

# Applications of Raman spectroscopy in art and archaeology

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 archeology 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.

One of the most important events dedicated to this subject today is the biennial International Congress on the Application of Raman Spectroscopy in Art and Archaeology (RAA). The RAA conferences promote Raman spectroscopy and play an important role in the increasing field of its application in Art and Archaeology. These prominent international events have a long tradition. Previously, they were held in London (2001),<sup>[1]</sup> Ghent (2003),<sup>[2]</sup> Paris (2005),<sup>[3]</sup> Modena (2007),<sup>[4]</sup> Bilbao (2009)<sup>[5]</sup> and Parma (2011).<sup>[6]</sup>

The seventh edition of the International Congress on the Application of Raman Spectroscopy in Art and Archeology (RAA 2013) was held in Ljubljana (Slovenia) from 2 to 6 September 2013. As in the previous editions, the scientific program was focused on the characterisation of materials (pigments, inks, photographic material, gemstones, stones, precious stones, glass, ceramics, etc.), conservation issues affecting cultural heritage (decaying, corrosion, etc.), surface-enhanced Raman spectroscopy (dyes, organic pigments, etc.), Raman spectroscopy of biological and organic materials (resins, fibers, ancient organic compounds, etc.), Raman spectroscopy in paleontology and paleoenvironment, new Raman instrumentation and Forensic applications in art and archaeology (e.g. falsification). These studies were presented along 5 plenary lectures, 40 oral presentations and 60 poster presentations. The number of active participants was 135 delegates from 32 countries among the 379 authors that presented at least one work to the congress.

At this point, we would like to mention Howell Gwynne M. Edwards, one of the 'fathers' of Raman spectroscopy applications to art and archaeology. Edwards retired in the year of the RAA 2013 edition, and it was an honour to host him in Ljubljana. The scientific and organizing committees acknowledged his lifetime work and gave him the stage to open the conference with an extremely interesting keynote lecture entitled Raman Spectroscopy of Extremophilic Biodeterioration: An Interface between Archaeology and the Preservation of Cultural Heritage. We believe that there is not a single scientist working in the field who would not have used at least one of his numerous publications for building the knowledge or as a good reference.

Because of the increasing need for well defined and quickly available reference spectra, the congress was completed by a special session and round table about the most important criteria and requirements for the building of a public database of standard Raman spectra of compounds related to cultural heritage and archaeology, presented by Infrared and Raman Users Group (IRUG) members, in order to give a contribution to the building of the

large, public, database of Raman spectra related to art, archaeology and conservation science by IRUG.

The RAA 2013 edition takes pride in the general comment of the participants: 'a very high scientific quality of the contributions', 44 of them are collected in this special issue, ordered in the different topics suggested to participants when this edition was announced.

## Characterisation of materials: gems, pigments and supports

Raman spectra of the new gemstone pezzottaite [Cs(Be<sub>2</sub>Li)Al<sub>2</sub>Si<sub>6</sub>O<sub>18</sub>] and Cs-beryl were studied and compared by Lambruschi *et al.*<sup>[7]</sup> The extended Raman spectrum of pezzottaite was reported for the first time. Characteristic peaks were identified in the region of fundamental H<sub>2</sub>O stretching vibrations: Pezzottaite showed two weak Raman modes while beryl exhibits a single intense band. The position of H<sub>2</sub>O bands also allowed identification of the orientation of H<sub>2</sub>O into the channels (i.e. type I or II), assigning type II for pezzottaite. Furthermore, to complement the Raman data, other diagnostic methods were used, such as electron microprobe analysis in wavelength dispersive mode, laser ablation inductively coupled plasma mass spectrometry and single-crystal X-ray diffraction (XRD) characterisation. On the basis of the study, the authors proposed a protocol to distinguish between beryl and pezzottaite by Raman spectroscopy.

Jeršek and Kramar<sup>[8]</sup> reported on the Raman investigation of a baroque chalice made in 1732, one of the most richly decorated chalices in Slovenia, containing 456 embedded gemstones. In addition to the Raman data, gemology microscopy and ultraviolet fluorescence were used. The investigation showed the composition of the gemstones, identifying 24 diamonds, 93 rubies, 4 sapphires, 152 emeralds, 101 almandine garnets, 6 grossular garnets, 68 amethysts, 6 citrines, one specimen of glass and one of agate. Interestingly, the yellow-orange gemstones, so far identified as citrines, were determined as grossular garnets. Furthermore, on the basis of identified inclusions and in combination with macroscopic observations and literature data, the origin of the gemstones, as well as the substitutes for the lost stones, were determined.

The Raman microspectroscopy results of the study of plasterwork decorations, located on the stalactite vaults of the Hall of the Kings in the Alhambra (Granada, Spain), were presented by Dominguez-Vidal *et al.*<sup>[9]</sup> Field investigations were first carried out *in situ* (portable Raman spectrometer at 785 nm). Then, a well-directed sampling, based on the results obtained, was performed. Finally, more information was obtained on that reduced number of samples by means of laboratory studies. Almost all the pigments present in the decorations of the hall were identified by *in situ* Raman microscopy: cinnabar, minium, carbon black, natural lapis lazuli and

synthetic ultramarine blue. However, the identification of blue-greenish and green pigments had to be performed on microsamples using a Raman microscope (excitation at 514 nm) revealing the presence of azurite (and its degradation compound clinoatacamite) and copper chlorides mixed with a small amount of lapis lazuli for green decorations. The stratigraphic study of the layers discovered the presence of redecorations with overlaying layers of pigments even of different colours.

