Chapter 10
Raman Analysis of Inorganic and Organic Pigments

Anastasia Rousaki and Peter Vandenabeele

Abstract Raman spectroscopy is one of the most favorable techniques applied in the art analysis field. Its unique characteristics, namely the organic and inorganic components identification, spatial resolution down to micrometers scale, control of the laser power and measuring conditions and fast identification are just some of the remarkable features of the technique. Moreover, Raman spectroscopy can be applied directly on the artefact and on the field, with mobile systems, without jeopardizing the integrity of the work of art. Other Raman approaches can be considered namely, microspatially offset Raman spectroscopy (micro-SORS) and surface-enhanced Raman spectroscopy (SERS) when it comes to the direct non-destructive stratigraphic analysis of art works and the characterization of organic compounds such as dyes.

Keywords Benchtop Raman spectroscopy · Mobile Raman spectroscopy · Microspatially offset Raman spectroscopy · Surface enhanced Raman spectroscopy · Resonance Raman spectroscopy

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10.1 Introduction

Over the years, Raman spectroscopy has grown to become a frequently applied technique that is available to conservation scientists. The approach has many advantages, such as allowing a relatively quick identification of the artists' pigments while being non-destructive. By focussing a low power laser beam on a sample or even directly on the artwork, it is possible to record a molecular spectrum of the pigments, accounting for their identification.

Almost a century ago, in 1923, based on theoretical considerations, the German scientist Adolf Smekal predicted the inelastic scattering of light interacting with molecules. It lasted until 1928, till the Raman effect was for the first time observed by the Indian physicist Chandrasekhara Venkata Raman and his student Kariamanikkam Srinivasa Krishnan. In 1930, Sir Raman was awarded the Nobel prize of physics for this discovery that was named after him. In the initial days of Raman spectroscopy, Raman spectra were recorded using filtered sunlight and required a large (room-size) spectrometer to record spectra of large volumes (ca. 600 ml) of pure liquids (Gardiner and Graves 1989; Vandenabeele 2013). Soon, the introduction of mercury arch lamps accounted for a more stable light source and allowed to record spectra of smaller volumes of liquids. Often, mercury lamps were spiral-shaped and the sample was positioned in the center of the lamp, allowing to record spectra in a 90°-geometry. Photographic plates were used as detectors. However, setting-up and aligning the spectrometer was a complex and time-consuming task, which hampered the broad application of Raman spectroscopy outside specialised laboratories. Often, scientists preferred the use of infrared spectroscopy as a way to identify molecules, in a more routine way.

As Raman spectroscopy requires the use of a monochromatic light source, the introduction of lasers – which are intense and monochromatic – to excite the molecules, the time required to record a Raman spectrum was drastically reduced. Moreover, steadily the introduction of optical components improved the sensitivity of the instrumentation. This included, amongst others the introduction of charge-coupled-device (CCD) detectors, that are sensitive in the visual region of the electromagnetic spectrum. Until recently, as no sensitive detectors were available in this spectral region, spectrometers using infrared excitation (1064 nm) relied on the Fourier-transform technology to record high-quality spectra. Also, the introduction of high-quality notch filters allowed that for many applications the large double-monochromator spectrometers could be replaced by more compact instruments. Another milestone in the development of Raman spectroscopy was the coupling of Raman spectrometers with microscope optics, allowing to record Raman spectra of small solid particles, while the introduction of fibre-optics probes accounted for a flexible set-up. Since the first decade of current century, smaller and mobile spectrometers were introduced, allowing the technique to move away from a strictly controlled laboratory environment, introducing the possibilities to perform *in situ* measurements.

Along with these technological evolutions, new possibilities of implementing Raman spectroscopy for the investigation of art objects, became increasingly more available. It was soon after the introduction of confocal Raman microscopy by

M. Delhaye and P. Dhamelincourt (1975) that they realised that this approach could be of great advantage for the analysis of micrometer-sized particles, like minute pigment grains. Moreover, the technique was also applied for the direct Raman analysis of small-sized mediaeval manuscripts (Best et al. 1992; Clark 1995a, b). Laboratories created their reference databases with Raman spectra of artists' materials (Table 10.1).

As the field of applications broadened, different methods of data processing were developed, including chemometrical approaches. As an example, when studying

Table 10.1 Overview of some published collections of reference spectra of artists' materials

Collection	Description	References
UCL- Raman Spectroscopic Library of Natural and Synthetic Pigments	Collection with downloadable Raman spectra of mostly inorganic pigments. Many spectra were recorded with an Ar⁺ laser, others with a HeNe laser. In a second paper, the database was extended with other laser wavelengths (http://www.chem.ucl.ac.uk/resources/raman/)	Bell et al. 1997; Burgio and Clark 2001
e-VISART database	Password protected database	Castro et al. 2005
ColoRaman	Raman and fluorescence spectroscopy of oil, tempera and fresco paint pigments	Burrafato et al. 2004
Medieval pigments	Collection of spectra of mediaeval pigments	Marucci et al. 2018
Natural organic binding media and varnishes	Collection and discussion of Raman spectra of artists' oils, polysaccharides, proteins and resins, recorded with 785 nm	Vandenabeele et al. 2000b; Daher et al. 2010
Archaeological resins	Collection of spectra of archaeological resins recorded with FT-Raman spectroscopy (1064 nm).	Edwards and Ali 2011
Mexican Copal resins	Local Mexican copal resins	Vandenabeele et al. 2003
RRUFF database	Extensive collection of spectra of minerals	Lafuente et al. 2016
Biological molecules	Raman spectral database of biomolecules	De Gelder et al. 2007
Natural silicate glasses	Collection of spectra of natural silicates	Giordano et al. 2019
Green minerals	Raman spectra of green mineral pigments	Coccato et al. 2016; Gilbert et al. 2003
Black pigments	Raman spectra and discussion of black pigments	Coccato et al. 2015
Synthetic Organic pigments	Collection of downloadable Raman spectra of synthetic organic pigments. https://soprano.kikirpa.be	Fremout et al. 2012
Azo-pigments	Spectra and discussion on azo-pigments	Vandenabeele et al. 2000a
Synthetic Organic pigments	Collection of synthetic organic pigments	Scherrer et al. 2009; Schulte et al. 2008
Cupper-phthalocyanine	Spectra and discussion on the discrimination between different forms of copper phthalocyanine pigment.	Defeyt et al. 2012

Raman spectra of glassy materials, it is possible to do a Raman band deconvolution and based on the polymerisation index, information on the glass composition and the production temperature can be obtained (Colomban 2003a; Colomban et al. 2006). On the other hand, the evolution towards the introduction of smaller instruments and the use of flexible probeheads counted for the development of the first mobile Raman instrument (Vandenabeele et al. 2004), dedicated to the analysis of artefacts. This allowed for the first on-site investigations, where direct analysis of the artworks could be performed, including the analysis of wall-paintings (Maguregui et al. 2012; Vandenabeele et al. 2005a, b; Vandenabeele et al. 2009) and the direct analysis of objects in a museum environment (Vandenabeele et al. 2007a, b; Vandenabeele et al. 2008).

In this chapter, we will first shortly discuss some theoretical aspects of the Raman effect, including some information on cases where the technique can be successfully applied, as well as some possible interferences. To obtain interesting results with Raman spectroscopy, it is of the utmost importance to select an appropriate approach. On the one hand, one can use benchtop instrumentation to perform molecular analysis with a spatial resolution down to ca. 1 μm, while on the other hand, when using mobile Raman instrumentation, the spot size is typically larger. Furthermore, microspatially offset Raman spectroscopy (micro-SORS) is described as an innovative technique towards the direct stratigraphic analysis, without sample requirements. Finally, when the focus is on the analysis of organic dyes, surface-enhanced Raman Spectroscopy (SERS) approaches can be implemented.

10.2   Theory of the Raman Effect

To understand the working principles of Raman spectroscopy, one should think about scattering; one of the most basic interactions of electromagnetic radiation with molecules. In other words, the Raman effect elegantly describes the inelastic scattering of the incident radiation from molecules (Lombardi 2007; Vandenabeele 2013). On the other hand, the elastic scattering of light is referred to as Rayleigh scattering (Vandenabeele 2013). The difference between the elastic and inelastic scattering is whether or not the vibrational energy of the system is changed or not. In the following paragraphs, only the basic scientific terminology will be given accompanied with the description of the phenomena relevant to Raman spectroscopy. Detailed information regarding the physical and chemical background of Raman spectroscopy can be found in dedicated literature (Cialla-May et al. n.d.; Ferraro and Nakamoto 2003; Lombardi 2007; Long 2002; McCreery 2000; Smith and Dent 2004; Tobias 1967; Vandenabeele 2013).

In order to understand the difference between elastic and inelastic scattering we need to imagine the interactions of photons with molecules. If the incident and the scattered photon have the same energy, Rayleigh scattering (*i.e.* elastic scattering) occurs (energy difference between incident and emitted photon equals 0) (Ferraro and Nakamoto 2003; McCreery 2000; Smith and Dent 2004; Tobias 1967;

Vandenabeele 2013). However, in some cases the incident photon collides with a molecule and the scattered one increases or decreases its energy, as the molecule transfers some of its vibrational energy from or to the photons. If the scattered photon increases its energy, anti-Stokes Raman scattering occurs and if the energy decreases the Stokes Raman scattering takes place. The intensity of the Raman scattering, plotted against the difference in energy, defined in wavenumbers (cm^{-1}), gives the Raman spectrum of the molecule (Vandenabeele 2013). Raman scattering is a weak phenomenon compared to Rayleigh scattering and thus the latter is supressed by appropriate filtering, not to overwhelm the entire spectrum (Vandenabeele 2013). A Raman spectrum is symmetrical: on the one hand some photons gain energy, while on the other hand some loose energy. As the loosing of energy is more abundant, the latter form, which is called Stokes Raman spectroscopy, is most frequently used in cultural heritage research. In Fig. 10.1, the most fundamental radiation-molecule interactions relevant to this chapter are described.

Raman scattering is occurring between vibrational/rotational states and so-called virtual states. The virtual state is not a solution of the time independent Schrödinger's equation and thus it is an 'imaginary' state The Raman Effect: A Unified Treatment of the Theory (Long 2002). As a consequence, the Raman shift is independent of the wavelength of the incident radiation. However, what is changing, is fluorescence emission (Fig. 10.1). With sufficient energy, a molecule can transit from the ground to the excited energy state, relax and return to the ground state.

With the appropriate laser and thus the appropriate energy, the molecule can be forced to be excited to an electronic state, instead of to a virtual one (Vandenabeele 2013). This transition enhances considerably the Raman signal, a process that is called resonance enhancement. If the energy of the laser is sufficiently low (i.e. at longer wavelengths), the molecules cannot be excited to the electronic state, hence
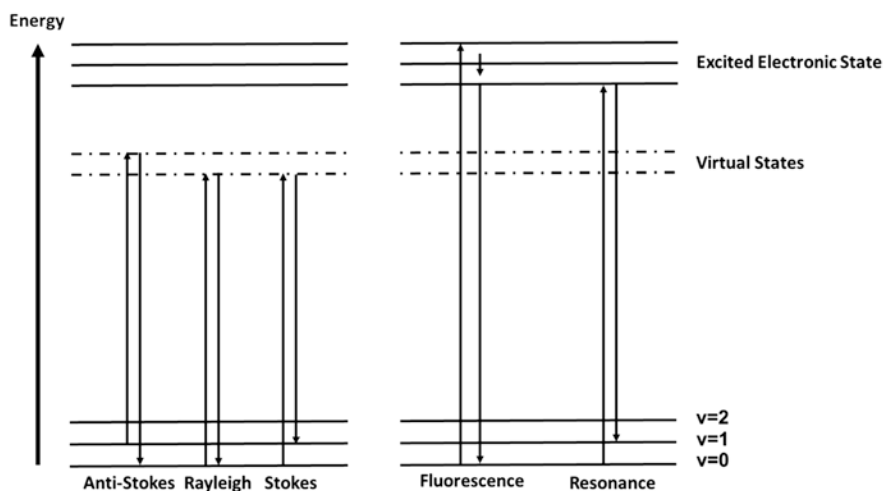

Fig. 10.1 Ideal energy diagram visualizing some of the fundamental radiation-molecule interactions

no fluorescence is observed. On the other hand, with lasers with a higher energy, it is more likely to achieve resonance Raman spectra of pigments used in cultural heritage objects (Clark and Franks 1975; Colomban 2003b). This technique is widely known as Resonance Raman spectrsocopy (RRS).

