Zavod za varstvo
kulturne dediščine Slovenije
Institute for the Protection of
Cultural Heritage of Slovenia

1913
2013

BOOK OF ABSTRACTS

RAA
2013

7th

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

2-6 September 2013

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Application of Raman Spectroscopy
in Art and Archaeology
Ljubljana, Slovenia, 2th–6th September 2013

Book of Abstracts
7th International Congress on the Application of Raman Spectroscopy in Art and Archaeology (RAA 2013),
Ljubljana (Slovenia), 2th–6th September 2013

Publisher: Institute for the Protection of Cultural Heritage of Slovenia
Editors: Polonca Ropret, Nadja Ocepek
Editorial Board: Klara Retko, Lea Legan, Tanja Špec, Črtomir Tavzes
Print: Birografika BORI d.o.o.
Copies: 400

Ljubljana 2013

The publication is published with the financial support of the Ministry of Culture, and is not payable.

REPUBLIC OF SLOVENIA
MINISTRY OF CULTURE

CIP - Kataložni zapis o publikaciji
Narodna in univerzitetna knjižnica, Ljubljana
543.424.3:7(082)
543.424.3:902(082)

INTERNATIONAL Congress on the Application of Raman Spectroscopy in Art and Archaeology (7 ; 2013 ; Ljubljana)
Book of abstracts / 7th International Congress on the Application of Raman Spectroscopy in Art and Archaeology, Ljubljana (Slovenia), 2th-6th September 2013 ; [editors Polonca Ropret, Nadja Ocepek]. - Ljubljana : Institute for the Protection of Cultural Heritage of Slovenia, 2013

ISBN 978-961-6902-38-0
1. Ropret, Polonca, kemik
268489728

The use of Raman spectroscopy for identifying and studying the material component of the objects of art and antiquities has flourished in recent years. The increasing importance of the application of Raman spectroscopy in art and archaeology is illustrated by an increasing number of research papers published each year, and by the scientific conferences and sessions that have been dedicated to this research area in the past decade.
The RAA conferences promote Raman spectroscopy and play an important role in the increasing field of its application in Art and Archaeology. The RAA is an established biennial international event. It brings together studies from diverse areas and represents dedicated work on the use of this technique in connection to the fields of art-history, history, archaeology, palaeontology, conservation and restoration, museology, etc. Furthermore, the development of new instrumentation, especially for non-invasive measurements, has received a great attention in the past years. These prominent, international events have a long tradition. Previously they were held in London (2001), Ghent (2003), Paris (2005), Modena (2007), Bilbao (2009), Parma (2011), and this year (2013) in Ljubljana.

The RAA 2013 conference received over 100 high quality contributions from different research laboratories all over the world, and this book of abstracts presents their latest advancements. One of the important topics is studies of deterioration induced by different environmental factors, such as biodeterioration, pollution, light and humidity exposure. The outcomes of these studies can give important information for designing safe conservation – restoration treatments and help in creating a better environment for cultural heritage objects, for their storage and display, all contributing to increasing of its sustainability. A great number of research contributions are presenting the latest achievements in the characterisation of traditional organic colorants by introducing new solutions for Surface enhanced Raman spectroscopic studies. This is an important topic that contributes to understanding not only the composition of the organic colorants, but also their production processes. The advancements in metals characterisation give important information to understanding of their corrosion processes and/or deliberate patinations by artists, which can give important input in designing further corrosion inhibition processes. A special topic is dedicated to the archaeometry research, from characterisation of ancient artefacts, their degradation processes, to finding possible solutions for their preservation. New, presented knowledge on gemstones characterisation, provenance, authenticity research, and furthermore, forensics applications, all attest of the wide applicability of Raman spectroscopy. The latest innovations in Raman instrumentation is presented by well – known companies in the field of Raman instruments, with a special emphasis in the development of portable, non-invasive instruments. Many research laboratories are taking the advantage of non-invasive instruments in order to keep the full integrity of works of art. However, the interpretation of the results is often challenging, which gives scientific contributions dealing with these questions a special, important place. Finally, the importance of a comprehensive Raman database is emphasised, and the latest work of the Infrared and Raman Users Group (IRUG) is presented, a database which we all help creating, and which can help in solving many questions that we all face.

We wish to thank all of the authors who submitted their latest research results and helped creating the scientific program of the RAA 2013 conference, as well as this Book of Abstracts.