Nineteen natural specimens of azurite from European mining locations (exploited in medieval times) were analysed by Aru *et al.*<sup>[10]</sup> using Raman microscopy to investigate the existence and identify the impurities. Malachite, hematite, goethite, cuprite, rutile and anatase were detected in a significant proportion of the specimens. Other minerals, detected less frequently, include quartz, calcite, cerussite, orthoclase, beudantite and jarosite. The most important finding was the nature of the black and orange-brown mineral grains; the classical assumption that such impurities in azurite pigments are mainly copper oxides (cuprite and tenorite) is partially incorrect as the orange-brown particles actually correspond to the iron oxides, goethite and hematite. These findings indicate that any iron oxides and malachite detected as minor impurities in azurite-containing museum objects should be taken as a consequence of the natural makeup of azurite specimens used for the pigments rather than a deliberate addition by the artist.

Micro-Raman spectroscopy and optical microscopy under visible and ultraviolet light were applied by Pięta *et al.*<sup>[11]</sup> to characterise the pigments, state of conservation and painting techniques used in the 17th century Golden Age panel painting 'Servilius Appius' (located at the Gdańsk History Museum), attributed to Isaac van den Blocke. Optical microscopy on sample cross sections revealed that samples were multilayered (four to six layers depending on the location in the painting). Individual layers of six samples were analysed by micro-Raman spectroscopy, discovering a rich palette of white, yellow (lead tin compounds), red, blue (azurite plus smalt) and black pigments. The results showed that the painting was in a good state of conservation, except for the corrosion of smalt and discoloration of the blue shade to a dirty grey-green (in the areas where the smalt was mixed with many different media) while regions in which smalt was mixed with a sufficient amount of lead white were generally well preserved.

The characterisation of Portuguese painting's ground layers from the 15th and 16th centuries (1450–1600), mainly those used by the Coimbra, Lisbon and Viseu workshops, was performed by Antunes *et al.*<sup>[12]</sup> using optical microscopy, micro-confocal Raman and Raman spectroscopic mapping, on cross sections from a set of six groups of representative paintings. Results were integrated with those obtained by micro-XRD and scanning electron microscopy (SEM)/energy dispersive X-ray spectroscopy (EDS) on the same samples. Calcium carbonate and sulfate, prepared by addition of animal glue, are used regularly in these layers and can be considered common in the Iberian Peninsula. The differences among the various workshops at that time are related to the diverse use and proportions of chalk/calcite (calcium carbonate), gypsum (di-hydrated calcium sulfate) and anhydrite (anhydrous calcium sulfate). In most cases, the ground layers are made of calcium sulfate in the form of the so-called gesso grosso (anhydrite with small amounts of gypsum). Only the Viseu paintings used calcium carbonate ground layers.

The chemical stability of chrome yellows, frequently used by painters of the Impressionism and Post-impressionism period, depends on the chemical composition ( $\text{PbCrO}_4$ ,  $\text{PbCr}_{1-x}\text{S}_x\text{O}_4$ ) and

crystalline structure (monoclinic or orthorhombic) of the material. Monico *et al.*<sup>[13]</sup> have explored the possibility to distinguish among different forms of this pigment by using Raman spectroscopy. First, three paintings conserved at the Van Gogh Museum (Amsterdam) were analysed *in situ* using a portable Raman spectrometer, while equivalent investigations employing laboratory instruments were performed. Previously, several oil paint model samples, made up of monoclinic and/or orthorhombic crystalline forms of  $\text{PbCrO}_4$  and  $\text{PbCr}_{1-x}\text{S}_x\text{O}_4$  ( $0.1 \leq x \leq 0.8$ ), were analysed using 785.0, 532.0, 514.5 and 488 nm excitations. The band shape and the position of the chromate bending modes proved to be more sensitive than the stretching modes (at 785 nm) to discriminate among the monoclinic  $\text{PbCrO}_4$ , the monoclinic  $\text{PbCr}_{1-x}\text{S}_x\text{O}_4$  ( $x < 0.25$ ) or the S-rich orthorhombic  $\text{PbCr}_{1-x}\text{S}_x\text{O}_4$  ( $x \sim 0.5$ ).

The series of the Sibyls from the church of San Pedro Telmo, one of the most important groups of paintings of Argentine colonial art, were analysed by Marte *et al.*<sup>[14]</sup> using Raman microscopy in combination with SEM-EDS and HPLC. Ten of the paintings were performed in the 18th century while those of Delphic and Tiburtine Sibyls were painted in 1864, during the first restoration of the series in Buenos Aires. There is a controversy about the origin (Andean workshop or Spanish source) of this group of paintings. The analysis revealed the presence of a mixture of barium sulfate, lead white and calcite in the preparation layers of the 19th century Sibyls in contrast to the clayish ground layer in the 18th century paintings. Traditional pigments such as vermilion, lead white, orpiment, indigo, lazurite (its presence in the Tiburtine painting is the first report of this blue pigment in Argentine colonial art) and Prussian blue were identified by Raman microscopy. However, the presence of a synthetic lead-based yellow pigment and the organic pigments alizarin and Indian yellow in the 18th century Sibyls strongly suggests their Spanish origin.

