Applications of Raman spectroscopy in art and archaeology

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

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

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

Due to the increasing need for well-defined and quickly available reference spectra, the congress was completed by a round table about the most important criteria and requirements for the building of a public database of standard Raman spectra of compounds related to cultural heritage and archaeology. The results of the open discussion have been then presented during the Infrared and Raman Users Group (IRUG) workshop in Philadelphia (USA, September 27–28, 2012) 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 database will include also the big collection of reference spectra of synthetic organic pigments presented by Fremout and Saverwyns[7] that was presented in this RAA 2011 Congress.

Advanced methods and techniques for complex mixtures

The development of new methods and data treatment of the spectral information will be a field of continuous research in the field of Cultural Heritage where real samples are always complex mixtures of original and degradations compounds that require new approach to be implemented in the daily practice of Raman spectroscopy. Some examples of these new developments have been selected for this special issue, including a new concept of detection limits for compound identification, a SERS method for dyestuffs analysis, the potential use of Fourier transform (FT)-Raman for quantitative analysis and the theoretical simulation of vibrational spectra to help in the assignment of Raman signals for unknown compounds.

The definition of Raman spectroscopic detection limits is not straightforward, especially in art analysis where the investigation of solid particles, often dispersed in a solid matrix of complex nature, is involved. Vandenabeele and Moens[8] discuss some ideas on the description of relative Raman band intensities and on how to include this in the definition of the limit of identification with the aim to initiate future discussions in the Raman spectrometry community about this concept and the associated concept of limit of identification of a product.

Casanova-Gonzalez et al.[9] have reported the SERS spectra of carminic acid, cochineal (Dactylopius coccus), achiote (Bixa orellana), muitle (Justicia spicigera), zacatlaxcalli (Cuscuta sp.), brazilwood (Caesalpinia echinata) and cempazuchitl (Tagetes erecta), recorded in aqueous solution and directly on dyed wool fibers, using silver colloids as SERS substrate. The acquired spectra will be used to analyse in a non-destructive way the wide variety of Mexican dyes used since early pre-Hispanic periods for coloring fibers, codex writing and mural painting cultural artifacts.

To determine the nature and the concentration of efflorescence salts, ionic chromatography (IC) is generally used although the method presents a number of drawbacks (long sample preparation times, different sample dilutions). As an alternative, Broggi et al.[10] proposed the application of FT-Raman spectroscopy to study the soluble ions constituting the most diffuse efflorescence salts in monuments and archeological sites. Calibration was set up by measuring the band integration area of each standard salt solution at the more intense and/or well-resolved band. Twelve control mixtures were tested, and the obtained results were comparable with the IC determinations performed on the same salt mixtures.

The work by Prencipe[11] shows the usefulness of theoretical ab initio calculations to establish the Raman shifts of crystalline materials. Such results are useful (1) for the correct assignment of the observed Raman signals to fundamental vibrational modes, (2) for the identification of modes too weak to be detected experimentally and (3) for the de-convolution of bands resulting from the overlap of several modes in the experimental spectra. The procedure is exemplified using jadeite ($NaAlSi_2O_6$).

The impacts from the environment

The environmental impacts on both movable and immovable items of Cultural Heritage were first considered in the past RAA 2009 Congress as a novel topic of interest. In this RAA 2011 edition, this topic has attracted the attention of a considerable number of contributors. Particulate matter, atmospheric acid gases and oxidants as well as organic compounds are the major environmental

stressors affecting to Cultural Heritage materials; they affect mainly to the outside parts of the Built Heritage and art objects exposed to the open air. The nature of the particulate matter can contribute not only to an aesthetical problem but to be the nucleus for further decaying processes in the surfaces of some materials. The aerosols containing CO_2 play an important role in the oxidation of metals (the initial acidity required to start most of the reactions of decaying is supplemented by this greenhouse acid gas). Moreover, infiltration waters carrying soluble ions are another source of important problems in building materials. Most of these effects are contained in the next nine contributions summarized below.