10.3 Laboratory Raman Spectroscopy

Benchtop Raman systems are stable spectrometers used for laboratory applications. These instruments are used extensively in archaeometrical research as they can provide fast analysis and reliable data. Nowadays, multi-laser systems are commercially available: these spectrometers are coupled with multiple laser sources covering the ultraviolet (UV) to the near-infrared (near-IR) region of the electromagnetic spectrum. In the Raman analysis of art objects, the most useful excitation wavelengths are situated from the visible to the near-IR region.

Laboratory Raman systems are securing wavenumber stability, a feature that is essential for the correct identification of the unknown (attributing the accurate wavenumber vibration to the correct substance). In many benchtop instruments, focusing of the laser beam is performed via a coupled Raman microscope, that allows to analyse directly the surface of the sample and/or artefact. Different objective lenses are attached on the microscope turret, changing the working distance (the larger the magnification the smaller the working distance) and the spatial resolution (depended on the objective lens and the laser wavelength). Indeed, micro-Raman spectroscopy instruments can achieve really small spatial resolutions comparable to the size of the pigments' granules (micrometre scale). Moreover, high-quality laboratory instruments are typically able to achieve high spectral resolutions, which can make it possible to discriminate between molecular vibrations that result in Raman signals that are just few wavenumbers (or less) apart.

A true confocal Raman microscope can achieve high lateral (XY) and depth (Z) resolutions by incorporating a confocal pinhole at the laser illumination path to detect only the signal from the focal plane. Any other Raman signal that originates from material that is above or below the focal plane, is removed.

The aforementioned advantageous features of benchtop Raman spectrometers are ideally coupled to the fact that the selection of excitation wavelength, laser power on the sample, measuring conditions (usually referring to the number of accumulations and measuring time) and the size of the confocal pinhole is controlled and selected upon the needs of the analysis. Thus, the user can select all possible settings and take full advantage to measure the scattering properties of the material under study, investigate resonance effects, avoid thermally induced degradation due to elevated laser power and/or measuring time etc.

A variation of solids, liquids and gasses can be characterized with micro-Raman spectroscopy. For art analysis research, both inorganic and organic materials found in works of art are successfully identified. The minimal amount of sample can be placed under the Raman microscope and can be measured without any sample preparation, while small artefacts can be positioned directly on the microscope stage. Due to the

high spatial resolution of the Raman technique, q-tip sampling (Vandenabeele et al. 1999) can be an alternative approach to the scrapping or razor sampling. For this, q-tips (cotton tipped swabs) are gently swabbed on the coloured surface. Removing just few pigment grains (theoretically a single grain is sufficient) allow to perform a micro-Raman analysis. When stratigraphic analysis is requested, cross sections are required. In order to direct the sections, these are embedded in resins and after curing and appropriate polishing the components of each layer can be differentiated. Raman micro-spectroscopy is an non-destructive technique when the size of the object allows its placement under the Raman microscope for direct analysis.

Since the first successful examples of Raman spectroscopy studies on pigment identification of colourful mediaeval manuscripts (Best et al. 1992; Clark 1995b; Guineau 1984; Guineau et al. 1986; Vandenabeele et al. 1999; Wehling et al. 1999), the technique has been applied to various pigments found on works of art including materials on: oil paintings (Benquerença et al. 2009), wall paintings (Vandenabeele et al. 2005a, b), rock art paintings (Hernanz et al. 2008, 2016; Morillas et al. 2018; Rousaki et al. 2015), ceramics (Lucas et al. 2018; Tomasini et al. 2020), porcelains (Jiang et al. 2018) etc.. Micro-Raman spectroscopy produces tremendous results on the synthetic organic pigments analysis (Scherrer et al. 2009; Schulte et al. 2008; Vandenabeele et al. 2000a) including plastics (Angelin et al. 2021) and graffiti/street art colours (Bosi et al. 2020; Cucci et al. 2016; La Nasa et al. 2021) with not only characterizing the main colorants but also allowing to discriminate between polymorphs (Defeyt et al. 2012, 2013).

Regarding the analysis of polymorphs found in modern artists' palette, indeed Raman spectroscopy is a very powerful tool for their non-destructive analysis and solid characterization. As an example the copper phthalocyanine (CuPc) blue compounds, a modern synthetic group of pigments, are among the most interesting pigments in art and art analysis. Not only can be found in different polymorphs characterized by different crystal arrangements, stability properties, shade among others (α form: PB15:0, PB15:1, PB15:2; β form: PB15:3, PB15:4 γ form: PB15:5 and ε form: PB15:6) but also can be used as dating and/or authenticity markers of the artefact (Defeyt et al. 2012, 2013; Defeyt and Strivay 2014; Kehe 1963). It was only in 1935 that the α form reached the market followed by the β form at the early 1950s and the ε form being commercially available in 1962 (Defeyt et al. 2012, 2013; Defeyt and Strivay 2014; Kehe 1963). Defeyt et al., in 2012 (Defeyt et al. 2012) and 2013 (Defeyt et al. 2013) used micro-Raman spectroscopy in combination with other techniques or alone for the identification of the α- β- and ε- form of copper phthalocyanine (CuPc) blue pigments. Moreover, for the latter forms she employed linear discriminant analysis (LDA) by using twelve Raman intensity ratios for the discrimination (Defeyt et al. 2013).

As most of the works of art are exposed to environmental conditions that introduce degradation of the pigments, Raman spectroscopy has proven a valuable tool on the study of alteration mechanisms. Many examples can be given, such as the study of the degradation of lead and copper (Costantini et al. 2020; Smith and Clark 2002), and iron based pigments (Costantini et al. 2020), experiments on the darkening of haematite and formation of coquimbite ($Fe_2(SO_4)3 \cdot 9H_2O$) on paintings from Pompei – a multi stepped procedure (Maguregui et al. 2014), degradation of the

blue colour found on Pompeian wall paintings (Prieto-Taboada et al. 2021), formation of copper oxalates on Cypriot wall painting (Nevin et al. 2008) etc.

Except from identifying the artist's palette and discovering the degradation processes, both having a great impact on conservation treatments, Raman spectroscopy is ideal for tracking possible forgeries and can contribute against the illegal trafficking of works of art. Titanium dioxide is a widely known white pigment used on art objects. Its most debated polymorphs are anatase and rutile whilst brookite seems less relevant to cultural heritage studies. Anatase and rutile seem to have a well-defined occurrence in the art world which coincides with its commercial availability (Edwards et al. 2006; Laver 1997) especially its use on easel paintings (Saverwyns 2010), on modern graffiti colours (or on modern and contemporary art) etc. Anatase, being a rare mineral, is expected not to be a major pigment in ancient art objects but rather an impurity, indicating when found as a pigment, a possible forgery (Edwards et al. 2006). However, this is debated as anatase has been found to be a pigment in antiquity artefacts (Edwards et al. 2006).

Tracking the manufacture and commercial availability dates of pigments throughout the centuries (Brown and Clark 2013; Eastaugh et al. 2008; Laver 1997) is of utmost importance when conducting research in order to identify copied work. Micro-Raman spectroscopy is a very useful technique for authentication studies as it proved very successful in the case of Russian avant-garde paintings characterization (Saverwyns 2010).

For Raman spectroscopy retrieving spectra with good signal-to-noise ratios is partially depending on the laser power and measuring time applied. But the retrieval of a Raman signal in general can be based also on resonance phenomena or fluorescence emission. Fluorescence emission can be avoided by selecting a laser in the near-IR region, typically with a 1064 nm wavelength. Fourier transformations (FT-) were incorporated to Raman spectroscopy and FT-Raman spectroscopy was used for the identification of various organic and inorganic pigments (Baran et al. 2010; Edwards et al. 2004). Recording spectra with near-infrared excitation requires typically liquid-nitrogen-cooled solid state semiconductors as detector, and as a consequence it has to rely on the FT-principle. When using excitation with visible lasers, dispersive Raman spectrometers can be used, with thermoelectrically cooled (TEC) charge-coupled device (CCD) detectors. Moving towards lower excitation energies helps to avoid fluorescence, but as the energy decreases the Raman scattering is decreasing. Indeed, the Raman signal is proportional to the 4th power of the excitation frequency. Thus for achieving a good quality signal elevated laser power should be introduced. (Bersani et al. 2016; Bersani and Lottici 2016; Conti et al. 2016a; Rousaki et al. 2018a). Besides the 1064 nm excitation usually coupled to semiconductor detectors, recently multi-channel detector chips became available, that are able to deal with this long-wavelength excitation, allowing to introduce the near-infrared dispersive Raman instrumentation.

Associating the chemical information with the spatial distribution of the unknown is an approach called mapping. Micro-Raman spectrometers, because of their stability, confocality and high spatial resolution, can retrieve quality mappings producing high quality molecular images. Most of the micro-Raman systems are using calibrated stages for positioning and focusing in the x,y and z axis, respectively. By

arranging a number of point measurements in the x,y space, these can be stored, combined and manipulated (with the appropriate chemometrical methods) to produce chemical images. Flat objects are always preferable when conducting Raman mappings, as otherwise correction for focusing needs to be incorporated.

Raman mappings can be performed on embedded samples, by using a (confocal) Raman microscope. Among others, a cross section from the cork model of the Pantheon in Rome made by Antonio Chichi was collected from the dome of the maquette and stratigraphically characterized to reveal the consequent layers and prior conservation treatments (Rousaki et al. 2019). Also, cross sections from the sixteenth century 'Portrait of a Youth' painting were characterized to map the materials used by the painter (Lau et al. 2008). High quality molecular mappings of areas of few cm^2 were performed in the case of a nineteenth century porcelain card in order for the spatial distribution of the pigments to be revealed (Deneckere et al. 2012). In Fig. 10.2 the optical microscope image with the measuring area is indicated against its molecular images.
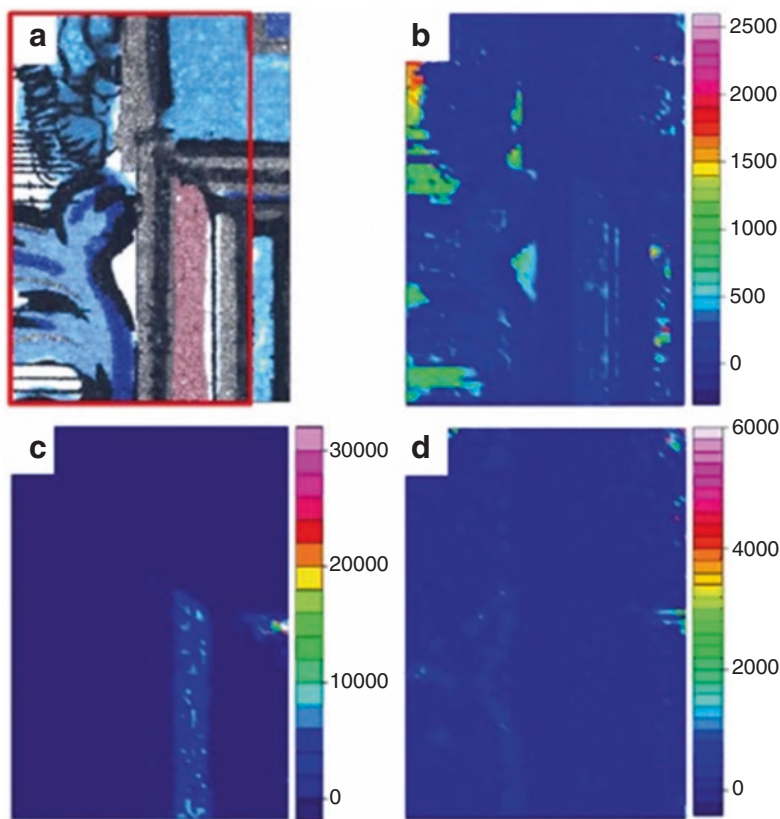
Fig. 10.2 (**a**) Optical microscope image of the area under study together with its molecular images constructed by intergrading the most prominent Raman band of (**b**) lead white ($2PbCO_3 \cdot Pb(OH)_2$); (**c**) vermillion (HgS) and (**d**) ultramarine ($Na_{8-10}Al_6Si_6O_24S_{2-4}$). (Reproduced from ref. (Deneckere et al. 2012) with permission from Springer Nature, Copyright 2011)