## Conservation issues (alteration/degradation processes) affecting cultural heritage

The study of the decayed gilded decorations of the stalactite vaults in the Hall of the Kings (Alhambra complex, Granada, Spain) has been carried out for the first time by de la Torre-López *et al.*<sup>[15]</sup> First, the *in situ* analysis by portable Raman spectroscopy enabled the identification of tin(II) oxide in the black areas nearby the golden flakes, suggesting the presence of an altered tin foil. Then, these decorations were characterised through the use of complementary non-destructive laboratory techniques on microsamples. Two main metallic structures were identified: (1) a thin (1–2  $\mu\text{m}$ ) gold leaf (probably original) and (2) redecorations with a laminated structure formed by a gold leaf placed over a thicker (10–15  $\mu\text{m}$ ) tin foil. Synchrotron Fourier-transform infrared microspectroscopy revealed the use of proteinaceous glue to fix the gold leaf directly on the plasterwork, whereas in the case of the laminated structures, either glue or a natural resin was found. Detachment of the metals as a result of the alteration of the organic materials (oxalate formation) and the oxidation of the tin foil was revealed by Raman microspectroscopy. Two technologies of false gilding were encountered: one based on a tin foil tinted to look like and the second with a tin-copper alloy (this appeared severely degraded to copper oxalate and tin(II) oxide).

Efflorescence from walls and wall paintings of two Pompeian houses were analysed in the field by Madariaga *et al.*<sup>[16]</sup> by using a portable Raman spectrometer (785 nm), assisted with a handheld ED-XRF spectrometer. Both exposed and protected rooms were

measured in different year seasons (May 2010 and September 2011 and 2012), considering different orientations. The efflorescence salts are formed through chemical attacks of acid gases ( $\text{CO}_2$ ,  $\text{SO}_2$  and  $\text{NO}_x$ ), acids from biological metabolism or transported by infiltration waters on the original compounds of the mortars. The rainwash of the newly formed salts and biominerals can be considered as the most serious problem for the conservation of the archaeological remains of Pompeii. The walls and wall paintings exposed to the rainwash are the worst preserved, probably because of a continuous cycle of acid attack to the original carbonate materials, involving loss of plaster. The walls affected by infiltration waters showed also a remarkable decaying as a result of the action of the efflorescence on the carbonate compounds acting as the binder of the mural painting remains in the houses of Pompeii.

The deterioration of a traditional pigment, malachite [ $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ ] in different binders, as a consequence of environmental effects acting on paint layers that were prepared according to traditional Baroque recipes, was studied by Špec *et al.*<sup>[177]</sup> Malachite has often been reported to be very permanent in all binding media; however, investigations of aged and non-aged paint layers by means of Raman microscopy have shown instability of the carbonate part of the molecule, especially when malachite is present in an egg yolk medium. Decomposition of the pigment and the formation of degradation products such as copper oxide (tenorite-CuO) were observed. The possible formation of another copper oxide, paramelaconite- $\text{Cu}_4\text{O}_3$ , was also taken into consideration. In order to obtain additional information on the degradation processes that affect malachite paint layers, supporting analytical methods, such as SEM and XRD, were used confirming the previous experimental Raman observations.

Weathering steel sculptures are part of urban landscapes in most of the western cities. Although weathering steel was designed to resist against the atmospheric impact, some papers described recently different decaying in such sculptures exposed to  $\text{Cl}^-$  and  $\text{SO}_2$ -rich urban atmospheres. Aramendia *et al.*<sup>[181]</sup> propose the use of the extended protective ability index (PAI), measured through quantitative Raman imaging, to correlate deterioration with the presence of different iron (oxy-hydr)oxides at the surface of the artworks. The classical PAI takes into account only the ratio between the mass of goethite and lepidocrocite. However, when weathering steel sculptures are exposed to such  $\text{Cl}^-$  and  $\text{SO}_2$ -rich atmospheres, other iron compounds are systematically detected, like hematite (in  $\text{SO}_2$ -rich atmospheres), akaganeite (in  $\text{Cl}^-$ -rich atmospheres) and magnetite. The extended PAI is calculated by dividing the mass fraction of the stable iron phase (goethite) between the sum of mass fractions of the non-stable iron phases (lepidocrocite + hematite + akaganeite + magnetite). PAI values obtained for the different artworks provided quantitative clues for the conservation diagnosis of the studied weathering steel sculptures.

It is known that bronze surfaces, as well as prepatinated surfaces on bronze, undergo chemical and visual changes when exposed to humid and polluted environments. To decrease those decaying processes, corrosion inhibitors started to be used some years ago, although the basic knowledge on their protective effect is not well clarified. To better understand the effectiveness of corrosion inhibitors on patinated bronze surfaces, Kosec *et al.*<sup>[19]</sup> studied the adequacy of twoazole type inhibitors. The inhibited layers were then protected by a water-repellant layer. In the case of the studied patinas, green chloride and green nitrate patinas, applied over the brown artist's patina, were tested, as well as brown patina and the patina that develops on bare bronze. The inhibition systems used on the different chemically

achieved patinas were characterised by Raman spectroscopy and electrochemical techniques. A chemical interaction of both inhibitors with copper and bronze was ascertained, confirming that the inhibitors were very effective.