As part of an air quality investigation, Potgieter-Vermaak et al.[12] collected size-segregated atmospheric particulate matter, in a room of the Alhambra Palace (Granada, Spain) at 100 km from the sea, during two sampling campaigns (summer and winter). Single-particle analyses were performed using micro-Raman spectroscopy (MRS) and electron probe X-ray microanalysis (EPXMA) to determine its potential degradation profile. The presence of various mixed salts of acidic and/or hygroscopic nature, such as sodium and ammonium nitrates and sulfates, especially in the finer fraction (to be as high as 50%), was noticeable. Apart from the potential chemical attack, the soiling due to carbonaceous matter deposition is a real concern; soot was identified by MRS and EPXMA in all size fractions, reaching values of up to 55%, and was often intertwined with soluble inorganic salts.

The evolution of green chloride and green nitrate patinas, produced artificially on brown patinated bronze, has been studied by Ropret and Kosec[13] using scanning electron microscopy (SEM), Raman spectroscopy and X-ray diffraction. Cuprite and cuprous sulfite were found on the brown patina, atacamite on the green chloride patina, and a mixture of gerhardite and rouaite on the blue to green nitrate type patina. Then, the green patinas were treated in a climatic chamber for 12 weeks in a controlled SO_2 atmosphere, observing clinoatacamite and paratacamite as the end corrosion products, after an intermediate brochantite stage on the green chloride and green nitrate type patinas. These accelerated experiments demonstrate the complex corrosion process of copper-based materials.

In a second work of the same research group, Kosec et al.[14] studied different types of bronze, brown patina and two green type patinas (green chloride and green nitrate patina) exposed to simulated urban acid rain, with the aim to monitor the transformation process of chemically formed patinas and of the bronze itself. The patinated samples were immersed in urban acid rain, which contained carbonates, nitrates and sulfates, for 35 days to study the morphological change of the patinated products. The structures of the patina and corrosion products were characterized by scanning electron microscopy and energy dispersive X-ray Spectrometry (SEM/EDX) and Raman spectroscopy. On the brown patina, brochantite and langite formed, together with cuprous oxide. Three corrosion products were confirmed on the green chloride patina, that is, cuprous oxide, brochantite/langite and atacamite. On the green nitrate patina cuprite, langite/brochantite and gerhardite/rouaite were identified.

To complement both works, Ospitali et al.[15] characterized Sn-based corrosion products using the hyphenated system SEM–energy dispersive spectrometry (EDS)–Raman structural and chemical analyser. Different Sn-containing compounds, mainly crystalline and nanosized tin dioxides, were detected in bronze patinas exposed to different environments like to the atmosphere (natural and accelerated ageing conditions)

and to the soil. These results showed that Sn(IV) oxide species in patinas have to be systematically taken into account in order to understand bronze corrosion mechanisms, even if they are poorly crystallized and difficult to identify. Moreover, this demonstrates that bronze corrosion can be fundamentally described as a decuprification phenomenon.

To ascertain the controversial origin of the calcium oxalate films, the settlement of their mineralogical composition and stratigraphy was investigated by Conti et al.[16] using micro-Raman mapping on cross section of samples taken from different facades of the Trento Cathedral, assisted with other techniques like optical microscopy and SEM/EDX. It was possible to directly define thickness, composition and stratigraphy of calcium oxalate films, identifying the newly formed crystalline phases and their distribution inside the stone. This allowed to correlate the films with the decay of the stone. In spite of the literature data, calcium oxalate phases are not always arranged in a recurrent stratigraphy, their distribution is very inhomogeneous within a few microns and any specific rule was observed for the presence of weddellite and whewellite in the oxalate films. Moreover, the presence of weddellite in the most external portion of the films was sometimes detected, and the reason for such occurrence in some external parts of the films still remains unknown.

