SPECIAL ISSUE
Raman in Art and Archeology (RAA 2019)

GUEST EDITORS
Martin A. Ziemann and Juan Manuel Madariaga
The Journal of Raman Spectroscopy is an international journal dedicated to the publication of original research at the cutting edge of all areas of science and technology related to Raman spectroscopy. The journal seeks to be the central forum for documenting the evolution of the broadly-defined field of Raman spectroscopy that includes an increasing number of rapidly developing techniques and an ever-widening array of interdisciplinary applications. Such topics include time-resolved, coherent and non-linear Raman spectroscopies, nanostructure-based surface-enhanced and tip-enhanced Raman spectroscopies of molecules, resonance Raman to investigate the structure-function relationships and dynamics of biological molecules, linear and nonlinear Raman imaging and microscopy, biomedical applications of Raman, theoretical formalism and advances in quantum computational methodology of all forms of Raman scattering, Raman spectroscopy in archaeology and art, advances in remote Raman sensing and industrial applications, and Raman optical activity of all classes of chiral molecules.

Special Issue: Raman in Art and Archeology (RAA 2019)
Guest Editors: Martin A. Ziemann and Juan Manuel Madariaga

The present study describes the first ever verified use of calomel as a white pigment on European works of art. 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, are presented. Both objects were unexpectedly found to contain calomel (Hg₂Cl₂), intentionally used as a white pigment.

New evidence for the intentional use of calomel as a white pigment 15–22
M. Crippa, S. Legnaioli, C. Kimbriel and P. Ricciardi

Applications of Raman spectroscopy in art and archaeology 8–14
M. A. Ziemann and J. M. Madariaga

The 10th edition of the International Congress on the Application of Raman Spectroscopy in Art and Archaeology (RAA2019) was held in Potsdam (Germany) from 3 to 7 September 2019, with eight keynote lectures, 35 oral presentations and 18 Poster Presentations. The number of active participants was 68 delegates from 20 countries among the 236 authors that presented at least one work.

Contents continued overleaf
The wavenumber of the bending and stretching regions, $\delta_{\text{max}}$ and $\nu_{\text{max}}$, and the polymerization index $I_p$ from Raman spectra of medieval émaux champlevés provide information on compositional differences in the glass matrix, namely, the alkaline components, which are difficult to detect by common laboratory X-ray fluorescence analysis.

The composition of 27 pigments commercialized by Kremer Pigmente has been investigated in detail. The information obtained by Raman spectroscopy and supported by other techniques such as FTIR, NIR, and FORS, have been compared with those reported on pigment datasheets available by the company. The final aim is to provide to stakeholders with various academic formations a useful characterization tool for the interpretation of pigment spectral information.

**Highlights**

- A set of 27 dry pigments was studied by different spectroscopic techniques.
- The main components were identified using available databases and literature.
- Some inconsistencies among obtained results and datasheet information were found.
- Additional components, not declared by the manufacturer, were also identified.

A set of decorative contemporary tile panels created by the Portuguese artist Maria Keil, for the Lisbon metro stations, was for the first time under a noninvasive analytical study. This study combines $\mu$-XRF and $\mu$-Raman analytical techniques for an elemental and structural composition characterisation of the tile's glazes. Results show that the artist has chosen a glassy matrix with a lead silicate glass base and a variety of pigments as well as pigments mixtures to enlarge the chromatic pallet of the glaze.

**Contents continued overleaf**
Raman spectroscopy is a convenient, efficient, and non-destructive technique that could estimate the metamictization degree of zircon, particularly for gem-class or historical samples. The full width at half maximum value of the $\nu_3$(SiO$_4$) band around 1000 cm$^{-1}$ can classify the structural state of zircon as crystallized (the full width at half maximum value is less than 5 cm$^{-1}$), intermediate (the full width at half maximum value ranges from 5 to 15 cm$^{-1}$), and metamict (the full width at half maximum value is more than 15 cm$^{-1}$). This study focuses on the zircon samples from Sri Lanka in the gemological collection of Abraham Gottlob Werner.