The corrosion behaviour of lead (Pb)-based alloys exposed to volatile acetic and formic acids was investigated by Ghiara *et al.*<sup>[20]</sup> The research was based on laboratory-made samples replicating specific types of Pb-based alloys, with antimony (Sb) and tin (Sn) as alloying elements. The model samples were exposed to concentrated acetic and formic acid vapours for 15 days. Each specimen was subjected to gravimetric measurements and periodically monitored by micro-Raman spectroscopy and SEM/EDX in order to understand the corrosion behaviour. Results showed the presence of typical corrosion products, like different hydrated forms of Pb and Sn acetates and formates. However, an increase in the volume and brittleness of some Sb-rich specimens as well as the presence metallic Sb was also found. The presence of such corrosion products must be considered when such objects have to be restored and particular attention should be given to conservation/stabilisation procedures.

Gutman *et al.*<sup>[21]</sup> studied a precious Gothic wall painting, discovered in 2012 during the restoration works at the Dominican Monastery in Ptuj (Slovenia) but dated back to 14th century, using optical and Raman microscopy to acquire information about the technology used, as well as to identify the deterioration products. The optical microscope revealed the use of a lime technique (several layers of fresh lime wash were overlaid on a dry mortar, followed by one single layer of paint). The pigments applied were all of inorganic origin: azurite, red and yellow ochres, cinnabar, red lead, lead white, lead-tin yellow type I and carbon black. The identification of the type I of lead-tin yellow in this wall painting of the 14th century is of a high importance because, until now, it was considered that it appeared on the market only in the first half of the 15th century. Lead white, red lead and lead-tin yellow type I are very rarely found in fresco paintings in Slovenia, what makes the wall paintings even more important. Moreover, black and brown grains of plattnerite ( $\text{PbO}_2$ ) were observed as a result of degradation of lead pigments.

Portable Raman spectroscopy, assisted with XRF, was used by Veneranda *et al.*<sup>[22]</sup> to investigate the original and decayed materials as well as the degradation phenomena affecting the middle age mural painting of the Assumption's church in Alaiza (Basque Country, Spain). Original compounds were identified and distinguished from (1) those materials used in recent restorations and (2) those considered as decaying compounds. This information was used to select the sampling areas to perform laboratory Raman measurements and soluble salt test in an attempt to clarify the degradation processes. The use of industrial common salt (unpurified NaCl) against the snow and ice, as well as common fertilisers such as  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$ , generates  $\text{Na}^+$  and  $\text{NH}_4^+$  cations together with  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  anions that ascent the basal part of the walls causing the decarbonation of calcite (acid-base reaction between  $\text{NH}_4^+$  and  $\text{CO}_3^{2-}$ ) and the subsequent disintegration of the mortar. Sulfate compounds were detected in the lower parts of the walls (below half a meter), while nitrate compounds were detected at heights greater than 1 m.

## Surface-enhanced Raman spectroscopy

Surface-enhanced Raman spectroscopy (SERS) was used to study the palette of the 19th century French impressionists and post-

impressionists, whose works represent one of the largest collections, owned by the Art Institute of Chicago. Pozzi *et al.*<sup>[23]</sup> utilised SERS for the analysis of red lake paint reconstructions prepared according to 19th century historical recipes. The results showed that after hydrolysis with hydrofluoric acid and application of the Lee–Meisel SERS substrate, the dyes can be successfully identified even in the presence of inorganic pigments, extenders, ground materials or binding media. The same procedure was then applied to analyse samples from Manet, Pissarro, Renoir, Monet and Gauguin paintings. It was shown that madder and cochineal lakes were extensively used, sometimes also in combination. The presented SERS protocol enabled to reduce the size of samples needed for analysis, leading to a successful identification of lake samples as small as  $20 \times 20 \mu\text{m}$ . The work added also important information to art historical data on the use of materials in the 19th century. According to the authors, it seems that only Vincent van Gogh deviated from the common practice of using mainly madder and cochineal lakes, adding eosin and, in a few cases, brazilwood lakes to his palette.

Idone *et al.*<sup>[24]</sup> explored the possibility to obtain the SERS spectra and a successful identification of lakes without any pretreatment of samples, by application of silver colloidal pastes as substrates. This application can be extremely interesting, especially in the investigation of cross sections of samples, where spatial information on the sequence of paint layers is important. The analytical procedure was successfully tested on cross sections of samples removed from the 13th century painted wooden statue and from the 16th century mural painting. However, some further work is still required in order to fully investigate the substrate's capabilities and how different variables, such as interaction with other compounds present in the paint layers' matrix, and interaction of the substrate itself with the dye molecule influence the enhancement.

A very interesting contribution to SERS studies was shown by Platania *et al.*<sup>[25]</sup> who developed a microextraction procedure for the analysis of mordanted dyes. Ethylenediaminetetraacetic acid (EDTA) was added to the previously developed Ag-agar gel substrate, which enhanced its capabilities to trap the analysed molecules inside the gel structure. Mordanted dyes on textile: silk, wool and printed cotton, as well as lakes on a mock-up panel painting were successfully analysed by SERS after the microextraction. Its extreme power lies in the fact that the extraction is very efficient, allowing the detection of very low concentrations, hydrolysis treatments such as exposure to hydrofluoric acid vapours prior the extraction of a dye are not necessary, and it can be used *in situ*, without any removal of samples from an artwork. Furthermore, the gel exhibits good possibilities of adding additional compounds to its structure, which could even further enhance the extractive performance of the gel, allowing the extraction of specific molecules in a mixture.