Innovative treatments which aim at modifying existing corrosion products into more stable and less soluble compounds while maintaining the surface's appearance are needed. Biological treatments based on such criteria are being developed for the preservation of metal artefacts. The work by Joseph et al.[17] presents the capacity of Beauveria bassiana to precipitate copper oxalates to stabilize soluble patinas (copper hydroxysulfates) or the transform active corrosion products (copper hydroxychlorides) in copper-based artifacts. Copper oxalates produce green compact patinas showing a high degree of insolubility and chemical stability even in very acidic atmospheres (pH < 3). In their work, cultures of B. bassiana were applied on copper-based coupons naturally aged in urban or marine environment. The results of Raman mapping, on cross-sectioned samples, clearly showed that the original patina was gradually transformed into copper oxalates and that the conversion is completed on the surface areas where B. bassiana grew. Raman mapping demonstrated here to be a valuable tool for precisely and non-destructively localizing corrosion products as well as for evaluating protective treatments on metal artefacts.

The last work on copper patinas was presented by Bongiorno et al.,[18] but in this case, the so-called 'artistic patina', an intentionally produced patina by the artist on copper based alloys, was investigated by MRS and SEM/EDX. Several types of patinas were experimentally produced in the laboratory using the torch technique and reactive solutions based on water as a solvent containing, respectively, copper nitrate, iron nitrate and potassium sulfide ('liver of sulfur'). Blue-green patinas showed the presence of copper oxides (Cuprite and Tenorite), probably due to the oxidizing treatment made with torch, and the presence of a copper nitrate (Rouaite) due to the compositional characteristics of the reactive solutions. Reddish-brown patina showed the presence of iron oxides and hydroxides (Magnetite, Limonite, Goethite) together with copper oxides (Cuprite). All the produced patinas were then aged in a salt spray chamber and studied with microscopic techniques, showing the formation of new highly soluble compounds (copper chlorides, such as Botallackite, Atacamite and Paratacamite, and copper sulfate, such as Posnjakite) that they do not protect the metallic substrate but delay its corrosion acting as a 'sacrificial layer'.

Admixtures have been used since the Roman civilization with the purpose of increasing mortar properties (hardening, strength, etc.). In ancient civilizations, natural admixtures such as eggs, urine, blood, etc., were used, while in current civilizations, synthetic complex compounds are employed. Properties of concretes are governed by its flow ability, which is related to the dispersion of the cement particles. Better fluidity is achieved by the addition of a type of cement admixtures named superplasticizers. The first structural Raman characterization of a superplasticizer, in the complex matrix of a commercial product, is presented by Cañamares et al.[19] A third generation (polycarboxylate-based) superplasticizer was studied at various experimental conditions, and two different structures were determined by comparison of the experimental Raman spectra (FT-Raman at excitation of 1064 nm) with the theoretical ones using the DFT calculations.

To characterize possible pathologies on cementitious materials from a historical 19th century lighthouse exposed to the open air, in Igueldo (San Sebastian, Spain), Morillas et al.[20] used Raman spectroscopy assisted with other analytical techniques. The spectroscopic observations were compared with quantitative concentration values of dissolved cations and anions, extracted with mili-Q water as soluble salts and treated by chemometric tools. The integrated analytical techniques were used to diagnose the influence of (1) marine aerosol as source of Cl^-, F^-, Mg^{2+}, Na^+ and K^+, (2) seagull droppings as source of NH_4^+ and NO_3^- and (3) original addition of sulphates to the cementitious materials, on the formation of decaying products such as chlorides, sulphates, nitrates, etc. The in-situ formed decaying compounds penetrate the pores when enough water is outside, promoting the formation of efflorescence crusts that are washed by the rain, in a cyclic pathway that affect the integrity of the lighthouse outdoor area (roof and walls), leading to the formation of cracks where the water containing soluble ions goes to the inner parts of the building.

Archaeological materials and findings

The application of Raman spectroscopy to the analytical characterization of archaeological materials is now well established although the common occurrence of fluorescence emission backgrounds, which arise from specimen degradation, absorption of impurities from the depositional environment or percolation of materials from the upper parts to the archaeological site is a problem for the analysis of some sample. That is why new improvements and experiences are required to solve such problems and to continue the research in this particular field. Four contributions are presented now, each covering a different type of material.