10.4 Direct and Mobile Raman Spectroscopy

It is undeniable that one of the most advantageous characteristics of Raman spectroscopy, is its mobility. Over the years, the spectrometers scaled down in size and became compact and/or autonomous in order to enhance the experience of non-destructive analysis. This was a milestone of the technique that was quickly embraced by the archaeometrical community. Indeed, nowadays one can say that there is a clear turn on the direct, non-invasive and/or on field analysis as extensive sampling on artefacts is faced with scepticism.

Review papers, dedicated partially or entirely on Raman spectroscopy mobile applications (Bersani et al. 2016; Colomban 2012; Vandenabeele et al. 2014; Vandenabeele and Donais 2016) underline not only the importance and the instrumental improvements of the technique itself but also reveal the huge amount of applications on works of art from prehistory until today. Thus, it is safe to say that a hundred years' technique or even almost two decades of Raman mobility successfully reflects on masterpieces of thousands of years old.

The nomenclature concerning the Raman spectrometers, for non-invasive analysis or direct analysis, is separating the systems in transportable, mobile, portable, handheld and palm sized (Lauwers et al. 2014b; Rousaki et al. 2018a; Vandenabeele et al. 2014; Vandenabeele and Donais 2016). Mobile spectrometers, compared to their benchtop counterparts, are suffering more from wavenumber instability and are more prompt to wavenumber fluctuations due to unstable environmental conditions etc., especially when they are brought on field. The correct and frequent calibration of the systems can compensate for the wavenumber instability. Calibration can be achieved by measuring a single product and verify the wavenumber position of the most prominent band against the theoretical value. This is not an exact calibration but rather a fast calibration check of the validity of the output of the spectrometer. Accurate calibration can be performed by measuring products with Raman signals covering a wide spectral region (Hutsebaut et al. 2005). Corrections, recalculations and final calibration of the x-axis can be performed by comparison with the theoretical positions (reference band positions) of the products used (Hutsebaut et al. 2005). Moreover, absolute calibration (to obtain the calibration in nm) can also be performed by using a light source, e.g. neon light calibration.

Mobile Raman spectrometers are usually single laser systems, although dual laser mobile systems exist on the market. They are dispersive instruments coupled to TEC CCD or TEC solid state (semiconductor) detectors, depending on the laser excitation used. Generally, they have lower spatial and spectral resolution than benchtop systems. The most common mobile instruments used in cultural heritage research are the ones attached to long fibre optics cables, thus enabling the characterization of surfaces that are situated away from the main unit. These systems are usually relatively compact and allow the full control of the measuring conditions by the operator. Without cameras or objective lenses and when the probehead is mounted on positioning accessories (e.g. tripods), the focusing of the beam is achieved by evaluating the signal-to-noise ratio in distinct positions. When focusing

by hand and positioning the probehead in close contact with the object, special caps can be slid over the probe's lens (Lauwers et al. 2014b; Rousaki et al. 2017b). Using these caps serves a twofold reason: they are introducing a known focal distance, thus enabling stable focusing and are simultaneously blocking the sunlight. For extra protection of the artefact, a thin layer of semi hard foam can be placed on top of the cap. The thickness of the foam must not interfere with the focal length of the lenses cap. If the caps are not used, blocking the ambient light can be achieved by using black non transparent thick cloths or measuring during the night. One should note, in Raman spectroscopy, blocking the environmental signal is very important as this can interfere seriously with the actual Raman signal, hampering the identification of the unknown.

Mobile Raman instruments can perform the analysis on field or in the laboratory directly on the artefact or even on samples and cross sections. Although their spot size is in the mm scale, when the fibre optics probehead is combined with magnification objectives, high magnifications can be reached. Handheld Raman spectrometers are less frequently mentioned in cultural heritage studies. These have fixed optical heads and the users have less freedom to change some measuring parameters (according to the model or the software mode).

In art analysis, the beginning of the 2000s signified the need of conducting direct analysis straight on the artefact. One solution explored the possibility of connecting fibre optics to an FT-Raman spectrometer (Vandenabeele et al. 2001). Among the paintings examined with this method were the Baby Elephant by Lucebert, La Toilette by Degas, La Mort d'un Esprit by Giorgio de Chirico, and La Promenade du Monstre by Rene Magritte. Three years later, in 2004, an in-house developed mobile Raman spectrometer dedicated to cultural heritage studies was realized (Vandenabeele et al. 2004).

Among others (Deneckere et al. 2010, 2011), this mobile art analyser (MArtA) was used for the identification of the pigments in Mad Meg ("Dulle Griet") by Pieter Bruegel the Elder (1561) (Van de Voorde et al. 2014) (Fig. 10.3). The Raman analysis which was conducted in the Museum Mayer van den Bergh in Antwerp, Belgium was accompanied by a handheld X-Ray fluorescence (XRF) spectrometer and a portable X-ray fluorescence/X-ray diffraction (XRF/XRD) instrument in order for the outcome of the direct and on field analysis to be complemented.

Since the first attempts for direct analysis with in-house or adapted solutions, mobile Raman spectrometers are now widely commercially available and researchers can opt for using a combination of systems according to the art project or investigation (Rousaki et al. 2020; Vandenabeele et al. 2007a, b). Mobile Raman spectroscopy is responsible for high-quality data retrieved from a numerous of masterpieces including pigments and degradation products of Pompeian wall paintings (Conti et al. 2015; Maguregui et al. 2012) and preserved Pompeian pigments (Marcaida et al. 2018), illuminated mediaeval manuscripts (Lauwers et al. 2014a), materials and weathering products of decorated plasterwork in the Alhambra (Dominguez-Vidal et al. 2012, 2014). Concerning three-dimensional (3D) objects, direct Raman analysis was able to identify materials used as original pigments and overpainting components of the interior and exterior of the cork maquette of the
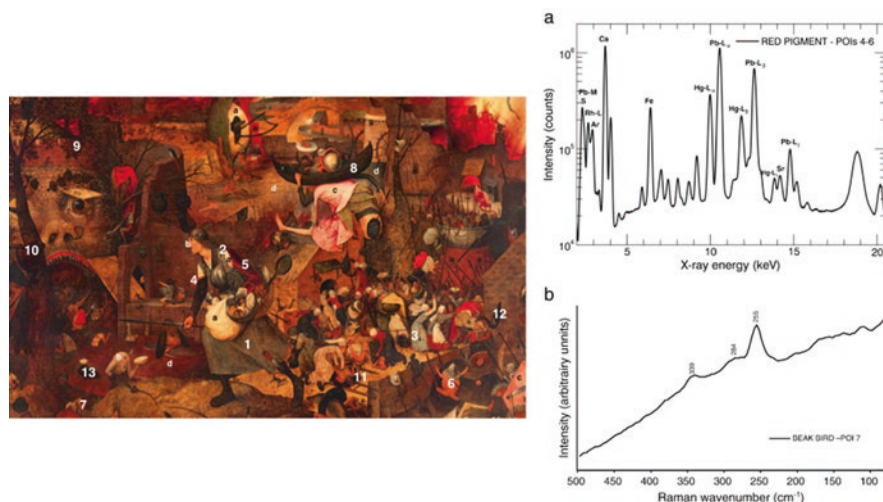
Fig. 10.3 (Left) Mad Meg ("Dulle Griet") by Pieter Bruegel the Elder with points of interest indicted on the painting (Right) (**a**) XRF sum-spectrum of the 4 and 5 points of interest (sleeves) and of the point of interest 6 (creature on the bridge) and (**b**) Raman spectrum confirming vermillion confirming as a red pigment on the surface of the painting (point of interest 7, (beak of the bird). (Adapted from ref. (Van de Voorde et al. 2014) with permission from Elsevier, Copyright 2014)

Pantheon in Rome made by Antonio Chichi (Rousaki et al. 2019). The long fibre optics probehead of the portable Raman instrument used was mounted on a articulating arm for positioning and focusing. The direct Raman study was accompanied with handheld X-ray fluorescence (hXRF), ultraviolet-induced visible fluorescence photography (UIVFP), digital microscopy (Hirox), micro-XRF and benchtop Raman spectroscopy. The results of this project, that also included computer tomography (CT)-scanning and 3D-scanning, assisted towards the restoration campaign of the cork model now exposed to the Ghent University Museum (GUM).

Remarkable results were produced from the direct Raman analysis of rock art paintings (Rousaki etal. 2017b; Tournié et al. 2011; Lahlil et al. 2012; Pitarch et al. 2014; Rousaki et al. 2018b). In particular, the pigments of the ancient population inhabited rock shelters in Patagonia (Argentina) were thoroughly investigated together with the conservation sate of the magnificent works of rock art (Rousaki et al. 2017b, 2018b). Portable Raman spectroscopy was able to identify the existence of a green earth pigment, a challenging task due to its poor Raman scattering capabilities (Fig. 10.4) (Rousaki et al. 2018b).

Concerning the Raman mapping of works of art performed with mobile Raman spectrometers, this still remains a challenging task. In 2016, the proof-of-concept of an *in situ* Raman mapping of a nineteenth century porcelain card, was published (Lauwers et al. 2016), suggesting possible hardware connections and processing tools.