Retko *et al.*<sup>[26]</sup> proposed a new SERS substrate, based on the photoreduction of silver nitrate by UV light and hydroxypropyl cellulose as a stabilising agent. The performance of the new substrate was successfully tested on the organic dye alizarin red S and two organic pigments: madder lake and alizarin crimson dark. Furthermore, colorants were successfully identified also in the prepared mock-up paint layers with different organic binders without any pretreatment and without any interfering signal in the SERS spectra from the media. Because of its viscosity, the substrate shows promising characteristics also for the analysis of cross sections of samples. Further work is still necessary in order to understand the complete reduction and nanoparticle formation mechanisms, as well as in the optimisation of the substrate's preparation and its testing on more complex chemical substances.

Thin-layer chromatography (TLC) in combination with SERS was applied to characterise a mauve laboratory prepared sample by Cañamares *et al.*<sup>[27]</sup> Mauve was synthesised in 1856 by Perkin and was the first synthetic organic dye. Its composition is mauveine A, B, B2 and C. Five fractions were separated by TLC, and further SERS measurements were performed directly on each spot on the TLC plate, which gave high-quality Raman spectra. Furthermore, the Raman band assignments were performed by density functional theory calculations.

Highly important developments towards the non-invasive and *in situ* SERS measurements by utilisation of portable Raman instrumentation were performed by Doherty *et al.*<sup>[28]</sup> The removable methylcellulose gel substrate was optimised, and a new gelatin substrate was introduced. A possible penetration of the substrate into the artwork surface was monitored by non-invasive portable nuclear magnetic resonance (NMR) profilometry. It was found that the methylcellulose substrates should not be used on paper objects as a result of their high penetration. To overcome this difficulty, a new gelatin substrate with adequate SERS activity was proposed. By application of the gelatin (gel G) substrate, it was possible to identify the azo dye orange 10, the xanthene PR81 and rhodamine 6B, while the substrate remained completely and only at the surface.

Roldan *et al.*<sup>[29]</sup> studied the natural sepia pigment by application of Raman, SERS, Fourier transform infrared spectroscopy (FTIR), Py-GC/MS and XRF. Sepia, in its natural form composed of eumelanin, is a challenging compound to identify in artworks as a result of its heterogeneity (it can contain also proteins, polysaccharides and lipids). Further complications in sepia identification arise also from its insolubility in most organic solvents, interference with the binder matrix and poor spectroscopic characteristics. As the SERS substrate, a hydroxylamine-reduced silver colloid was used for the characterisation of natural sepia pigments, a synthetic sepia sample and two sepia inks applied on paper and exposed to accelerated aging. Density functional theory calculations along with the previous spectroscopic studies helped in the band assignments of the investigated compounds. Further information on the presence of lipids, cholesterol derivatives and polysaccharides were gained by applying Py-GC/MS, while XRF measurements showed that the elemental composition depends on the extraction procedure applied during the pigment preparation. Finally, the developed SERS procedure was successfully used also for the sepia identification in the 19th century drawing by the artist R.F. Blum.

Several dark red microsamples from nine illuminated manuscripts of three important medieval Portuguese monasteries (St. Mamede of Lorvao, Holy Cross of Coimbra and St. Mary of Alcobaca) were analysed by Castro *et al.*<sup>[30]</sup> using a multianalytical approach to identify the dyes, fillers, binders and other additional paint components. SERS and microspectrofluorimetry were used for the first time to characterise lac dye paints, while Raman microscopy ( $\mu$ -RS) and micro-FTIR ( $\mu$ -FTIR) were employed to detect binders and fillers. SERS was able to offer a conclusive molecular fingerprint of lac dye. Microspectrofluorimetry provided useful information on the global formulation of the red paints.

## Raman spectroscopy of biological and organic materials

It is well known that endolithic microorganisms can penetrate actively into the rocks giving rise to biodeterioration phenomena.

Consequently, endolithic traces can be found on stones, as a result of current or past biological colonisation. Raman spectroscopy was used by Casanova-Municchia *et al.*<sup>[31]</sup> to analyse four different lithotypes of rocks, gathered from stone monuments and natural outcrops in temperate and mediterranean bioclimates, having endolithic microorganism colonisation (cyanobacteria, fungi and lichens). Scytonemin, anthraquinone compounds and carotenoids were detected as biomarkers, characteristic of microorganisms adapted to strong UV radiation and dry conditions. The results of this work identified for the first time traces of endolithic microorganisms on stone monuments located in temperate and mediterranean bioclimate, where extreme climate conditions are not foreseen. Moreover, different geo-markers such as goethite and lepidocrocite were also identified, probably present because of the mobilisation of iron by lichen metabolic activity.