The first in-situ micro-Raman spectroscopic study of prehistoric drawings found in the cave of Rouffignac-Saint-Cernin (Dordogne, France) was carried out by Lahlil et al.[21] Rouffignac cave art, assigned to the upper Magdalenian Paleolithic period (13 500–12 000 BP), is constituted of more than 250 drawings and engraving including 158 mammoths. There are about a hundred drawings, all made of black pigments. Until now, destructive chemical analyses performed on one sample, as well as recent micro X-ray fluorescence in-situ analyses have shown that the drawings contain manganese oxides. This new study of the Rouffignac cave using a portable Raman instrument (in-situ XRF and X-ray diffraction were also performed to compare results) confirmed that the black manganese oxides romanechite and pyrolusite were used as pigments by prehistorical artists. Carbon and carotenoids have been found locally. Differences between the various figures are

highlighted, and hypotheses about the drawings production are proposed.

Significant paintings from the Tito Bustillo (Ribadesella, Asturias) and El Buxu (Cardes, Asturias) caves, renowned archaeological sites of the Cantabrian Palaeolithic cave art, were studied by MRS. Auxiliary techniques like infrared spectroscopy, X-ray diffraction, X-ray photoelectron spectroscopy and SEM–EDX were also used by Hernanz et al.[22] Hematite (α-Fe_2O_3) of three granular sizes (<1, <10 and $<30\mu m$) is the main red component of these paintings. Wüstite, amorphous carbon and Mn are additional components of some pigments. Hydroxyapatite was also detected in one pictograph. Calcite, α-quartz and clay minerals were used as filler materials. Particles of anatase are present in some cases, but any organic binder was detected. Considering the main components, granular size, contents of hematite disordered structures and secondary phases with Ni and Mn, it is concluded that none of the pigments extracted from the Tito Bustillo and El Buxu caves were prepared from the ochre quarry of the Tito Bustillo cave.

A representative set of eight lithic tools, suitably selected among the very rich Palaeolithic industry collected over the past years in different archaeological sites of the Guadalteba County (Málaga, Spain), has been non-destructively investigated by means of Raman spectroscopy, using both portable and benchtop Raman spectrometers, by Hernandez et al.[23] α-quartz was confirmed as the raw material in all the cases, although a small amount of moganite was also evidenced as a distinctive fingerprint in these chert samples. Crusts were mainly made of calcite in all the cases, sometimes accompanied by other minerals such as barite or anatase. This first Raman spectroscopic study on chert and sandstone artefacts from the Guadalteba suggests a further and more thorough archaeometric investigation of these lithic tools based on sets of Raman measurements (Raman mapping) on each specimen rather than on single-point Raman experiments such as in the present case, given the wide macroscopic heterogeneity of this kind of samples (color, grain size, transparency, etc.).

Finally the work of Edwards et al.[24] on the Raman spectroscopic analysis of biomaterial found in the cranial cavity of a decapitated skull dating from the Iron Age, some 2500 years ago, must be highlighted. The survival of brain tissue showed the presence of degraded protein, consistent with it. The novel observation of characteristic Raman spectroscopic signatures of biochemicals produced by cyanobacteria, namely carotenoids and scytonemin, both in the brain tissue and in the surrounding deposits from the cranium, is consistent with the waterlogged depositional environment in which the human skeletal remains were found. The Raman spectral data were in support of biochemical, morphological and radiographic analyses of this biomaterial, which therefore can be described as brain that has been significantly reduced in volume inside the cranial cavity.

Paintings: pigments, dyes and binders

The study of the antique paintings is one of the most evident examples of the interaction between scientific analysts, art historians and archaeologists, required not only to understand the problem but also to make optimum use of the harvested data. Zoppi et al.[25] studied several fragments of wall paintings of Phaistos (Crete); the results gave new indications about the painting technique and could be related to the cultural exchanges in the Mediterranean area, between the Cretan and Aegean Bronze Age.