Fluorescence emission is a valid problem in mobile Raman spectroscopy and new approaches have been suggested for overcoming such a disadvantage. 1064 nm
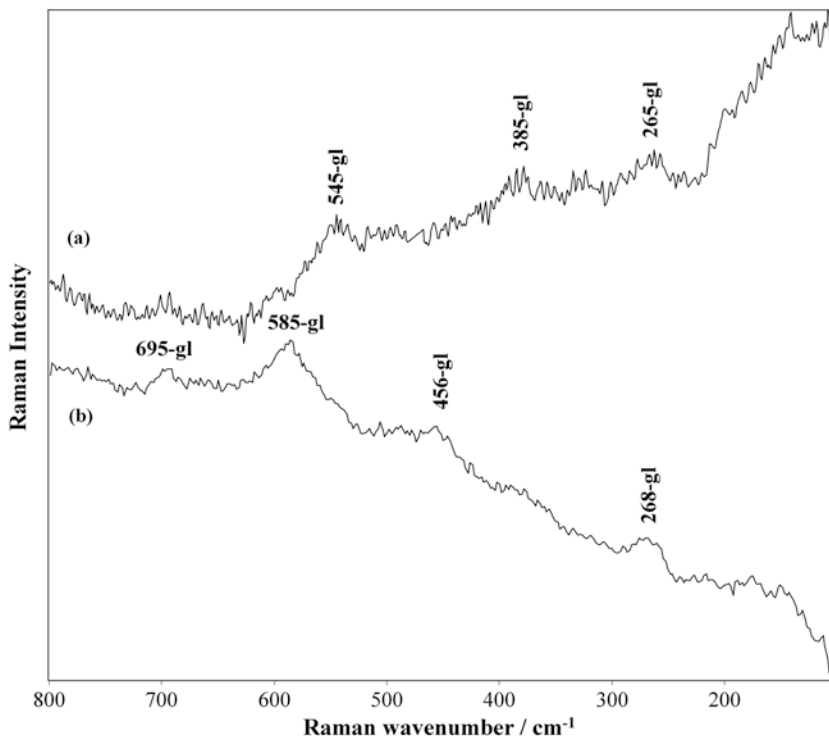
Fig. 10.4 Raman spectra collected with (**a**) with the 785 nm and (**b**) with the 532 nm laser of the Nr. 10 green rock art painting from the shelter Angostura Blanca, Chubut province. Portable Raman spectroscopy point out the likely presence of glauconite (gl), (K,Na) $(Fe^{3+},Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$. (Reproduced from ref. [Rousaki et al. 2018b] with permission from Elsevier, Copyright 2018)

dispersive mobile Raman spectrometers can be used by the scientists profiting from the long wavelength excitation characteristics. As the 1064 nm excitation was associated with FT-spectrometers (required optics and interferometers), the entire unit was able to be scaled down by swapping from FT- to dispersive systems and from cooling with liquid nitrogen to TEC-solid state detectors. The loss of scattering capabilities is compensated with increased laser powers and measuring times (Conti et al. 2016a; Rousaki et al. 2020).

For advancing the analysis and processing experience, it was introduced on the market a handheld Raman spectrometer using the sequentially shifted excitation technology (SSE™) (patent number: US8570507B1) (Rousaki et al. 2020) [Bravo by Bruker]. This is a compact spectrometer with a fixed optical head and a fixed operational power at 100 mW, in-built calibration and a software that autonomously collects the Raman spectra (except when it is positioned on its docking stage where the user can decide for the measuring time of the data). It is a dual laser system, projecting its results in a wide spectral region. The shifted excitation procedure

corrects for fluorescence emission allowing the actual Raman signal, from the measured object, to be revealed (Cooper et al. 2013; Rousaki et al. 2020). The system is tested on cultural heritage objects and materials such as mosaics (Rousaki et al. 2020), a series of laboratory samples and colourful sculptures (Conti et al. 2016a), works of art from some of the New York City museums (Pozzi et al. 2019), organic components found in modern art (Vagnini et al. 2017), etc.

10.5 Non-invasive Stratigraphic Analysis: SORS

Art and Raman spectroscopy is a combination of fields and disciplines that is proven to give fruitful results. Until recently, the concept of stratigraphic analysis of complex layered structures found on works of art was exclusively accomplished by the use of benchtop Raman instruments. For carrying out the analysis, the painting, sculpture or object should be sampled in a specific manner (cross sections) in order for the stratigraphy to be revealed. The sample should then be embedded and polished. As direct research is gaining steam in the art analysis world, new techniques are immerging. Raman spectroscopy is one of the first techniques to embrace the 'new trends' in archaeometry and propose new concepts of non-invasive and non-destructive, direct stratigraphic analysis.

P. Matousek et al. (Eliasson et al. 2014; Matousek et al. 2005) in 2005, proposed the concept of spatially offset Raman spectroscopy (SORS) as a method for deeper-than-the-surface analysis. In SORS the laser beam and the collection zone are spatially separated. The larger the separation and/or the spatial offset the greater the subsurface information. And although, the technique can be applied when the thickness for the layers are at the millimetres or centimetres range (Eliasson and Matousek 2007; Rousaki et al. 2018a; Stone et al. 2007), its application on cultural heritage object was questionable.

The typical thicknesses of the layers of work of art objects are at the micrometre scale. One simple drawback; when applying SORS without any modification on micrometre thick layers, could have been the altered retrieval of signal; a rough sum of subsequent layers. Moreover, as many pigments are sensitive under the laser, restrictions should be made in both the laser frequency, laser power and measuring time. To overcome possible obstacles, microspatially offset Raman spectroscopy (micro-SORS) was proposed as an alternative for work of art analysis, when the sublayers are situated under turbid/opaque one (Bersani et al. 2016; Botteon et al. 2020a, b; Conti et al. 2015; Conti et al. 2015c; Conti et al. 2020; Matousek et al. 2016; Rousaki et al. 2018a). Micro-SORS is using the same basic idea of SORS, the spatial separation of the illumination and signal retrieval zone adapted to the needs of archaeometric research (micrometres spatial offsets, lower laser powers etc.) (Rousaki et al. 2018a). Furthermore, focusing through objectives reduces the volume size of the collection zones significantly. The most straightforward approach/variant of micro-SORS is when this is applied via conventional unmodified micro-Raman spectrometers. *Defocusing* micro-SORS can be achieved by distancing in

steps, the objective lens from the focusing position of the microscope (Bersani et al. 2016; Conti et al. 2015b; Conti et al. 2020; Matousek et al. 2016). On the other hand, *full* micro-SORS demands the modification of the apparatus, to separate the beam delivery from the signal collection areas by using different lenses (Bersani et al. 2016; C. Conti et al. 2015; Conti et al. 2020). In the miniaturized variant of micro-SORS, namely fibre-optics micro-SORS (Vandenabeele et al. 2017), two glass fibres are spatially separated; one to deliver and one to collect the Raman signal. The delivery fibre is unmovable while the collection glass fibre is mounted on a translation stage. The spot size is roughly equal with the diameter of the fibres used. As micro-SORS is still under investigation and research other approaches have been proposed in the literature (Buckley et al. 2016; Khan et al. 2016; Liao et al. 2016; Matthiae and Kristensen 2019).

Micro-SORS methods, with applications on cultural heritage research, have been tested on artificial samples (Conti et al. 2014, 2016c, 2017) and art works including sculptures (Conti et al. 2015a) and street murals (Botteon et al. 2018). Extensive research has been done for studying the possibilities and abilities of micro-SORS for subsurface analysis of painted structures (Conti et al. 2016b, d, e; Matousek et al. 2015), for combining confocal XRF with micro-SORS (Conti et al. 2018), for exploring the diffusion profile, of products used in conservation, into a matrix (Botteon et al. 2020a, b) etc.

In respect to subsurface mapping this has been tested on artificial samples using the *full* micro-SORS variant (Botteon et al. 2017) or on real samples using the *defocusing* variant (Rousaki et al. 2017a). For the latter a nineteenth century porcelain card was used as an ideal object for such research. The experiments were separated in two stages: one to retrieve and evaluate the *defocusing* Raman signal from subsequent layers from differently coloured zones and two to perform the *defocusing* Raman mapping and construct the sublayers images. In Fig. 10.5 the distribution of vermillion (normalized to lead white) is given is the focused position and in two different *defocusing* ones.

In the imaged position (Fig. 10.5a), vermillion is situated on the correct zone, while by increasing defocusing its signal is losing intensity (Fig. 10.5b, c). Indeed, lead white is situated below all the couloured zones of the porcelain card (Rousaki et al. 2017a). In terms of portability towards the *in situ* investigations the defocusing
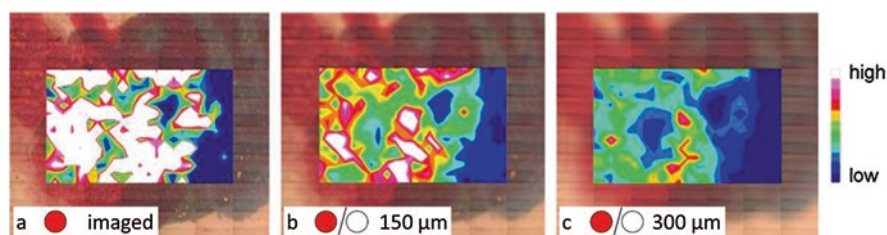
Fig. 10.5 Spatial distribution of vermillion normalized to lead white on an area of a nineteenth century porcelain at (**a**) zero offset or focusing position; (**b**) 150 μm and (**c**) 300 μm. (Adapted from ref. (Rousaki et al. 2017a) with permission from the Royal Society of Chemistry, Copyright 2017)

and the full micro-SORS variants have successfully demonstrated (Botteon et al. 2020a, b; Realini et al. 2016, 2017).

In order to achieve subsurface contrast between layers, frequency offset Raman spectroscopy (FORS) has been proposed (Sekar et al. 2017). This approach is based on the idea that the optical properties of the medium are changing upon shifting the laser frequency thus achieving sublayer information (Sekar et al. 2017). Moreover, it was reported that a FORS-SORS method is producing increased enhancement (Sekar et al. 2017).

10.6 Surface-Enhanced Raman Spectroscopy (SERS)

Raman spectroscopy is an ideal first choice technique for the identification of inorganic and organic materials in cultural heritage objects. However, especially for the analysis of organic components often fluorescence occurs. Therefore, for this analysis, one can simply benefit from changing the laser wavelength to supress fluorescence phenomena and retrieve the actual Raman signal. Although this is valid for some classes of organics or synthetic organic molecules, 'traditional' Raman spectroscopy seems to lack sensitivity to identify several organic colorants such as the natural dyes. Complications especially arise when the concentration of the colorant is low or if this colorant is largely dispersed inside the artwork's layers. Moreover, often these colorants don't have very good Raman scattering capabilities. The development of surface–enhanced Raman spectroscopy (SERS) produced successful results on materials like dyes, by enhancing considerably their Raman signal.

Fleischmann et al. (Fleischmann et al. 1974), in 1974, observed the enhancement of the Raman signal of pyridine on silver, creating the base of SERS experiments. A bit over a decade later, B. Guineau and V. Guichard (1987) reported its application on cultural heritage objects, characterizing madder. Nowadays, SERS is widely applied and extensively researched for the characterization of organic colorants. Even though, separation techniques seems to produce better discrimination between dyestuffs, SERS is considered more cost efficient, less invasive or less destructive and faster (Casadio et al. 2016; Pozzi and Leona 2016).

In SERS, both chemical and field enhancement are effectively occurring, for describing the analyte-metal interaction and the increase of the power of the electromagnetic field (wavelength depended), respectively (Vandenabeele 2013). Parameters of outmost importance are the preparation and application of the metallic substrate on which the analyte is to be absorbed (Agarwal et al. 2014; Cañamares et al. 2009; Leona 2009; Leona et al. 2006; Pozzi and Leona 2016; Retko et al. 2014; Sessa et al. 2018; Zalaffi et al. 2020) and the meticulous, sometimes aggressive, sample treatment and sophisticated methodologies (Bruni et al. 2011; Chen et al. 2006; Jurasekova et al. 2010; Pozzi et al. 2012; Pozzi and Leona 2016). The technique has been demonstrated and applied widely on samples and real works of art identifying dyes and lakes (Campanella et al. 2020; Cañamares et al. 2006;

Casadio et al. 2010; Gui et al. 2013; Leona et al. 2011; Newman et al. 2007; Pozzi et al. 2013, 2014; Sessa et al. 2018; Zoleo et al. 2020).

Several methodological approaches and techniques for upgrading the SERS experience have been proposed in literature, including laser-ablation surface-enhanced Raman spectroscopy (Cesaratto et al. 2014; Londero et al. 2013) and the implementation of the appropriate laser excitation for surface-enhanced resonance Raman spectroscopy (SERRS) (Leona 2009).

Towards the direct analysis of art objects by using SERS, some approaches include mobile, removable film (Doherty et al. 2011), inkjet colloidal application (Benedetti et al. 2014) and application of tip-enhanced Raman spectroscopy (TERS) with even a combination of TERS and atomic force microscopy (AFM) (Kurouski et al. 2014).