The detection of copper resinate in paintings (a green pigment widely used by the 16th century painters) is up to this time an analytical challenge. The oldest recipes suggest the preparation of copper resinate by mixing verdigris with terpenic resins as Venice turpentine (conifer resins) on hot ashes. Conti *et al.*<sup>[32]</sup> examined the Raman features of copper resinate on three painted layers prepared by mixing the pigments with a suitable amount of linseed oil. The mock paint films were spread on ground glass supports and aged under laboratory conditions (25 °C, 55% relative humidity) for a month and then analysed. Another set of analyses was performed after 1 year of such natural aging observing no significant changes in obtained spectra. The Raman features with seven laser sources (488, 514, 532, 633, 785 and 830 nm in dispersive Raman scattering mode and 1064 nm in FT-Raman mode) were compared with verdigris. The excitation at 830 nm gives the richest spectrum of copper resinate while 488 nm is the most suitable for verdigris. The obtained results were applied in the analysis of a chip extracted from a famous Caravaggio's painting.

Metal carboxylates (metal soaps) form naturally when free fatty acids react with metal cations and may also be found as additives or degradation products. To increase the knowledge of such compounds, 22 metal carboxylates were synthesised and their Raman and FTIR spectra assembled in a reference database by Otero *et al.*<sup>[33]</sup> Metal salts of cations commonly present in oil paintings were used, including lead, zinc, calcium, cadmium, copper and manganese. The fatty acids studied were palmitic, stearic and oleic. Azelaic acid, a product resulting from autoxidation of polyunsaturated acids, was also included. Metal carboxylates were characterised by  $\mu$ -Raman and  $\mu$ -FTIR spectroscopy, and their structures were confirmed by XRD. Raman enabled the differentiation of the carbon chain length in the C–C stretching region (1120–1040  $\text{cm}^{-1}$ ) and IR distinguished the metal cation in the  $\text{COO}^-$  stretching absorption region (1650–1380  $\text{cm}^{-1}$ ), being complementary techniques (with the aid of chemometrics) for a full identification of the metal carboxylates in complex aged paints. The model gave a high confidence level for the identification of copper palmitate and copper azelate in two 19th century Portuguese oil paintings.

The characterisation of materials involved in painted works of art provides a better knowledge of artworks through the understanding of artistic and technological processes. Daher *et al.*<sup>[34]</sup> studied complex systems made of a multilayered coloured background, covered with varnish layers from some pieces selected from a large corpus of French decorative arts objects from 18th century museum collections, with the aim to understand the artistic and technological processes in the decorative arts field during the 18th century. Specific materials such as lake pigments, binders

and varnishes were studied by means of a set of experimental setups (FT-Raman at 1064 nm, SERS with a 458 nm excitation wavelength, infrared using a micro-ATR mode) and the best set of analytical parameters for each technique and each analysed sample. The results obtained allowed to identify and characterise multilayered paint systems as well as varnish compositions using specific data treatment methodology.

Madden *et al.*<sup>[35]</sup> studied the early 20th century aviation plastics and leverages, including goggles, flight helmets, airplane windows and canopies, all belonging to the largest air and space collection of the Smithsonian institution. For that purpose, Fourier transform and portable dispersive Raman spectrometers were utilised successfully analysing polymers and plasticisers. The Raman measurements allowed the identification of glass, laminated safety glass, plasticised cellulose nitrate, plasticised cellulose acetate and poly (methyl methacrylate). Furthermore, the Raman data contributed information that is of extreme importance in the interpretation of technological history.

## Raman spectroscopy in paleontology and prehistoric art

Coelacanth fossils from the Romualdo and Brejo Santo Geological formations in Brazil were studied by Freire *et al.*<sup>[36]</sup> By utilisation of Raman, IR and XRD measurements, it was found that the coelacanth processes of fossilisation occurred in different manners depending on the environmental conditions the fossils were exposed to. In the Romualdo formation, the fossils are composed of both hydroxyapatite and calcite, while the matrix shows the presence of calcite and quartz. In the Brejo Santo Geological formation, the fossils are constituted of hydroxyapatite, while the matrix is mainly formed of calcite, quartz and albite.

Montoro *et al.*<sup>[37]</sup> studied polymerisation process of communic acids that are considered as precursors to form fossil resins class Ia and Ib. Three isomers of communic acid: trans-, cis- and iso-/mirceo-communic acid were exposed to a controlled temperature treatment in the laboratory. The temperature-induced reactivity in side chain conjugated double bonds and a loss of conjugation in the side chain was successfully followed by Raman spectroscopy, as a weakening of the relative intensities of specific Raman modes could be followed. The formation of fossil resin occurs in two reactive steps. It was found that for trans- and cis- isomers, the initial polymerisation with 1,2-addition to the conjugated double bond is followed by a maturation reaction. When comparing the three isomers, both reactive steps occur at different temperatures. The Raman data were also confirmed by DSC results.

*In situ* investigation of rock art paintings by utilisation of micro-Raman spectroscopy ( $\mu$ -RS) can be faced with several problems: sunlight, wind, dust and crusts. These problems were addressed by Hernanz *et al.*<sup>[38]</sup> giving a special focus on the presence of crusts. The objects of the study were five rock art sites in Spain. At the surface of the rock paintings as well as in the stratigraphic layers of the crusts, several minerals were found: whewellite, gypsum, calcite, clay, dolomite,  $\alpha$ -quartz, anatase and haematite, while haematite and amorphous carbon were found to compose the red and black pictographs. The *in situ* Raman studies were complemented also by energy dispersive X-ray fluorescence and diffuse reflectance infrared Fourier transform spectroscopy, whereas microstratigraphic measurements were performed by  $\mu$ -RS and SEM combined with EDS.