Even the most antique and well-known pigments, such as hematite and carbon, still require deep studies to understand their sources, preparation methods and their uses in historical and pre-historical times. Tomasini et al.[26] suggest a characterization by means of Raman spectra of different pigments based on carbon to distinguish between the various kind of carbonaceous materials used in pictorial and archaeological samples.

The analysis of the materials used in ancient artworks must not be limited to the substances intentionally used by the artists, because preservation along the time depends also on the surrounding materials, on the environmental agents and on the man-made alterations they suffer. Thus, the alteration products and the deterioration agents should be identified and studied to fulfill with the complete characterization of all materials present. This cannot be afforded with the use of a single technique and usually a multi-technique approach is required. Irazola et al.[27] showed how the combination of portable instrumentation (Raman, energy-dispersive X-ray fluorescence – EDXRF-, infrared diffuse reflectance – DRIFT-spectrometry) and laboratory instruments, like Raman imaging and SEM–EDS can be fruitfully used to assess the conservation state of 16th century wall paintings located in two churches of the Biscay County (north of Spain), where decaying products such as nitrates and oxalates, derived from physicochemical processes on the raw materials, were detected.

The coupling between micro-Raman and chromatographic techniques is another powerful multi-analytical approach to obtain a contemporary identification of organic and inorganic pigments as well as of binders, leading even to the identification of the artist technique. Minceva-Sukarova et al.[28] used MRS, pyrolysis gas chromatography–mass spectrometry (Py/GC/MS) and GC/MS for the characterization of pigments and binders used in the wall paintings ascribed to the works of the prominent 19th century Macedonian iconographer, Dicho Zograph. The use of a huge palette of pigments was confirmed, including both traditional pigments, used from antiquity, and synthetic pigments, dating back from XIX–XX centuries.

Raman spectroscopy was often used to identify traces of recent restorations, when any documentation on the history of the artifact can be obtained. This is the case reported by Cazzanelli et al.,[29] where many recent restoration compounds were found in the painting 'Rebecca at the well', of a Neapolitan anonymous preserved in the MAON museum of Rende (Cosenza, Italy), were identified. Pessanha et al.[30] reported on the study of a pair of Japanese folding screens belonging to the early 17th century present in the Museu Nacional Soares dos Reis (Oporto); the use of different wavelengths as Raman excitation, together with elemental analysis (XRF), allowed a complete characterization of the materials present on the surface of the folding screens, giving precious information on a restoration work conducted 'in the western countries', not recorded in historical sources.

As in many other fields of the knowledge, most of the recent developments of the Raman analysis are related to the use of the increasing power of the computers in the interpretation of the data. The study of modern dyes is often complex due to the presence of a large number of Raman bands, typical of the used organic molecules. When mixtures are present, the identification of the minor phases is very difficult, because the bands of the different dyes lie often in the same regions. González-Vidal et al.[31] proposed a methodology for the automatic identification of the components of pigments mixtures starting from the Raman spectra.

Raman spectroscopy has the invaluable ability to investigate, in completely non-contact and non- destructive way, precious art objects. If the artifacts are small enough to be placed under the microscope objective, high-resolution laboratory micro-Raman apparatus could be used to obtained well-defined data in a safe way. Burgio et al.[32] made an extensive comparison between portrait miniatures realized between 16th and 17th centuries by well-known miniaturists and preserved in the Victoria and Albert Museum in London. This wide and detailed campaign of measurements allowed to define the evolution of the artists palettes, giving a possible paternity for some miniatures of uncertain attribution.

Another example of use of micro-Raman laboratory equipment without sampling is shown by Aceto et al.,[33] reporting the results of a campaign of measurement carried on a series of early printed decorated books. Due to the large number of studied decorations, it was not possible to analyse all the different shades and colors of all the pages. The combined use of fiber optic reflectance spectroscopy with micro-Raman and XRF was very effective to quickly identify in situ the colors, leading to the complete characterization of the palette used in all the analysed books.