10.7 Conclusions

Almost a century after the discovery of the Raman effect, Raman spectroscopy has grown to be one of the core stone techniques applied in cultural heritage studies. Its undeniable that advantages together with the variation of the Raman approaches developed, bring the technique in the front line of analytical studies. Moreover, the hardware advantages of the last two decades detach the method from its traditional immobile approach and brought it on the field, allowing measuring directly on the artefact and breaking out from the laboratory. Furthermore, the implementation of SERS for the identification of dyes, a very important class of organic colorants and the development of novel techniques such as micro-SORS proves the versatility of Raman spectroscopy.

Although, Raman spectroscopy shares some undeniably powerful characteristics, the users should be very cautious before starting a Raman analysis. In general, the laser power should be kept under control and sufficiently low in order not to invoke alterations on the measuring sample or object. Moreover, the Raman data should be meticulously treated not only against a spectral library of pure substances but considering also the literature. Lastly, one should be aware of spectral interferences, such as noise, fluorescence background and fluorescence bands, cosmic rays, ambient light etc when interpreting the Raman spectra.

Conclusively, Raman spectroscopy is able to answer contemporary conservation questions and create pathways for the identification of inorganic and organic pigments and colorants found on artistic masterpieces.

References

Agarwal, N.R., Tommasini, M., Fazio, E., Neri, F., Ponterio, R.C., Trusso, S., et al.: SERS activity of silver and gold nanostructured thin films deposited by pulsed laser ablation. Appl. Phys. A Mater. Sci. Process. **117**, 347–351 (2014). https://doi.org/10.1007/s00339-014-8401-8

Angelin, E.M., França de Sá, S., Picollo, M., Nevin, A., Callapez, M.E., Melo, M.J.: The identification of synthetic organic red pigments in historical plastics: developing an in situ analytical protocol based on Raman microscopy. J. Raman Spectrosc. **52**, 145–158 (2021). https://doi.org/10.1002/jrs.5985

Baran, A., Fiedler, A., Schulz, H., Baranska, M.: In situ Raman and IR spectroscopic analysis of indigo dye. Anal. Methods. **2**, 1372 (2010). https://doi.org/10.1039/c0ay00311e

Bell, I.M., Clark, R.J.H., Gibbs, P.J.: Raman spectroscopic library of natural and synthetic pigments (pre-≈ 1850 AD). Spectrochim. Acta A Mol. Biomol. Spectrosc. **53**(12), 2159–2179 (1997)

Benedetti, D.P., Zhang, J., Tague, T.J., Lombardi, J.R., Leona, M.: In situ microanalysis of organic colorants by inkjet colloid deposition surface-enhanced Raman scattering. J. Raman Spectrosc. **45**, 123–127 (2014). https://doi.org/10.1002/jrs.4424

Benquerença, M.-J., Mendes, N.F.C., Castellucci, E., Gaspar, V.M.F., Gil, F.P.S.C.: Micro-Raman spectroscopy analysis of 16th century Portuguese Ferreirim Masters oil paintings. J. Raman Spectrosc. **40**, 2135–2143 (2009). https://doi.org/10.1002/jrs.2383

Bersani, D., Lottici, P.P.: Raman spectroscopy of minerals and mineral pigments in archaeometry. J. Raman Spectrosc. **47**, 499–530 (2016). https://doi.org/10.1002/jrs.4914

Bersani, D., Conti, C., Matousek, P., Pozzi, F., Vandenabeele, P.: Methodological evolutions of Raman spectroscopy in art and archaeology. Anal. Methods. **8**, 8395–8409 (2016). https://doi.org/10.1039/C6AY02327D

Best, S.P., Clark, R.J., Withnall, R.: Non-destructive pigment analysis of artefacts by Raman microscopy. Endeavour. **16**, 66–73 (1992). https://doi.org/10.1016/0160-9327(92)90004-9

Bosi, A., Ciccola, A., Serafini, I., Guiso, M., Ripanti, F., Postorino, P., et al.: Street art graffiti: discovering their composition and alteration by FTIR and micro-Raman spectroscopy. Spectrochim. Acta. Part A Mol. Biomol. Spectrosc. **225**, 117474 (2020). https://doi.org/10.1016/j.saa.2019.117474

Botteon, A., Conti, C., Realini, M., Colombo, C., Matousek, P.: Discovering hidden painted images: subsurface imaging using microscale spatially offset Raman spectroscopy. Anal. Chem. **89**, 792–798 (2017). https://doi.org/10.1021/acs.analchem.6b03548

Botteon, A., Colombo, C., Realini, M., Bracci, S., Magrini, D., Matousek, P., et al.: Exploring street art paintings by microspatially offset Raman spectroscopy. J. Raman Spectrosc. **49**, 1652–1659 (2018). https://doi.org/10.1002/jrs.5445

Botteon, A., Colombo, C., Realini, M., Castiglioni, C., Piccirillo, A., Matousek, P., et al.: Non-invasive and in situ investigation of layers sequence in panel paintings by portable microspatially offset Raman spectroscopy. J. Raman Spectrosc. **51**, 2016–2021 (2020a). https://doi.org/10.1002/jrs.5939

Botteon, A., Yiming, J., Prati, S., Sciutto, G., Realini, M., Colombo, C., et al.: Non-invasive characterisation of molecular diffusion of agent into turbid matrix using micro-SORS. Talanta. **218**, 121078 (2020b). https://doi.org/10.1016/j.talanta.2020.121078

Brown, S., Clark, R.J.H.: Anatase: Important industrial white pigment and date-marker for artwork. Spectrochim. Acta. Part A Mol. Biomol. Spectrosc. **110**, 78–80 (2013). https://doi.org/10.1016/j.saa.2013.03.041

Bruni, S., Guglielmi, V., Pozzi, F., Mercuri, A.M.: Surface-enhanced Raman spectroscopy (SERS) on silver colloids for the identification of ancient textile dyes. Part II: pomegranate and sumac. J. Raman Spectrosc. **42**, 465–473 (2011). https://doi.org/10.1002/jrs.2736

Buckley, K., Atkins, C.G., Chen, D., Schulze, H.G., Devine, D.V., Blades, M.W., et al.: Non-invasive spectroscopy of transfusable red blood cells stored inside sealed plastic blood-bags. Analyst. **141**, 1678–1685 (2016). https://doi.org/10.1039/C5AN02461G

Burgio, L., Clark, R.J.H.: Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation. Spectrochim. Acta A Mol. Biomol. Spectrosc. **57**(7), 1491–1521 (2001)

Burrafato, G., Calabrese, M., Cosentino, A., Gueli, A.M., Troja, S.O., Zuccarello, A.: ColoRaman project: Raman and fluorescence spectroscopy of oil, tempera and fresco paint pigments. J. Raman Spectrosc. **35**(10), 879–886 (2004)

Campanella, B., Botti, J., Cavaleri, T., Cicogna, F., Legnaioli, S., Pagnotta, S., et al.: The shining brightness of daylight fluorescent pigments: Raman and SERS study of a modern class of painting materials. Microchem. J. **152**, 104292 (2020). https://doi.org/10.1016/j.microc.2019.104292

Cañamares, M.V., Garcia-Ramos, J.V., Domingo, C., Sanchez-Cortes, S.: Surface-enhanced Raman scattering study of the anthraquinone red pigment carminic acid. Vib. Spectrosc. **40**, 161–167 (2006). https://doi.org/10.1016/j.vibspec.2005.08.002

Cañamares, M.V., Leona, M., Bouchard, M., Grzywacz, C.M., Wouters, J., Trentelman, K.: Evaluation of Raman and SERS analytical protocols in the analysis of Cape Jasmine dye (Gardenia augusta L.). J. Raman Spectrosc. **41** (2009). https://doi.org/10.1002/jrs.2462

Casadio, F., Leona, M., Lombardi, J.R., Van Duyne, R.: Identification of organic colorants in fibers, paints, and glazes by surface enhanced Raman spectroscopy. Acc. Chem. Res. **43**, 782–791 (2010). https://doi.org/10.1021/ar100019q

Casadio, F., Daher, C., Bellot-Gurlet, L.: Raman spectroscopy of cultural heritage materials: overview of applications and new frontiers in instrumentation, sampling modalities, and data processing. Top. Curr. Chem. **374**, 62 (2016). https://doi.org/10.1007/s41061-016-0061-z

Cesaratto, A., Leona, M., Lombardi, J.R., Comelli, D., Nevin, A., Londero, P.: Detection of organic colorants in historical painting layers using UV laser ablation surface-enhanced Raman microspectroscopy. Angew. Chem. Int. Ed. **53**, 14373–14377 (2014). https://doi.org/10.1002/anie.201408016

Castro, K., Pérez-Alonso, M., Rodríguez-Laso, M.D., Fernández, L.A., Madariaga, J.M.: On-line FT-Raman and dispersive Raman spectra database of artists' materials (e-VISART database). Anal. Bioanal. Chem. **382**(2), 248–258 (2005)

Chen, K., Leona, M., Vo-Dinh, K.-C., Yan, F., Wabuyele, M.B., Vo-Dinh, T.: Application of surface-enhanced Raman scattering (SERS) for the identification of anthraquinone dyes used in works of art. J. Raman Spectrosc. **37**, 520–527 (2006). https://doi.org/10.1002/jrs.1426

Cialla-May, D., Schmitt, M., Popp, J.: Theoretical principles of Raman spectroscopy. Phys Sci Rev. **4**, 20170040 (n.d.). https://doi.org/10.1515/psr-2017-0040

Clark, R.J.: Pigment identification on medieval manuscripts by Raman microscopy. J. Mol. Struct. **347**, 417–427 (1995a). https://doi.org/10.1016/0022-2860(95)08564-C

Clark, R.J.H.: Raman microscopy: application to the identification of pigments on medieval manuscripts. Chem. Soc. Rev. **24**, 187 (1995b). https://doi.org/10.1039/cs9952400187

Clark, R.J.H., Franks, M.L.: The resonance Raman spectrum of ultramarine blue. Chem. Phys. Lett. **34**, 69–72 (1975). https://doi.org/10.1016/0009-2614(75)80202-8

Coccato, A., Jehlicka, J., Moens, L., Vandenabeele, P.: Raman spectroscopy for the investigation of carbon–based black pigments. J. Raman Spectrosc. **46**(10), 1003–1015 (2015)

Coccato, A., Bersani, D., Coudray, A., Sanyova, J., Moens, L., Vandenabeele, P.: Raman spectroscopy of green minerals and reaction products with an application in cultural heritage research. J. Raman Spectrosc. **47**(12), 1429–1443 (2016)

Colomban, P.: Polymerization degree and Raman identification of ancient glasses used for jewelry, ceramic enamels and mosaics. J. Non-Cryst. Solids. **323**, 180–187 (2003a). https://doi.org/10.1016/S0022-3093(03)00303-X

Colomban, P.: Lapis lazuli as unexpected blue pigment in Iranian Lâjvardina ceramics. J. Raman Spectrosc. **34**, 420–423 (2003b). https://doi.org/10.1002/jrs.1014

Colomban, P.: The on-site/remote Raman analysis with mobile instruments: a review of drawbacks and success in cultural heritage studies and other associated fields. J. Raman Spectrosc. **43**, 1529–1535 (2012). https://doi.org/10.1002/jrs.4042

Colomban, P., Tournie, A., Bellot-Gurlet, L.: Raman identification of glassy silicates used in ceram-ics, glass and jewellery: a tentative differentiation guide. J. Raman Spectrosc. **37**, 841–852 (2006). https://doi.org/10.1002/jrs.1515