Two classes of ancient ceramic artefacts from Motya (Sicily, Italy) and Khirbet al-Batrawy (Jordan) were studied by Medeghini *et al.*<sup>[39]</sup>  $\mu$ -RS was applied to study the mineralogical composition of these ceramics as well as the technological aspects of their production. The capabilities of the technique are also discussed, suggesting that  $\mu$ -RS is a suitable technique to investigate the mineralogical assemblage of the bulk, the nature of the black gloss and superficial decorations. Also, its capability to identify the mineral phases in traces can contribute to the provenance assessment of the raw materials. It also shows a great potential in the analysis of coarse-grain and low-fired ceramics, while in the characterisation of fine and vitrified pottery class has its limitations.

A very interesting investigation of the origin of the blue colour of the enamelled glass pieces of the Melfi castle (south of Italy) was presented by Caggiani *et al.*<sup>[40]</sup> Raman and SEM were used to identify the rock used as the raw material as well as to investigate if the mineral bearing the blue colour of the artefacts could be other than lazurite. Several materials were studied: two volcanic rocks, lapis lazuli and archaeological glass with blue enamels. The colouration mechanism was studied by application of temperature-dependent Raman measurements and Raman mapping on single lazurite crystals, h ayne crystals, rocks and the enamels. Among others, it was found that after the temperature increased above 700 °C, the colour in average increased and that the content and position of inclusions may play a crucial role in the intensity of the final colour. Finally, it was determined that the Melfi blue enamels were produced using lapis lazuli as the raw material.

Coccatto *et al.*<sup>[41]</sup> characterised seven gem quality green 'jade' samples and three green jade samples of archaeological importance by application of Raman spectroscopy. The results showed that five samples of gem quality and two samples of archaeological interest were 'jadeite jade', while two samples of gem quality and one sample of archaeological interest were found to be 'omphacite jade'. The Raman results were confirmed by classical gemology, EDXRF, UV-Vis-NIR absorption, FTIR in absorption and micro-FTIR in reflectance, proving that Raman is an efficient technique for their investigation. However, further studies are necessary in order to set the limits of the separation of the omphacite and jadeite minerals.

## New Raman instrumentation and applications

Utilisation of portable Raman instruments equipped with fibre optic probes for the *in situ* analysis of artefacts can be quite challenging. The difficulties may arise when positioning these probes to set the focal distance, angle of analysis and holding the probe steady. Several solutions had been proposed, but they might result in a less portable system or inability to perform depth profiling. The Short Communication by Madden *et al.*<sup>[42]</sup> presents a new adjustable focal length adapter. This accessory enables a good positioning of a fibre optic probe against the object and adjusts the focal distance into the material, especially important for the investigation of transparent layers.

Direct identification of pigments in mediaeval illuminated manuscripts was one of the first applications of Raman spectroscopy in art and archaeology. In previous *in situ* analysis of handwritings, the equipment was typically provided with a single excitation source. In the work presented by Lauwers *et al.*<sup>[43]</sup>, a portable dual Raman spectrometer was used to characterise the pigments employed in De Civitate Dei (Library in Bruges, Ms.106), an important illuminated mediaeval manuscript. A setup that allowed stable positioning of the equipment with the two lasers, which are part of

the instrument, was implemented to perform the measurements. Pigments such as lead white ( $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ ), lead-tin yellow type I ( $\text{Pb}_2\text{SnO}_4$ ), malachite ( $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ), azurite ( $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ ), mosaic gold ( $\text{SnS}_2$ ), vermilion ( $\text{HgS}$ ), carbon black (C) and red lead ( $\text{Pb}_3\text{O}_4$ ) were identified. These pigments were often used in mediaeval artworks and contribute to the enrichment of information of the materials used by the illuminator. Moreover, characteristics important for these *in situ* measurements using a dual-Raman spectrometer are discussed.

Much of current research on artworks is focused on the development of non-invasive spectroscopic methods to look at the composition of artists' materials qualitatively, little has been performed to analyse them quantitatively. Pallipurath *et al.*<sup>[44]</sup> investigated the use of Fourier Transform Raman spectroscopy, in isolation and in conjunction with complementary fibre optic reflectance spectroscopy, to look at the spectral changes that occur with varying the paint/binder ratio in model historic lead-based paints. When used in conjunction with multivariate analysis, they demonstrated that it can be possible to obtain a semi-quantitative estimation of the composition of a paint film from its Fourier Transform Raman spectrum, given a set of suitable reference spectra recorded from paints produced within the workable mixture range. This represents a tentative first step towards a semi-automated and quantitative method for analysing cultural heritage objects, which may help boost our understanding of their history and enable conservators to make more informed decisions so as to ensure their preservation.

The Raman spectral differences among the synthetic ultramarine blue (from the J. B. Guimet manufacturer) and three natural ultramarine blues (lazurites from different geographical sources: Chile, Afghanistan and Siberia) have been investigated by De Torres *et al.*<sup>[45]</sup> The synthetic ultramarine blue used as reference pigment was identified in an artwork created around 1917 by the Catalan modernist painter Ramon Casas i Carbo. The comparison of this synthetic pigment with the three natural lapis lazuli was performed using a home-made rigorous methodology based on the Euclidean distance between homologue spectral segments (or intervals). Based on the results presented, it is notable that the  $2\nu_1 + \nu_2$  vibrational mode can be used to differentiate among the ultramarine pigments, except in the comparison of the Chilean-Siberian lazurites, in which the highest difference is obtained in the  $\nu_2$  and  $\nu_1-\nu_2$  vibrational modes.