Raman microscopic measurements were used to analyse the detailed chemical composition and structure of three old papers dating from the 15th and 19th centuries. Raman mapping measurements were performed on the surface and along the cross-section of the papers. The resulting Raman images visualised the detailed chemical structure of the papers. The results of the paper analysis are discussed in connection with their use for the detailed characterisation and dating of paper.

Ariadne’s house is in the Regio VII of the Archaeological Park of Pompeii (Italy). As it is exposed to external alteration agents (rainfall, water infiltration and atmospheric pollution), the mural paintings located in this important residence clearly show the effects of ongoing degradation processes.

Influence of metamictization on the gemological properties of natural zircon: A Raman spectroscopic study of zircons in the gemological collection of Abraham Gottlob Werner

S. Gao and G. Heide

New insights into paper—Chemical paper analysis using Raman microscopy

E. Pigorsch

Understanding the degradation of the blue colour in the wall paintings of Ariadne’s house (Pompeii, Italy) by non-destructive techniques

N. Prieto-Taboada, S. Fdez-Ortiz de Vallesjuelo, A. Santos, M. Veneranda, K. Castro, M. Maguregui, H. Morillas, G. Arana, A. Martellone, B. de Nigris, M. Osanna and J. M. Madariaga

Contents continued overleaf
The present contribution focuses the attention on the mural paintings of two among the oldest Cappadocia churches, belonging to the group of “proto-Byzantine paintings.” These materials have never been extensively investigated before and represent a starting point of paramount importance to understand the evolution of both materials and techniques during the ages in this extraordinary region of central Turkey.

Portable Raman spectroscopy is used to perform a suitable diagnosis on the conservation state of elements (facades, structures and mortars) made of reinforced concrete, a common material in built heritage elements from the beginning of the 20th century. The methodology combines the use of Raman information with basic chemistry to explain the formation of decayed compounds through the reaction of chemicals of the surrounding environment with original built materials.

A depth profile-scanning study of an 18th-century gun-powder horn as well as reference Baltic amber samples was performed using a Raman confocal microscope equipped with a 785-nm laser. It was found that spectra collected from the surface are different than those from the bulk. The main changes are observed in the 1,700–1,400 cm⁻¹ range and are caused by degradation of the amber.

Spectroscopic investigation of Cappadocia proto-Byzantine paintings 95–108
M. Sbroscia, C. Pelosi, G. Agresti, A. Paolucci, P. Pogliani, L. Ruggiero and A. Sodo

Portable Raman can be the new hammer for architects restoring 20th-century built heritage elements made of reinforced concrete 109–122
I. Ibarrondo, U. Balziskueta, I. Martínez-Arkarazo, C. García-Florentino, G. Arana, A. Azkarate and J. M. Madariaga

The surface degradation of Baltic amber: The depth-profiling analysis and its application to historical object 123–129
A. Rygula, A. Klisieńska-Kopacz, P. Krupska, E. Kuraś and J. M. del Hoyo-Meléndez
The potential of photoreduced SERS substrate for the detection of the organic colourants (in mixtures) in lipid and proteinaceous paint layers is presented. Three different organic colourants and the cross-section of the sample from a polychrome work of art were included in the study. As the analyses by means of SERS are (minimally) invasive, the potential of noninvasive reflection FTIR analyses for the identification of organic colourants was tested as well.

SERS procedure using photoreduced substrates and reflection FTIR spectroscopy for the study of natural organic colourants 130–144
K. Retko, L. Legan and P. Ropret

The successful use of Raman microscopy for the in situ identification of organic red pigments in historical plastic objects is demonstrated. An in situ multi-analytical protocol for the study of organic red pigments is proposed. The novelty of the protocol lies on the analytical sequence of the techniques, combination of the information collected by elemental and vibrational analyses and final molecular identification of the organic red pigments by Raman.

The identification of synthetic organic red pigments in historical plastics: Developing an in situ analytical protocol based on Raman microscopy 145–158
E. M. Angelin, S. França de Sá, M. Picollo, A. Nevin, M. E. Callapez and M. J. Melo

Micro-Raman and VIS–NIR reflectance spectroscopy were applied in age determination of inks used in blue ballpoints pens. Principal component analysis was used to the classification of various blue ballpoints inks. Partial least squares models allow to obtain correlations between ∆E and Raman and reflectance spectra. The proposed nondestructive method allows to estimate the age of samples exposed to the sunlight.