Conti, C., Colombo, C., Realini, M., Zerbi, G., Matousek, P.: Subsurface Raman analysis of thin painted layers. Appl. Spectrosc. **68**, 686–691 (2014). https://doi.org/10.1366/13-07376

Conti, C., Colombo, C., Realini, M., Matousek, P.: Subsurface analysis of painted sculptures and plasters using micrometre-scale spatially offset Raman spectroscopy (micro-SORS). J. Raman Spectrosc. **46**, 476–482 (2015a). https://doi.org/10.1002/jrs.4673

Conti, C., Realini, M., Colombo, C., Sowoidnich, K., Afseth, N.K., Bertasa, M., et al.: Noninvasive analysis of thin turbid layers using microscale spatially offset Raman spectroscopy. Anal. Chem. **87**, 5810–5815 (2015b). https://doi.org/10.1021/acs.analchem.5b01080

Conti, C., Realini, M., Colombo, C., Matousek, P.: Comparison of key modalities of micro-scale spatially offset Raman spectroscopy. Analyst. **140**, 8127–8133 (2015c). https://doi.org/10.1039/C5AN01900A

Conti, C., Botteon, A., Bertasa, M., Colombo, C., Realini, M., Sali, D.: Portable sequentially shifted excitation Raman spectroscopy as an innovative tool for in situ chemical interrogation of painted surfaces. Analyst. **141**, 4599–4607 (2016a). https://doi.org/10.1039/C6AN00753H

Conti, C., Botteon, A., Colombo, C., Realini, M., Matousek, P.: Fluorescence suppression using micro-scale spatially offset Raman spectroscopy. Analyst. **141**, 5374–5381 (2016b). https://doi.org/10.1039/C6AN00852F

Conti, C., Realini, M., Botteon, A., Colombo, C., Noll, S., Elliott, S.R., et al.: Analytical capabil-ity of defocused µ-SORS in the chemical interrogation of thin turbid painted layers. Appl. Spectrosc. **70**, 156–161 (2016c). https://doi.org/10.1177/0003702815615345

Conti, C., Realini, M., Colombo, C., Botteon, A., Bertasa, M., Striova, J., et al.: Determination of thickness of thin turbid painted over-layers using micro-scale spatially offset Raman spec-troscopy. Philos. Trans. R. Soc. A Math. Phys. Eng. Sci. **374**, 20160049 (2016d). https://doi.org/10.1098/rsta.2016.0049

Conti, C., Realini, M., Colombo, C., Botteon, A., Matousek, P.: Contrasting confocal with defocus-ing microscale spatially offset Raman spectroscopy. J. Raman Spectrosc. **47**, 565–570 (2016e). https://doi.org/10.1002/jrs.4851

Conti, C., Botteon, A., Colombo, C., Realini, M., Matousek, P.: Investigation of heterogeneous painted systems by micro-spatially offset Raman spectroscopy. Anal. Chem. **89**, 11476–11483 (2017). https://doi.org/10.1021/acs.analchem.7b02700

Conti, C., Botteon, A., Colombo, C., Realini, M., Matousek, P., Vandenabeele, P., et al.: Contrasting confocal XRF with micro-SORS: a deep view within micrometric painted stratigraphy. Anal. Methods. **10**, 3837–3844 (2018). https://doi.org/10.1039/C8AY00957K

Conti, C., Botteon, A., Colombo, C., Pinna, D., Realini, M., Matousek, P.: Advances in Raman spectroscopy for the non-destructive subsurface analysis of artworks: micro-SORS. J. Cult. Herit. **43**, 319–328 (2020). https://doi.org/10.1016/j.culher.2019.12.003

Cooper, J.B., Abdelkader, M., Wise, K.L.: Sequentially shifted excitation Raman spectroscopy: Novel algorithm and instrumentation for fluorescence-free Raman spectroscopy in spectral space. Appl. Spectrosc. **67**, 973–984 (2013)

Costantini, I., Lottici, P.P., Bersani, D., Pontiroli, D., Casoli, A., Castro, K., et al.: Darkening of lead- and iron-based pigments on late Gothic Italian wall paintings: energy dispersive X-ray fluorescence, µ-Raman, and powder X-ray diffraction analyses for diagnosis: presence of β-PbO 2 (plattnerite) and α-PbO 2 (scrutinyite). J. Raman Spectrosc. **51**, 680–692 (2020). https://doi.org/10.1002/jrs.5817

Cucci, C., Bartolozzi, G., De Vita, M., Marchiafava, V., Picollo, M., Casadio, F.: The colors of Keith Haring: a spectroscopic study on the materials of the mural painting Tuttomondo and on reference contemporary outdoor paints. Appl. Spectrosc. **70**, 186–196 (2016). https://doi.org/10.1177/0003702815615346

Daher, C., Paris, C., Le Hô, A.S., Bellot-Gurlet, L., Échard, J.P.: A joint use of Raman and infrared spectroscopies for the identification of natural organic media used in ancient varnishes. J. Raman Spectrosc. **41**(11), 1494–1499 (2010)

De Gelder, J., De Gussem, K., Vandenabeele, P., Moens, L.: Reference database of Raman spectra of biological molecules. J. Raman Spectrosc. **38**(9), 1133–1147 (2007)

Defeyt, C., Strivay, D.: PB15 as 20th and 21st artists' pigments: conservation concerns. E-Preserv. Sci. **11**, 6–14 (2014)

Defeyt, C., Vandenabeele, P., Gilbert, B., Van Pevenage, J., Cloots, R., Strivay, D., et al.: Contribution to the identification of α-, β- and ε-copper phthalocyanine blue pigments in modern artists' paints by X-ray powder diffraction, attenuated total reflectance micro-fourier transform infrared spectroscopy and micro-Raman spectroscopy. J. Raman Spectrosc. **43**, 1772–1780 (2012). https://doi.org/10.1002/jrs.4125

Defeyt, C., Van Pevenage, J., Moens, L., Strivay, D., Vandenabeele, P.: Micro-Raman spectroscopy and chemometrical analysis for the distinction of copper phthalocyanine polymorphs in paint layers. Spectrochim. Acta. Part A Mol. Biomol. Spectrosc. **115**, 636–640 (2013). https://doi.org/10.1016/j.saa.2013.04.128

Delhaye, M., Dhamelincourt, P.: Raman microprobe and microscope with laser excitation. J. Raman Spectrosc. **3**, 33–43 (1975). https://doi.org/10.1002/jrs.1250030105

Deneckere, A., Schudel, W., Van Bos, M., Wouters, H., Bergmans, A., Vandenabeele, P., et al.: In situ investigations of vault paintings in the Antwerp cathedral. Spectrochim. Acta. Part A Mol. Biomol. Spectrosc. **75**, 511–519 (2010). https://doi.org/10.1016/j.saa.2009.10.032

Deneckere, A., Leeflang, M., Bloem, M., Chavannes-Mazel, C.A., Vekemans, B., Vincze, L., et al.: The use of mobile Raman spectroscopy to compare three full-page miniatures from the breviary of Arnold of Egmond. Spectrochim. Acta. Part A Mol. Biomol. Spectrosc. **83**, 194–199 (2011). https://doi.org/10.1016/j.saa.2011.08.016

Deneckere, A., Vekemans, B., Voorde, L., Paepe, P., Vincze, L., Moens, L., et al.: Feasibility study of the application of micro-Raman imaging as complement to micro-XRF imaging. Appl. Phys. A Mater. Sci. Process. **106**, 363–376 (2012). https://doi.org/10.1007/s00339-011-6693-5

Doherty, B., Brunetti, B.G., Sgamellotti, A., Miliani, C.: A detachable SERS active cellulose film: a minimally invasive approach to the study of painting lakes. J. Raman Spectrosc. **42**, 1932–1938 (2011). https://doi.org/10.1002/jrs.2942

Dominguez-Vidal, A., Jose de la Torre-Lopez, M., Rubio-Domene, R., Ayora-Cañada, M.J.: In situ noninvasive Raman microspectroscopic investigation of polychrome plasterworks in the Alhambra. Analyst. **137**, 5763 (2012). https://doi.org/10.1039/c2an36027f

Dominguez-Vidal, A., de la Torre-López, M.J., Campos-Suñol, M.J., Rubio-Domene, R., Ayora-Cañada, M.J.: Decorated plasterwork in the Alhambra investigated by Raman spectroscopy: comparative field and laboratory study. J. Raman Spectrosc. **45**, 1006–1012 (2014). https://doi.org/10.1002/jrs.4439

Eastaugh, N., Walsh, V., Chaplin, T.D., Siddall, R.: The Pigment Compendium – A Dictionary of Historical Pigments. Butterworth-Heinemann, Oxford (2008)

Edwards, H.G., Ali, E.M.: Raman spectroscopy of archaeological and ancient resins: problems with database construction for applications in conservation and historical provenancing. Spectrochim. Acta A Mol. Biomol. Spectrosc. **80**(1), 49–54 (2011)

Edwards, H.G.M., Jorge Villar, S.E., Eremin, K.A.: Raman spectroscopic analysis of pigments from dynastic Egyptian funerary artefacts. J. Raman Spectrosc. **35**, 786–795 (2004). https://doi.org/10.1002/jrs.1193

Edwards, H.G.M., Nik Hassan, N.F., Middleton, P.S.: Anatase – a pigment in ancient artwork or a modern usurper? Anal. Bioanal. Chem. **384**, 1356–1365 (2006). https://doi.org/10.1007/s00216-005-0284-2

Eliasson, C., Matousek, P.: Noninvasive authentication of pharmaceutical products through packaging using spatially offset Raman Spectroscopy. Anal. Chem. **79**, 1696–1701 (2007). https://doi.org/10.1021/ac062223z

Eliasson, C., Matousek, P., Leona, M., Stenger, J., Ferloni, E., Jurasekova, Z., et al.: Numerical Simulations of subsurface probing in diffusely scattering media using spatially offset Raman Spectroscopy. J. Raman Spectrosc. **43**, 1–29 (2014). https://doi.org/10.1515/psr-2017-0040

Ferraro, J.R., Nakamoto, K.: Introductory Raman Spectroscopy, 2nd edn. Elsevier, Amsterdam (2003). https://doi.org/10.1016/B978-0-12-254105-6.X5000-8

Fleischmann, M., Hendra, P.J., McQuillan, A.J.: Raman spectra of pyridine adsorbed at a silver electrode. Chem. Phys. Lett. **26**, 163–166 (1974). https://doi.org/10.1016/0009-2614(74)85388-1

Fremout, W., Saverwyns, S.: Identification of synthetic organic pigments: the role of a comprehensive digital Raman spectral library. J. Raman Spectrosc. **43**(11), 1536–1544 (2012)

Gardiner, D.J., Graves, P.R. (eds.): Practical Raman Spectroscopy. Springer, Berlin/Heidelberg (1989). https://doi.org/10.1007/978-3-642-74040-4

Gilbert, B., Denoël, S., Weber, G., Allart, D.: Analysis of green copper pigments in illuminated manuscripts by micro-Raman spectroscopy. Analyst. **128**(10), 1213–1217 (2003)

Giordano, D., González-García, D., Russell, J.K., Raneri, S., Bersani, D., Fornasini, L., Di Genova, D., Ferrando, S., Kaliwoda, M., Lottici, P.P., Smit, M., Dingwell, D.B.: A calibrated database of Raman spectra for natural silicate glasses: implications for modelling melt physical properties. J. Raman Spectrosc. **51**, 1822–1838 (2019)

Gui, O.M., Fălămaș, A., Barbu-Tudoran, L., Aluaș, M., Giambra, B., Cîntă Pînzaru, S.: Surface-enhanced Raman scattering (SERS) and complementary techniques applied for the investigation of an Italian cultural heritage canvas. J. Raman Spectrosc. **44**, 277–282 (2013). https://doi.org/10.1002/jrs.4186

Guineau, B.: Microanalysis of painted manuscripts and of colored archeological materials by Raman laser microprobe. J. Forensic Sci. **29**, 471–485 (1984)

Guineau, B., Guichard, V.: Identification des colorants organiques naturels par microspectrometrie Raman de resonance et par effet Raman exalte de surface (SERS); Exemple d'application à l'étude de tranchefiles de reliures anciennes teintes à la garance. ICOM Comm. Conserv. In 8th Triennal Meeting, vol. 2, Sydney, Australia, 1987, pp. 659–666.