In the study of books and manuscripts, Raman spectroscopy is able to identify also inks, in addition to pigments and dyes. Nastova et al.[34] studied illuminated medieval old-Slavonic manuscripts, and they found iron-gall inks, sometimes mixed with carbon inks. The comparison of the pigments and inks identified in these two analysed Slavonic manuscript showed a good correspondence to the ones used in Western Europe in the same period, except for green colors, obtained with indigo and yellow ochre instead of indigo and orpiment, and for the underlayer to the green pigment (yellow ochre instead of lead white or lead tin yellow).

Due to the diffuse use of very brilliant, heavy metal-based pigments, illuminated manuscripts and mural paintings are often subjected to particular degradation processes. During the study of a Medieval Cistercian 12th century manuscript, Muralha et al.[35] found the transformation of white lead carbonate into black lead sulfide galena. Blackening phenomena of metal-based pigments are often present in polluted environments, as revealed by Maguregui et al.[36] during a measurement campaign performed in Pompeii by using portable Raman and XRF instrumentation; red cinnabar (HgS) was found to degrade in metallic Hg and in different Hg compounds; also hematite (α-Fe$_2$O$_3$), claimed to be a stable pigment in most of the artists materials treatises, was found to be reduced partially into magnetite (Fe$_3$O$_4$) under the action of SO$_2$ acid gas. However, blackening and chromatic alterations could happen even in non-polluted environments, as reported by Aceto et al.[37] in the analysis of painted meridians and religious wall paintings present in the mountain hamlet of Ala di Stura, at 1080 m a.s.l. in the Lanzo Valleys (Italy); in this case, unstable lead red and white pigments were transformed in black lead sulfide and lead oxide (plattnerite), while the blue copper carbonate azurite was transformed in a green hydroxychloride.

Paintings from the XIX-XX century have been performed using, in addition to the traditional natural inorganic pigments, new synthetic organic and inorganic materials. Up to now, the majority of the published Raman studies are devoted to materials used in ancient artworks, but the most recent materials still need an adequate characterization. Casadio et al.[38] studied by Raman spectroscopy a family of cobalt-based synthetic pigments; the comparison of the spectra obtained on the reference materials with the ones obtained on modern paintings allowed the identification of cobalt titanate green in Jasper Johns palette and of cobalt violet light and cobalt violet dark among the pigments used by

Pablo Picasso. Defeyt et al.[39] used various techniques to identify the different crystalline phases of the largely diffuse blue dye copper phtalocyanine, in order to have a tool for a fine dating of modern paintings; Raman spectroscopy resulted the most efficient technique for the detection of this dye in artists' paints, but the combination with XRD and IR spectroscopy is suggested to obtain a precise identification of its crystalline structure.

Contemporary art is often made by 'poor materials', with complex and largely variable composition, as in the case of pen drawings. Sodo et al.[40] reported, for the first time, Raman spectra of 'original' and 'laboratory' drawings made by marker pens. The 'original' ones are part of a collection of more than 500 original drawings of the famous movie director Federico Fellini.

Ceramics, glasses and gemstones

Ceramics are very complex objects to study. The ceramic body could be considered as a man-made metamorphic rock, containing residuals of the raw materials (clays and other minerals), crystalline and amorphous neo-formation phases, fluxing agents such as feldspars, re-used fragments of older ceramics (chamotte) and other inclusions. In addition, many different types of pigments were used for decorations, and external coatings (glaze, engobe) are often present. Such complex artifacts require a multi-technique approach to perform the adequate characterization of original and altered compounds. Up to six works are now discussed, highlighting different aspects of such complex ceramic and glass samples.

Sanchez Vizcaino et al.[41] made a combined use of micro-Raman and energy dispersive X-ray microfluorescence (μEDXRF) to analyse ceramic and glass vessel fragments found in the Iberian cemetery of Tutugi (4th–3rd century BC, Galera, Granada, Spain), paying a particular attention on the nature of pigments. The high Raman signal usually obtained from heavy minerals and the ability of Raman spectroscopy to discriminate between phases with very similar composition, even within the same family (i.e. feldspars), made this technique very effective in the study of the tempers of ancient light-clay products.

