, whose ratio ($A_{500}/A_{1000}$) gives the polymerisation index $I_p$ was extracted from the data. Next to the signal of the glass network, Raman spectra of enamels may contain signals from crystalline phases generally associated with opacifying or colouring agents or unreacted raw ingredients. These comparably sharp signals need to be recognised since they interfere with the Raman signal of the silica network.

The aim of this study was to examine if the compositional differences of the enamels can be detected by Raman spectroscopy. Raman and energy dispersive x-ray analysis have been applied to a small selection of nine medieval *émail champlevé* objects from the Kunstgewerbemuseum, Staatliche Museen zu Berlin SPK.

Figure 1 shows the Raman results of two analysed objects. The wavenumber of the Si-O stretching signal $\upsilon_{max}$ is plotted against the polymerisation index $I_p$ and are compared to the values of glass families reported in the literature [4]. Most colours of the object O1973,186 (angel) have the composition of soda lime glass with mineral soda and are opacifyed with antimonate compounds. In the $\upsilon_{max}$ vs. $I_p$ plot most analysis fall together quite close to the corresponding glass family. Analyses from green and red enamel differ. Two of the analyses performed on the green enamel do not fall together with the other soda lime glass, suggesting a more varied composition. Indeed, bindhemite ($PbSb_2O_7$) was detected as opacifier in the green, and it is likely that partial dissolved bindhemite has locally changed the glass network by increasing the lead content and hence resulting in a $\upsilon_{max}$ value typical for lead containing glass. The red enamel of the "angel" is a potash lime glass and therefore the extracted features are clearly different from the other soda lime enamels. The object W1984,25 (ornament) has as well a large number of data points which correspond to soda lime glass with mineral soda. However, a more in depth evaluation allows to observe that the turquoise enamels were produced mixing two different type of glasses. The first is a soda lime glass with mineral soda and opacified with calcium antimonates, whereas the second is a soda-lead glass, possibly produced with plant ash soda, and opacified with tin oxide. The white enamels, finally, only present this second glass type.

The analysis of medieval enamels by Raman spectroscopy allows the identification of compositional differences in the glass used to produce them, namely the alkaline components and the lead content. The challenges with this analytical approach are the necessity to obtain "good quality spectra" without crystalline components, a reliable background subtraction and the limited number of established glass families, which are not in every case close enough to the composition of the studied enamels.


Inventory Nr. O.1973,186

Half figure of an angel, *émail champlevé*, around 1170, probably Cologne

Inventory Nr. W.1984,25

Part of an ornament with *émail champlevé*, around 1230, probably Treves

**Figure 1.** Two objects and the their respecive results of $I_p$ and $\upsilon_{max}$ for different spot analyis. The grey shapes in the graphs represent the ares for certain glass families reported in the literature [4].

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# Insight into concrete deterioration with Raman spectroscopy

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Alkali-silica reaction (ASR) is a serious problem concerning the deterioration of concrete. This leads to significant maintenance and reconstruction costs for concrete infrastructures all over the world. The geographical regions, which play a major role in concrete deterioration, are for example coastal areas or in general, areas with a high air humidity/salinity due to closeness of rivers or lakes [1]. The samples analyzed within this study are assessed to be potentially susceptible to ASR.

Concrete is basically made of different types of aggregates, cement and water. Concerning its susceptibility to ASR the aggregates are the main risk factor, as they vary in their reactivity. Depending on their mineralogical composition they could be classified as non-reactive, medium- or highly reactive. Some varieties are difficult to assess, as they react slow, respectively late or only when additional factors like alkali-supply (e.g. de-icing salt) or mechanical loading (fatigue) foster the reaction. Most types of aggregates contain nanocrystalline siliceous phases which have a high potential to be dissolved at high pH of the concrete pore solution. If this is the case, this may lead to the formation of deleterious alkali silica gel, when alkalis coming either from the pore solution of the concrete (mainly cement alkalis) or from outer factors like de-icing salt in winter (on roads) or saline environment [1]. This reaction product itself deserves space and can absorb moisture, which result in additional expansion and cracking of the concrete.

The amorphous ASR-gel is comparable to the structure of silicate glasses which are also composed of $SiO_4$-network with four bridging oxygens (BO) per $SiO_4$-tetrahedron. The number of BO's is indicated as Q-species ($Q_n$), where "n" describes the number of BOs. During the ASR, large cations ($Na^+$, $K^+$, $Ca^{2+}$) induce a depolymerization of the network and split the oxygen bonds until there are 0-4 BO's per $SiO_4$-tetrahedron left [2]. In table 1 the most intense peaks of each Raman spectrum were assigned to the Q-species. Raman spectroscopy is an ideal opportunity to analyze especially amorphous gel structures like the ASR-gel and the smallest changes in its network-structure. The characteristic Raman spectra of these gels show two broad bands in the 800 to 1200 cm$^{-1}$ range and the 400 to 700 cm$^{-1}$ range, indicating the Q-species of the amorphous $SiO_4$-network. [3,4] The aim of this study is to determine dependencies between the depolymerization degree derived from Raman spectroscopic data and the chemical and microstructural characteristics of ASR-gels evolved from various aggregates in concrete.