Guineau, B., Coupry, C., Gousset, M.T., Forgerit, J.P., Vezin, J.: Identification de bleu de lapis-lazuli dans six manuscrits à peintures du XIIe siècle provenant de l'abbaye de Corbie. Scriptorium. **40**, 157–171 (1986)

Hernanz, A., Gavira-Vallejo, J.M., Ruiz-López, J.F., Edwards, H.G.M.: A comprehensive micro-Raman spectroscopic study of prehistoric rock paintings from the Sierra de las Cuerdas, Cuenca, Spain. J. Raman Spectrosc. **39**, 972–984 (2008). https://doi.org/10.1002/jrs.1940

Hernanz, A., Chang, J., Iriarte, M., Gavira-Vallejo, J.M., de Balbín-Behrmann, R., Bueno-Ramírez, P., et al.: Raman microscopy of hand stencils rock art from the Yabrai Mountain, Inner Mongolia Autonomous Region, China. Appl. Phys. A. **122**, 699 (2016). https://doi.org/10.1007/s00339-016-0228-z

Hutsebaut, D., Vandenabeele, P., Moens, L.: Evaluation of an accurate calibration and spectral standardization procedure for Raman spectroscopy. Analyst. **130**, 1204 (2005). https://doi.org/10.1039/b503624k

Jiang, X., Ma, Y., Chen, Y., Li, Y., Ma, Q., Zhang, Z., et al.: Raman analysis of cobalt blue pigment in blue and white porcelain: a reassessment. Spectrochim. Acta. Part A Mol. Biomol. Spectrosc. **190**, 61–67 (2018). https://doi.org/10.1016/j.saa.2017.08.076

Jurasekova, Z., del Puerto, E., Bruno, G., García-Ramos, J.V., Sanchez-Cortes, S., Domingo, C.: Extractionless non-hydrolysis surface-enhanced Raman spectroscopic detection of historical mordant dyes on textile fibers. J. Raman Spectrosc. **41**, 1455–1461 (2010). https://doi.org/10.1002/jrs.2651

Kehe, H.J.: Phthalocyanine compounds (Moser, Frank H.; Thomas, Arthur L.). J. Chem. Educ. **40**, A974 (1963). https://doi.org/10.1021/ed040pA974.2

Khan, K.M., Ghosh, N., Majumder, S.K.: Off-confocal Raman spectroscopy (OCRS) for sub-surface measurements in layered turbid samples. J. Opt. **18**, 095301 (2016). https://doi.org/10.1088/2040-8978/18/9/095301

Kurouski, D., Zaleski, S., Casadio, F., Van Duyne, R.P., Shah, N.C.: Tip-Enhanced Raman Spectroscopy (TERS) for in situ identification of indigo and iron gall ink on paper. J. Am. Chem. Soc. **136**, 8677–8684 (2014). https://doi.org/10.1021/ja5027612

La Nasa, J., Campanella, B., Sabatini, F., Rava, A., Shank, W., Lucero-Gomez, P., et al.: 60 years of street art: a comparative study of the artists' materials through spectroscopic and mass spectrometric approaches. J. Cult. Herit. **48**, 129–140 (2021). https://doi.org/10.1016/j.culher.2020.11.016

Lafuente, B., Downs, R.T., Yang, H., Stone, N.: The power of databases: the RRUFF project. In: Armbruster, T., Danisi, R.M. (eds.) Highlights in Mineralogical Crystallography, pp. 1–29. Walter de Gruyter GmbH (2016)

Lahlil, S., Lebon, M., Beck, L., Rousselière, H., Vignaud, C., Reiche, I., Menu, M., Paillet, P., Plassard, F.: The first in situ micro-Raman spectroscopic analysis of prehistoric cave art of Rouffignac St–Cernin, France. J. Raman Spectrosc. **43**, 1637–1643 (2012)

Lau, D., Villis, C., Furman, S., Livett, M.: Multispectral and hyperspectral image analysis of elemental and micro-Raman maps of cross-sections from a 16th century painting. Anal. Chim. Acta. **610**, 15–24 (2008). https://doi.org/10.1016/j.aca.2007.12.043

Lauwers, D., Cattersel, V., Vandamme, L., Van Eester, A., De Langhe, K., Moens, L., et al.: Pigment identification of an illuminated mediaeval manuscript De Civitate Dei by means of a portable Raman equipment. J. Raman Spectrosc. **45**, 1266–1271 (2014a). https://doi.org/10.1002/jrs.4500

Lauwers, D., Hutado, A.G., Tanevska, V., Moens, L., Bersani, D., Vandenabeele, P.: Characterisation of a portable Raman spectrometer for in situ analysis of art objects. Spectrochim. Acta. Part A Mol. Biomol. Spectrosc. **118**, 294–301 (2014b). https://doi.org/10.1016/j.saa.2013.08.088

Lauwers, D., Brondeel, P., Moens, L., Vandenabeele, P.: In situ Raman mapping of art objects. Philos. Trans. R. Soc. A Math. Phys. Eng. Sci. **374**, 20160039 (2016). https://doi.org/10.1098/rsta.2016.0039

Laver, M.: Titanium dioxide whites. In: FitzHugh, E.W. (ed.) Artist's Pigment A Handbook of Their Historical Character, vol. 3, pp. 295–339. National Gallery of Art, Washington & Oxford University Press, Oxford (1997)

Leona, M.: Microanalysis of organic pigments and glazes in polychrome works of art by surface-enhanced resonance Raman scattering. Proc. Natl. Acad. Sci. **106**, 14757–14762 (2009). https://doi.org/10.1073/pnas.0906995106

Leona, M., Stenger, J., Ferloni, E.: Application of surface-enhanced Raman scattering techniques to the ultrasensitive identification of natural dyes in works of art. J. Raman Spectrosc. **37**, 981–992 (2006). https://doi.org/10.1002/jrs.1582

Leona, M., Decuzzi, P., Kubic, T.A., Gates, G., Lombardi, J.R.: Nondestructive identification of natural and synthetic organic colorants in works of art by surface enhanced Raman scattering. Anal. Chem. **83**, 3990–3993 (2011). https://doi.org/10.1021/ac2007015

Liao, Z., Sinjab, F., Gibson, G., Padgett, M., Notingher, I.: DMD-based software-configurable spatially-offset Raman spectroscopy for spectral depth-profiling of optically turbid samples. Opt. Express. **24**, 12701 (2016). https://doi.org/10.1364/OE.24.012701

Lombardi, J.R.: In: Brown, T.G., Creath, K., Kogelnik, H., Kriss, M.A., Schmit, J., Weber, M.J. (eds.) Radiation Interaction with Molecules Opt. Encyclopedia, pp. 2603–2635. Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim (2007). https://doi.org/10.1002/9783527600441.oe082

Londero, P.S., Lombardi, J.R., Leona, M.: Laser ablation surface-enhanced Raman microspectroscopy. Anal. Chem. **85**, 5463–5467 (2013). https://doi.org/10.1021/ac400440c

Long, D.: The Raman Effect: A Unified Treatment of the Theory of Raman Scattering by Molecules. Wiley, Chichester (2002)

Lucas, H.B., Silva, H.J.A., Tasayco, C.M.S., Munayco, P., Faria, J.L.B.: Archaeological pottery from Nasca culture studied by Raman and Mössbauer spectroscopy combined with X-ray diffraction. Vib. Spectrosc. **97**, 140–145 (2018). https://doi.org/10.1016/j.vibspec.2018.06.010

Maguregui, M., Knuutinen, U., Martínez-Arkarazo, I., Giakoumaki, A., Castro, K., Madariaga, J.M.: Field Raman analysis to diagnose the conservation state of excavated walls and wall

paintings in the archaeological site of Pompeii (Italy). J. Raman Spectrosc. **43**, 1747–1753 (2012). https://doi.org/10.1002/jrs.4109

Maguregui, M., Castro, K., Morillas, H., Trebolazabala, J., Knuutinen, U., Wiesinger, R., et al.: Multianalytical approach to explain the darkening process of hematite pigment in paintings from ancient Pompeii after accelerated weathering experiments. Anal. Methods. **6**, 372–378 (2014). https://doi.org/10.1039/C3AY41741G

Marcaida, I., Maguregui, M., Morillas, H., Prieto-Taboada, N., de Vallejuelo, S.F.-O., Veneranda, M., et al.: In situ non-invasive characterization of the composition of Pompeian pigments preserved in their original bowls. Microchem. J. **139**, 458–466 (2018). https://doi.org/10.1016/j.microc.2018.03.028

Marucci, G., Beeby, A., Parker, A.W., Nicholson, C.E.: Raman spectroscopic library of medieval pigments collected with five different wavelengths for investigation of illuminated manuscripts. Anal. Methods. **10**(10), 1219–1236 (2018)

Matousek, P., Clark, I.P., Draper, E.R.C., Morris, M.D., Goodship, A.E., Everall, N., et al.: Subsurface probing in diffusely scattering media using spatially offset Raman spectroscopy. Appl. Spectrosc. **59**, 393–400 (2005). https://doi.org/10.1366/0003702053641450

Matousek, P., Conti, C., Colombo, C., Realini, M.: Monte Carlo simulations of subsurface analysis of painted layers in micro-scale spatially offset Raman spectroscopy. Appl. Spectrosc. **69**, 1091–1095 (2015). https://doi.org/10.1366/15-07894

Matousek, P., Conti, C., Realini, M., Colombo, C.: Micro-scale spatially offset Raman spectroscopy for non-invasive subsurface analysis of turbid materials. Analyst. **141**, 731–739 (2016). https://doi.org/10.1039/C5AN02129D

Matthiae, M., Kristensen, A.: Hyperspectral spatially offset Raman spectroscopy in a microfluidic channel. Opt. Express. **27**, 3782 (2019). https://doi.org/10.1364/OE.27.003782

McCreery, R.: Raman Spectroscopy for Chemical Analysis. Wiley, New York (2000)

Morillas, H., Maguregui, M., Bastante, J., Huallparimachi, G., Marcaida, I., García-Florentino, C., et al.: Characterization of the Inkaterra rock shelter paintings exposed to tropical climate (Machupicchu, Peru). Microchem. J. **137**, 422–428 (2018). https://doi.org/10.1016/j.microc.2017.12.003

Nevin, A., Melia, J.L., Osticioli, I., Gautier, G., Colombini, M.P.: The identification of copper oxalates in a 16th century Cypriot exterior wall painting using micro FTIR, micro Raman spectroscopy and Gas Chromatography-Mass Spectrometry. J. Cult. Herit. **9**, 154–161 (2008). https://doi.org/10.1016/j.culher.2007.10.002

Newman, J., Chen, K., Leona, M., Vo-Dinh, T.: Surface-enhanced Raman scattering for identification of organic pigments and dyes in works of art and cultural heritage material. Sens. Rev. **27**, 109–120 (2007)

Pitarch, A., Ruiz, J.F., Fdez-Ortiz De Vallejuelo, S., Hernanz, A., Maguregui, M., Madariaga, J.M.: In situ characterization by Raman and X-ray fluorescence spectroscopy of post-Paleolithic blackish pictographs exposed to the open air in Los Chaparros shelter (Albalate del Arzobispo, Teruel, Spain). Anal. Methods. **6**, 6641–6650 (2014)