Fintor and Gyalai[42] were able to discriminate, through micro-Raman analysis of the temper grains, Terra Sigillata samples coming from different regions of North-Eastern Hungary. In particular, they found that temper grains of samples from Pfaffenhofen and Westerndorf contain more calcic minerals, including plagioclases and heavy minerals (augite, diopside, actinolite, apatite and titanite) while the ones from Rheinzabern contain mostly potassium feldspars and only anatase and rutile as heavy minerals.

In case of large objects, too precious to be moved from the museums, it is possible to use mobile equipments. Ferrer et al.[43] used an optical fiber Raman system to investigate the composition of yellow and orange colors of XVI and XVII centuries ceramics into the 'Museo de Cerámica de Barcelona' (Spain). That work showed how Raman spectroscopy is very effective in the detection of ceramic pigments based on lead, tin and antimony, allowing to discriminate among the complex family of ternary and quaternary yellow compounds used in Renaissance and Baroque polychrome ceramics.

Zuluaga et al.[44] used a combination of micro-Raman, XRD and SEM–EDX to differentiate between alkaline glazed and lead glazed potteries, in the analysis of late medieval Christian and Muslin pottery from Northern Spain. The glazes were discriminated by Raman spectroscopy through the analysis of the Si–O bending and stretching bands, in terms of the different SiO_4 tetrahedra Q^n units. The glass structure and the variation of degree of polymerization as a function of potassium content were studied by De Ferri et al.[45] in medieval-like glass samples and compared with ancient K-based glasses; the Raman study of the aging process of the glass samples allowed to reveal the neo-formation of crystalline phases together with the structural changes of the glass. Di Martino et al.[46] focused their attention on rare inclusions in ancient glass mosaic tesserae belonging to Daphni Monastery (Greece, XI century); the presence of metallic silicon crystals embedded in the glass matrix supports the hypothesis of local glass making in contrast with raw materials supplied only from Middle East or Egypt.

Raman spectroscopy is widely used in gemology field, and three works are included in this special issue. Giarola et al.[47] showed some examples about the ability of this technique to gather information on the nature and genesis of the gemstones by analyzing the inclusions through a confocal Raman microscope; they also showed how it is easy to unmask sophisticated fakes or imitations such as a 'doublet', the classical assembled gemstones.

The use of some additional optics, such as L-shaped lens, allows us to study gems mounted on artifacts or archaeological objects, as it was shown by Karampelas et al.[48]; they studied the gems adorning two chalices from the Benedictine Abbey of Einsiedeln (Switzerland) in a completely non-invasive way. The use of three different laser sources made possible the identification of all the gemstones, even in case of strong fluorescence.

Even organic gemological materials can be studied by means of Raman spectroscopy. Łydżba-Kopczyńska et al.[49] analysed over 100 objects of unique amber jewelry, dated back to early Iron Age, discovered in Domaslaw in Lower Silesia (Poland). The comparison with reference materials from previously selected amber deposits confirmed the Baltic origin for the archeological jewelry.

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 artifacts, representing the current state of the art in the application of this vibrational technique in Art and Archaeology. Some of them make use of other non-destructive or micro-destructive instrumental techniques to support the Raman information. Others highlight the possibilities of field analysis, performed in a non-destructive way, to obtain critical information for further studies on these Cultural Heritage artifacts. Others incorporate chemical modelling and/or chemometric analysis to explain and interpret the presence of unexpected materials together with the original ones. However, all of them have in common the Raman information as the core of the works.

The high quality and the amount of spectroscopic information from Raman and other techniques allow us to have a better knowledge of the Art and Archaeological items we need to analyse. However, to obtain the whole picture on the analysed artifacts, we need to exchange our knowledge with other scientists (spectroscopists, chemists, geologists, biologist, environmentalists, etc.) and professionals in the side of Humanities (historians, restorers, archaeologists, etc.) in an interdisciplinary approach. The contribution of the people attending the RAA2011 Congress to a research conducted in that collaborative way has been clearly shown, and we hope to increase such cooperation in the works to be presented in the forthcoming RAA2013 in Ljubljana, Slovenia.

Acknowledgements

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