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OP: Oral Presentation
P: Poster Presentation

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POSTER SESSION 1

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ORAL SESSION 3

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POSTER SESSION 2

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ORAL SESSION 5
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Friday, September 6, 2013

ORAL SESSION 7
Non-invasive Raman Investigation

ROUND TABLE – Raman spectral database

Pigments from Templo Pintado (Pachacamac, Perú) investigated by Raman Microscopy

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Pachacamac is a complex and vast archaeological site on the coast of Perú, 31 km south from Lima (Lat.12° 15' 29" South Long. 76° 54' 00" West). Its origin goes back to 200 CE and was taken over from the Ychma by the Incas around 1470 CE. As a religious and pilgrimage site, among the most significant buildings are the Templo Pintado (Painted Temple) and Templo del Sol (Temple of the Sun). The former is a 50 m high and 100 m wide adobe pyramid, with 3 sides made of a succession of giant steps (1 m high); the fronts of such staggered building are decorated with people, plants, birds and fish paintings,

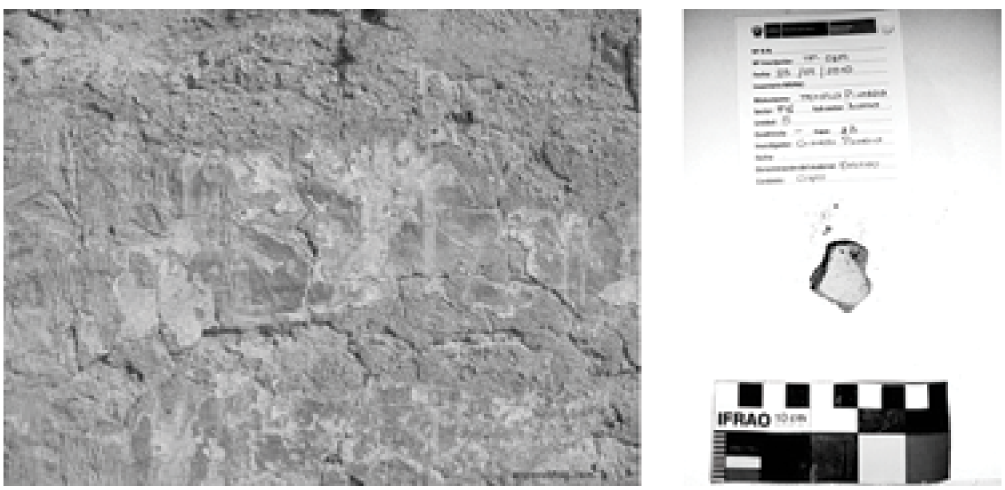

Figure 1. Painted wall at Templo Pintado, showing severe deterioration (left) and adobe fragment with a bluish-green paint (right).

colored in red, yellow and bluish-green mineral pigments, outlined in black[1](Fig. 1). The current efforts in the preservation of such magnificent archaeological site demand a better understanding on the materials and techniques originally employed. This work reports the results of pigment analysis using Raman Microscopy and XRD.

The investigated samples were 5 painted adobe fragments from Templo Pintado (north wall) and 4 minerals collected in quarries at the site area (Table 1). The painted fragments were investigated by Raman Microscopy (632.8 nm, 785 nm and 1064 nm excitation) and the reference minerals were also characterized by XRD.

Table 1. Samples identification and description

Sample ID	Sample Description
TP-029a	Painted fragment (several layers): red, pale yellow and bluish-green
TP-029b	Painted fragment: red and orange pigments
TP-029c	Painted fragment: red paint
TP-029d	Painted fragment: bluish-green paint with black trace
TP-029e	Stone bluish-green fragment with porous and irregular surface
MC1	Yellow pigment from quarry
MC2	Red pigment from quarry
MC3	Pale yellow pigment from quarry
MC4	Pale red pigment from quarry

The main issues to be addressed in the present investigation are: (i) the minerals from the quarries (MC1 to MC4) and the pigments in the painted fragments (TP-029a to TP-029e) are the same? (ii) the bluish-green pigment on sample TP-029d and TP-029e are the same? (iii) the black colored pigment in sample TP-029d is carbon? (iv) which organic binders, if any, were used to prepare the paintings?
An extensive Raman Microscopy investigation revealed that the red pigments were hematite[2] (α-Fe_2O_3) in both MC and TP samples, but bands assigned to α-quartz (465 cm^{-1}) and magnesium sulfate (main band at 1006 cm^{-1}) were also identified. Curiously, XRD did not show the presence of any crystalline compound (including hematite) in none of the red samples (MC2 and MC4). Cinnabar was not detected. Black pigment in TP-029d is carbon (broad bands at ca.1360 and 1580 cm^{-1}), although in a much smaller extension, magnetite (Fe_3O_4)was also identified; it is very likely that the latter is a contamination, considering the minerals used in the paint. Concerning the bluish-green pigment, despite the luminescent background it was possible to identify celadonite ($K(Mg,Fe^{2+})Fe^{3+}(Si_4O_{10})(OH)_2$) in both painted adobe and stone fragment, using Raman Microscopy and XRD. Furthermore, in the bluish area of the adobe fragment, a very small (300-400 µm) piece of bright blue bird feather was found.
In conclusion, Raman Microscopy and XRD were used to show that the minerals collected in quarries at the Pachacamac site and the paints on the adobe fragments are mostly silicates; in the case of the red pigment, hematite was identified by Raman Microscopy but not by XRD, indicating a low degree of crystallinity. It is thus very likely that the pigments used in Templo Pintado were from the local quarries. It was also shown that the bluish-green pigment in sample TP-029d and TP-029e are the same and corresponds to celadonite. A small fragment of blue bird feather suggests that the walls decorations had more than mineral pigments. Finally, the pigment in the black trace in sample TP-029d is carbon.