## Forensic applications in art and archaeology and authenticity research

The analytical parameters influencing the variability of Raman spectra of car paint samples were studied by Lambert *et al.*<sup>[46]</sup> Through 32 experiments and 160 measurements, including chemometrics, it was found that the only factor that significantly influences the Raman spectra variability is the sample preparation. No sample preparation gives less variability than the analysis on cross sections, even in the case of clearcoat presence. Furthermore, the surface roughness of samples exhibits a higher variability than the polished samples. The recommendations presented in the work should be especially taken into account when preparing databases.

Bersani *et al.*<sup>[47]</sup> studied 14 not certified emeralds, non-destructively, by application of Raman microspectrometry. The obtained results showed eight emeralds and six fakes, identified as garnet, glass and quartz. Furthermore, two of the emeralds were defined as synthetic, hydrothermally grown. The investigation of the fluid

and solid inclusions and of the Cr<sup>3+</sup> photoluminescence revealed important information on the genesis and provenance of the natural emeralds. This can further help in the authenticity investigations. Finally, for some of the samples, it was possible to define the orientation of the gem cut, when taking into account Raman spectra in different geometries.

Schotsmans *et al.*<sup>[48]</sup> were dealing with the characterisation of white substances in burials. Fourteen white residues were analysed, all belonging to archaeological and forensic sites. It was highlighted that lime could easily be mistaken for other materials, such as gypsum, brushite or cerussite. The identified materials can give important information on the taphonomic processes of burials and their funerary context. FT-Raman spectroscopy was applied to study the conversion from calcium hydroxide to calcium carbonate, which could also be considered for dating purposes. However, several factors, such as the influence of microenvironment on the rate of conversion need to be considered, and more research is needed in order to use lime hardening as a dating method.

For a fast and reliable discrimination of sapphire from its imitations, Barone *et al.*<sup>[49]</sup> studied the applicability of a portable Raman spectrometer, which turned out to be efficient enough for that purpose. This was also confirmed by micro-Raman spectroscopy, which was successful also in the study of inclusions and enhancement treatments that gave more data also for the discrimination of natural and synthetic gems, as well as the origin of the natural ones. A doublet assembled gem, composed of glass and garnet, was also characterised, revealing that garnet consists of almandine and pyrope. The successful utilisation of the portable Raman equipment in the field of gems characterisation is highly relevant in cases of gems mounted in precious and unmovable artworks.

Raman microscopy and FTIR were used by Chaplin *et al.*<sup>[50]</sup> to study in depth a pastel painting considered to had been painted by renowned Russian artist Natalia Goncharova in c. 1913. The Raman analyses of the palette used for the pastel painting established to consist of the following nine pigments: titanium dioxide white (rutile), zinc white, barium white, carbon-based black, phthalocyanine blue and green, hematite, a monoazo yellow (PY74) and dioxazine violet (PV23). The presence of this form of the dioxazine violet pigment indicates the pastel to have been painted after 1952. Further, the use of oil as the binding medium in the pastel also indicates an execution date of post-c.1950. The original date given to the painting as c.1913 is therefore incorrect, and it seems unlikely that this painting is her work. This result highlights the need for reliable and perceptive dating procedures for valuation purposes.

## Conclusion and future prospects

The 44 works included in this special issue are excellent examples of the innovative applications of Raman spectroscopy from prehistoric samples to present-day artefacts and represent mostly the current state of the art in its application to Art and Archaeology. Some papers highlight the possibilities of field analysis, performed in a non-destructive way, to obtain critical information for further studies on these cultural heritage artefacts. Others incorporate chemical modelling and/or chemometric analysis to explain and interpret the presence of unexpected materials together with the original ones. Even some papers deal with the use of complementary non-destructive as well as microdestructive instrumental techniques to support the Raman information. However, all of them have in common Raman spectroscopy as the core of the

manuscripts included in this special issue. The contribution of the people attending the RAA2013 Congress to a collaborative research among scientists from different fields (restorers, spectroscopists, chemists, geologists, biologist, environmentalists, etc.) has been clearly shown, and we hope to increase such cooperation in the works to be presented in the forthcoming RAA2015 in Wrocław, Poland.

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**Polonca Ropret<sup>a,b\*</sup>**  
**Juan Manuel Madariaga<sup>c,d</sup>**

\* Correspondence to: Polonca Ropret, Conservation Center, Institute for the Protection of the Cultural Heritage of Slovenia, Poljanska 40, 1000 Ljubljana, Slovenia  
E-mail: polona.ropret@rescen.si

<sup>a</sup>Conservation Center, Institute for the Protection of the Cultural Heritage of Slovenia, Poljanska 40, 1000 Ljubljana, Slovenia

<sup>b</sup>Museum Conservation Institute, Smithsonian Institution, 4210 Silver Hill Rd., Suitland, MD, 20746, USA

<sup>c</sup>Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country (UPV/EHU), P.O. Box 644, 48080, Bilbao, Spain

<sup>d</sup>Chair of Territory, Landscape and Heritage, University of the Basque Country (UPV/EHU), P.O. Box 450, 01080 Vitoria-Gasteiz, Spain

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