| Raman range (cm$^{-1}$) | assignment |
|---|---|
| 400 - 450 | $Q_4$ |
| 450 - 600 | $Q_3$ |
| 600 - 650 | $Q_2$ |
| 650 - 660 | $Q_2$ of CSH |
| 660 - 700 | $Q_1$ of CSH |
| 700 - 750 | $Q_1$ |

**Table 1.** Raman ranges (cm-1) and assignments to Q-species of the main peaks in Raman spectra

The most affected parts of deteriorated concrete samples were extracted and embedded in fluorescent epoxy for a better identification of the ASR-gel under convenient polarizing microscope (figure 1; left) followed by SEM in combination with EDX to determine the chemical composition of the ASR-gel.

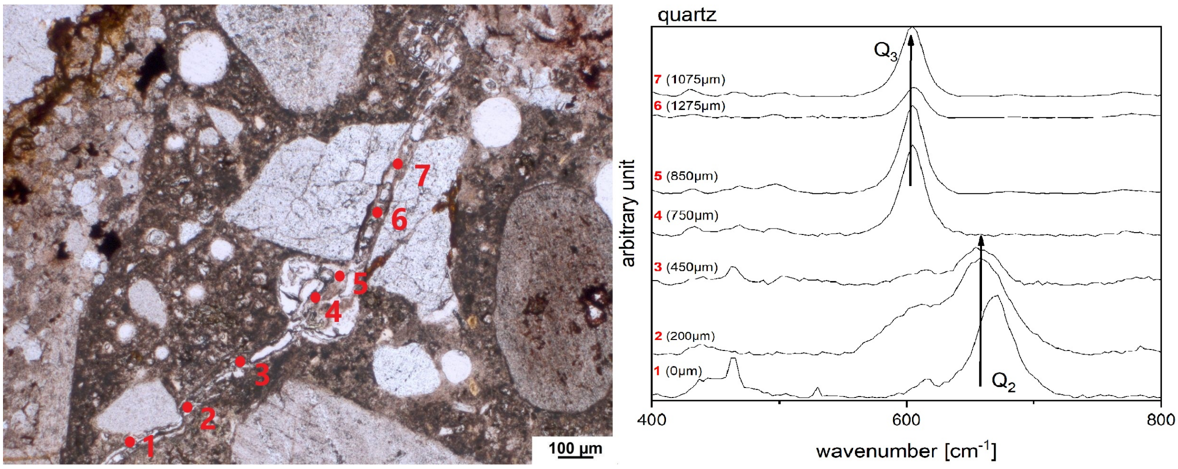

**Figure 1**. Left: Example of a representative overview of a thin section (under polarisation microscope) of concrete; crack partly filled with ASR reaction product and partly with epoxy of the preparation. The red points indicate the measured profile and the numbers the ID of the measured point. Right: stacked Raman spectra of all measured points of one sample for visual clarity of the shift of the bands. All the spectra are background corrected. The numbers on the left side represent the order of measurement with the distance between each measured point on the sample in parentheses

The analysis with Raman spectroscopy reveals depolymerization in the silicate framework caused by an increase in alkali content, manifested as a gradual shift of predominant peaks (figure 1; right). As a result, distinctions in the microstructure and the chemical composition of the ASR-gels evolving from different aggregates were detected. Furthermore, the reaction products show an increasing Ca/Si-ratio with progressive crack length whereas the (Na+K)/Si-ratio decrease. Finally, the results are expected to enable profound correlations between chemical composition and change of spectral features, improving future evaluation of ASR reactivity. Further research mainly addresses the investigation of the ASR-gel structure after treatment with different accelerated test methods, comparing the reaction products with those resulting from real exposition. It is assumed that Raman spectra have the potential to evaluate differences between various approaches, delivering criteria for the assessment of the practical relevance and significance of the accelerated testing procedures.

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These abstracts result from the 10th International Congress on the Application of Raman Spectroscopy in Art and Archaeology held 03.09. – 07.09.2019 in Potsdam (Germany).

The RAA is an established biennial international conference series. Since the beginning in 2001, the RAA conferences promote Raman Spectroscopy and play an important role in increasing the field of its applications in art history, history, archaeology, palaeontology, conservation and restoration, museology, degradation of cultural heritage, archaeometry, etc. Furthermore, the development of new instrumentation, especially for non-invasive measurements, receives great attention.

The Congress covers all topics of Raman spectroscopic applications in art and archaeology and focuses on the following themes:

- Material characterization and degradation processes
- Conservation issues affecting cultural heritage
- Raman spectroscopy of biological and organic materials
- Surface enhanced Raman spectroscopy
- Chemometrics in Raman spectroscopy
- Development of Raman techniques
- New Raman instrumentation and applications in cultural heritage objects investigations
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