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[1] J. C. Muelle, R. Wells, *Revista del MuseoNacional*. **1939**, *8*, 265.
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The Infrared and Raman Users Group Web-based Raman Spectral Database

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Raman spectroscopy is a well-known powerful technique for the analysis of cultural heritage materials. The number of Raman systems installed in museum and academic laboratories has grown over the past decade. Despite this popularity, there remains a lack of readily-accessible, relevant, peer-reviewed, Raman reference data on known substances to serve as comparisons for samples taken from works of art and archaeological artifacts.

To help meet this need, the Infrared and Raman Users Group (IRUG) has partnered with the Philadelphia Museum of Art (PMA) on a project to create a Raman spectral database to be housed on the IRUG website at www.irug.org. This project is supported by a National Leadership Grant for Advancing Digital Resources awarded by the Institute of Museum and Library Services (IMLS) to the PMA in 2009.[1] It is the second database project to be undertaken by IRUG, which previously developed and distributed several infrared (IR) compilations, the latest containing over 2,100 peer-reviewed spectra of carbohydrates, minerals and pigments, oils and fats, natural and synthetic resins, and waxes. When completed, the Raman database is expected to become a similar fundamental resource for the international cultural heritage community.

The new Raman web-based database software allows users to create personal accounts for online submission, peer-review, editing, storage, and downloading of data (see Figure 1). As with the IRUG online IR database, spectra will be submitted in the non-proprietary raw JCAMP-DX (ASCII text) format, along with supporting information regarding the sample, sampling and data acquisition. After on-line peer review and quality assurance, spectra will be distributed in the IRUG JCAMP-DX format as discreet data records.[2] Additional project deliverables include: a software interface for public keyword and (digital) spectral searches of the database; a searchable Raman bibliography with peer-reviewed, downloadable, open-source PDF papers; and a glossary of chemical structures and terms.

IRUG has worked with Endertech, a Los Angeles based web design and software development company, to develop the Raman database and associated functionalities using MySQL® open-source database management system. Thus far, over 600 Raman spectra have been collected from various contributors worldwide to form the foundation of the database. Database beta testing and refinement currently are underway. The target date for launching the database is fall 2013. Individuals interested in participating should contact their respective IRUG Regional Chair: Beth Price, Americas; Marcello Picollo, Asia and

Australia; Boris Pretzel, Europe and Africa; or the IRUG Raman Committee Chair, Suzanne Lomax.

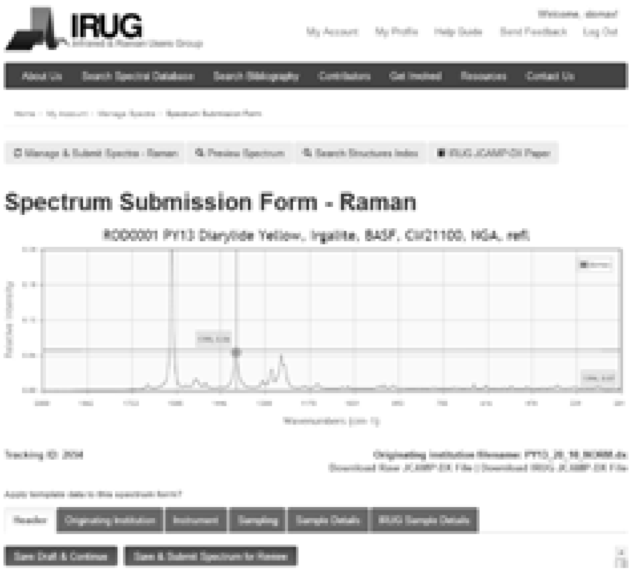

Figure 1. Screenshot of redesigned IRUG website showing online Raman spectrum submission form and interactive spectrum accessed from a user personal account.

Acknowledgements

This project is supported by the Institute of Museum and Library Services; National Center for Preservation Training & Technology; The Dow Chemical Company, Advanced Materials and Corporate Information Technology Divisions; Philadelphia Museum of Art; Victoria and Albert Museum; National Gallery of Art, Washington; and Institute of Applied Physics “Nello Carrara”, National Research Council. The authors also recognize Abigail Teller, Lauren Klein, Terra Huber, and Heather Brown for their important contributions.

References

[1] The IMLS is the primary source of federal support in the United States for libraries and museums. Its mission is to create strong libraries and museums that connect people to information and ideas; to sustain heritage, culture, and knowledge; to enhance learning and innovation; and to support professional development. For more information, see http://www.imls.gov (accessed 19/08/2013).

[2] JCAMP-DX (Joint Committee on Atomic and Molecular Physical Data Exchange) is a file specification. For full information on the IRUG JCAMP-DX protocol, see B. A. Price, B. Pretzel, S. Q. Lomax, C. Davis, J. Carlson, Revised JCAMP-DX Spectral File Format for Submissions to the Infrared & Raman Users Group (IRUG) Spectral Database, http://www.irug.org/ed2k/jcamp.asp (accessed 19/08/2013).

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