Application of chemometric methods for the determination of fading and age determination of blue ballpoint inks 159–169
B. Łydżba-Kopczyńska, T. Czaja, R. Cieślą and G. Rusek
This work presents the first archaeometry study performed on glass beads recovered from the Vaccaean necropolis of “Las Ruedas” (IV-I BC, Valladolid, Spain). The glass network structure and presence of pigments on these glass beads have been analyzed by Raman spectroscopy. The analysis of the $\nu$ (Si-O) stretching modes and $\delta$ (Si-O) bending modes on the Raman spectra allows identifying diverse potential provenances and compositions, as well as the use of pigments such as CaSb$_2$O$_6$ and Naples yellow.

Exploiting the characterization of a group of Southern Italy glazed and enamelled pottery, the paper shows the wide range of information that can be extracted by a Raman spectroscopy investigation on this kind of samples. Data concerning the production technology, the main glassy matrices, opacifiers, colouring materials and additional crystalline phases at the body-glaze interface were collected. 

**Highlights**
- Medieval and renaissance pottery from Southern Italy were analysed
- Raman analyses provided unexpected results and answers to archaeological questions.
- SnO$_2$ Raman bands confirmed the grouping of Montella samples in three classes.
- Neofomed phases due to reactions during the production processes were discovered.
- Different cobalt-based phases were found in the blue enamels.

In order to overcome the limitation of the classic approaches for fine-grained depurated archaeological ceramics, Raman spectroscopy has been applied on the small mineral phases in archaeological pottery. The mineral phases studied, difficult to study with optical microscopy (OM), can be used as thermometer, or to assess the provenance. Among those, newly formed feldspars with their peculiar Raman fingerprint can provide useful information about the technological processes used in the manufacture of the pottery wares. A comparative evaluation among micro-Raman spectroscopy and OM, X-ray diffraction (XRD) and scanning electron microscope energy dispersive spectrometry (SEM-EDS) further helps to unveil the characteristic of original feldspars and newly formed ones.

**Contents continued overleaf**
Some iron nails extracted from the Urbieta shipwreck and conserved in the Archaeological Museum of Bilbao are studied in this work. Raman spectroscopy identified the raw materials employed in these pieces as well as decayed compounds. This work confirms that Raman spectroscopy is a suitable technique to analyze buried metallic pieces and to detect remains of past conservation treatments.

This work presents a methodological approach based on Raman spectroscopy analysis of carbonaceous matter in black limestones used in antiquity as decorative stones for provenance determination of ancient artefacts. The obtained results demonstrated that the use of Raman parameters typical of low-ordered carbon matter is an effective tool in provenancing black decorative limestones in non-destructive way, supporting also the creation of reference plots to which refer future Raman-based provenance studies.

In the absence of any final product and any other archaeological indication on the productive function of a furnace, precursors must be chemically identified by sampling the operating top. Geological maps must be preliminarily studied to rule out possible interferences with productive precursors. Optical microscopy inspection of the sampled findings must be used to rule out the metal melting function, and the remaining discrimination between calcara and kiln for ceramics must be established via Raman and FT-IR spectroscopy.

Discovering the colours of industrial heritage characterisation of paint coatings from the powerplant at the Levada de Tomar 208–216
I. Tissot, J. F. Fonseca, M. Tissot, M. Lemos, M. L. Carvalho and M. Manso

On the productive function of furnaces in archaeological sites 217–229
M. Rossi, N. De Riso, M. Caterino, G. Ferraro, L. Cicala, B. Ferrara, V. Gassner and A. Vergara

The interaction of sediments with the archeological iron remains from the recovery shipwreck of Urbieta (Gernika, North of Spain) 230–240
E. Estalayo, J. Aramendia, L. Bellot-Gurlet, L. Garcia, I. García-Camino and J. M. Madariaga

Raman spectroscopy as a tool for provenancing black limestones (bigi morati) used in antiquity 241–250
S. Raneri, F. Košek, L. Lazzarini, D. Wielgosz-Rondolino, J. Jehlicka and F. Antonelli