Pozzi, F., Leona, M.: Surface-enhanced Raman spectroscopy in art and archaeology. J. Raman Spectrosc. **47**, 67–77 (2016). https://doi.org/10.1002/jrs.4827

Pozzi, F., Lombardi, J.R., Bruni, S., Leona, M.: Sample treatment considerations in the analysis of organic colorants by surface-enhanced Raman scattering. Anal. Chem. **84**, 3751–3757 (2012). https://doi.org/10.1021/ac300380c

Pozzi, F., Lombardi, J.R., Leona, M.: Winsor & Newton original handbooks: a surface-enhanced Raman scattering (SERS) and Raman spectral database of dyes from modern watercolor pigments. Herit. Sci. **1**, 23 (2013). https://doi.org/10.1186/2050-7445-1-23

Pozzi, F., van den Berg, K.J., Fiedler, I., Casadio, F.: A systematic analysis of red lake pigments in French Impressionist and Post-Impressionist paintings by surface-enhanced Raman spectroscopy (SERS). J. Raman Spectrosc. **45**, 1119–1126 (2014). https://doi.org/10.1002/jrs.4483

Pozzi, F., Basso, E., Rizzo, A., Cesaratto, A., Tague Jr., T.J.: Evaluation and optimization of the potential of a handheld Raman spectrometer: in situ, noninvasive materials characterization in artworks. J. Raman Spectrosc. **50**, jrs.5585 (2019). https://doi.org/10.1002/jrs.5585

Prieto-Taboada, N., Fdez-Ortiz de Vallejuelo, S., Santos, A., Veneranda, M., Castro, K., Maguregui, M., et al.: Understanding the degradation of the blue colour in the wall paintings of Ariadne's house (Pompeii, Italy) by non-destructive techniques. J. Raman Spectrosc. **52**, 85–94 (2021). https://doi.org/10.1002/jrs.5941

Realini, M., Botteon, A., Conti, C., Colombo, C., Matousek, P.: Development of portable defocusing micro-scale spatially offset Raman spectroscopy. Analyst. **141**, 3012–3019 (2016). https://doi.org/10.1039/C6AN00413J

Realini, M., Conti, C., Botteon, A., Colombo, C., Matousek, P.: Development of a full micro-scale spatially offset Raman spectroscopy prototype as a portable analytical tool. Analyst. **142**, 351–355 (2017). https://doi.org/10.1039/C6AN02470J

Retko, K., Ropret, P., Cerc Korošec, R.: Surface-enhanced Raman spectroscopy (SERS) analysis of organic colourants utilising a new UV-photoreduced substrate. J. Raman Spectrosc. **45**, 1140–1146 (2014). https://doi.org/10.1002/jrs.4533

Rousaki, A., Bellelli, C., Carballido Calatayud, M., Aldazabal, V., Custo, G., Moens, L., et al.: Micro-Raman analysis of pigments from hunter-gatherer archaeological sites of North Patagonia (Argentina). J. Raman Spectrosc. **46**, 1016–1024 (2015). https://doi.org/10.1002/jrs.4723

Rousaki, A., Botteon, A., Colombo, C., Conti, C., Matousek, P., Moens, L., et al.: Development of defocusing micro-SORS mapping: a study of a 19th century porcelain card. Anal. Methods. **9**, 6435–6442 (2017a). https://doi.org/10.1039/C7AY02336G

Rousaki, A., Vázquez, C., Aldazábal, V., Bellelli, C., Carballido Calatayud, M., Hajduk, A., et al.: The first use of portable Raman instrumentation for the in situ study of prehistoric rock paintings in Patagonian sites. J. Raman Spectrosc. **48**, 1459–1467 (2017b). https://doi.org/10.1002/jrs.5107

Rousaki, A., Moens, L., Vandenabeele, P.: Archaeological investigations (archaeometry). Phys. Sci. Rev. **3** (2018a). https://doi.org/10.1515/psr-2017-0048

Rousaki, A., Vargas, E., Vázquez, C., Aldazábal, V., Bellelli, C., Carballido Calatayud, M., et al.: On-field Raman spectroscopy of Patagonian prehistoric rock art: pigments, alteration products and substrata. TrAC Trends Anal. Chem. **105**, 338–351 (2018b). https://doi.org/10.1016/j.trac.2018.05.011

Rousaki, A., Pincé, P., Lycke, S., Harth, A., Martens, M., Moens, L., et al.: In situ and laboratory analysis on the polychromy of the Ghent Pantheon cork model by Antonio Chichi. Eur. Phys. J. Plus. **134**, 375 (2019). https://doi.org/10.1140/epjp/i2019-12754-3

Rousaki, A., Costa, M., Saelens, D., Lycke, S., Sánchez, A., Tuñón, J., et al.: A comparative mobile Raman study for the on field analysis of the Mosaico de los Amores of the Cástulo Archaeological Site (Linares, Spain). J. Raman Spectrosc. **51**, 1913–1923 (2020). https://doi.org/10.1002/jrs.5624

Saverwyns, S.: Russian avant-garde … or not? A micro-Raman spectroscopy study of six paintings attributed to Liubov Popova. J. Raman Spectrosc. **41**, 1525–1532 (2010). https://doi.org/10.1002/jrs.2654

Scherrer, N.C., Stefan, Z., Francoise, D., Annette, F., Renate, K.: Synthetic organic pigments of the 20th and 21st century relevant to artist's paints: Raman spectra reference collection. Spectrochim. Acta Part A Mol. Biomol. Spectrosc. **73**, 505–524 (2009). https://doi.org/10.1016/j.saa.2008.11.029

Schulte, F., Brzezinka, K.W., Lutzenberger, K., Stege, H., Panne, U.: Raman spectroscopy of synthetic organic pigments used in 20th century works of art. J. Raman Spectrosc. **39**, 1455–1463 (2008). https://doi.org/10.1002/jrs.2021

Sekar, S.K.V., Mosca, S., Farina, A., Martelli, F., Taroni, P., Valentini, G., et al.: Frequency offset Raman spectroscopy (FORS) for depth probing of diffusive media. Opt. Express. **25**, 4585 (2017). https://doi.org/10.1364/OE.25.004585

Sessa, C., Weiss, R., Niessner, R., Ivleva, N.P., Stege, H.: Towards a Surface Enhanced Raman Scattering (SERS) spectra database for synthetic organic colourants in cultural heritage. The effect of using different metal substrates on the spectra. Microchem. J. **138**, 209–225 (2018). https://doi.org/10.1016/j.microc.2018.01.009

Smith, G.D., Clark, R.J.H.: The role of H2S in pigment blackening. J. Cult. Herit. **3**, 101–105 (2002). https://doi.org/10.1016/S1296-2074(02)01173-1

Smith, E., Dent, G.: Modern Raman Spectroscopy – A Practical Approach. Wiley, Chichester (2004). https://doi.org/10.1002/0470011831

Stone, N., Baker, R., Rogers, K., Parker, A.W., Matousek, P.: Subsurface probing of calcifications with spatially offset Raman spectroscopy (SORS): future possibilities for the diagnosis of breast cancer. Analyst. **132**, 899 (2007). https://doi.org/10.1039/b705029a

Tobias, R.S.: Raman spectroscopy in inorganic chemistry. J. Chem. Educ. **44**, 70 (1967). https://doi.org/10.1021/ed044p70

Tomasini, E., Palamarczuk, V., Zalduendo, M.M., Halac, E.B., Porto López, J.M., Fuertes, M.C.: The colors of San José pottery from Yocavil valley, Argentine Northwest. Strategy for the characterization of archaeological pigments using non-destructive techniques. J. Archaeol. Sci. Rep. **29**, 102123 (2020). https://doi.org/10.1016/j.jasrep.2019.102123

Tournié, A., Prinsloo, L.C., Paris, C., Colomban, P., Smith, B.: The first in situ Raman spectroscopic study of san rock art in South Africa: procedures and preliminary results. J. Raman Spectrosc. **42**, 399–406 (2011)

Vagnini, M., Gabrieli, F., Daveri, A., Sali, D.: Handheld new technology Raman and portable FT-IR spectrometers as complementary tools for the in situ identification of organic materials in modern art. Spectrochim. Acta. Part A Mol. Biomol. Spectrosc. **176**, 174–182 (2017). https://doi.org/10.1016/j.saa.2017.01.006

Van de Voorde, L., Van Pevenage, J., De Langhe, K., De Wolf, R., Vekemans, B., Vincze, L., et al.: Non-destructive in situ study of "Mad Meg" by Pieter Bruegel the Elder using mobile X-ray fluorescence, X-ray diffraction and Raman spectrometers. Spectrochim. Acta Part B At. Spectrosc. **97**, 1–6 (2014). https://doi.org/10.1016/j.sab.2014.04.006

Vandenabeele, P.: Practical Raman Spectroscopy – An Introduction. Wiley, Chichester (2013). https://doi.org/10.1002/9781119961284

Vandenabeele, P., Donais, M.K.: Mobile spectroscopic instrumentation in archaeometry research. Appl. Spectrosc. **70**, 27–41 (2016). https://doi.org/10.1177/0003702815611063

Vandenabeele, P., Wehling, B., Moens, L., Dekeyzer, B., Cardon, B., von Bohlen, A., et al.: Pigment investigation of a late-medieval manuscript with total reflection X-ray fluorescence and micro-Raman spectroscopy. Analyst. **124**, 169–172 (1999). https://doi.org/10.1039/a807343k

Vandenabeele, P., Moens, L., Edwards, H.G.M., Dams, R.: Raman spectroscopic database of azo and application to modern art studies. J. Raman Spectrosc. **31**, 509–517 (2000a). https://doi.org/10.1002/1097-4555(200006)31:6<509::AID-JRS566>3.0.CO;2-0

Vandenabeele, P., Wehling, B., Moens, L., Edwards, H., De Reu, M., Van Hooydonk, G.: Analysis with micro-Raman spectroscopy of natural organic binding media and varnishes used in art. Anal. Chim. Acta. **407**(1–2), 261–274 (2000b)

Vandenabeele, P., Verpoort, F., Moens, L.: Non-destructive analysis of paintings using Fourier transform Raman spectroscopy with fibre optics. J. Raman Spectrosc. **32**, 263–269 (2001). https://doi.org/10.1002/jrs.691

Vandenabeele, P., Grimaldi, D.M., Edwards, H.G., Moens, L.: Raman spectroscopy of different types of Mexican copal resins. Spectrochim. Acta A Mol. Biomol. Spectrosc. **59**(10), 2221–2229 (2003)

Vandenabeele, P., Weis, T.L., Grant, E.R., Moens, L.J.: A new instrument adapted to in situ Raman analysis of objects of art. Anal. Bioanal. Chem. **379**, 137–142 (2004). https://doi.org/10.1007/s00216-004-2551-z

Vandenabeele, P., Bodé, S., Alonso, A., Moens, L.: Raman spectroscopic analysis of the Maya wall paintings in Ek'Balam, Mexico. Spectrochim. Acta. Part A Mol. Biomol. Spectrosc. **61**, 2349–2356 (2005a). https://doi.org/10.1016/j.saa.2005.02.034

Vandenabeele, P., Lambert, K., Matthys, S., Schudel, W., Bergmans, A., Moens, L.: In situ analysis of mediaeval wall paintings: a challenge for mobile Raman spectroscopy. Anal. Bioanal. Chem. **383**, 707–712 (2005b). https://doi.org/10.1007/s00216-005-0045-2

Vandenabeele, P., Castro, K., Hargreaves, M., Moens, L., Madariaga, J.M., Edwards, H.G.M.: Comparative study of mobile Raman instrumentation for art analysis. Anal. Chim. Acta. **588**, 108–116 (2007a). https://doi.org/10.1016/j.aca.2007.01.082

Vandenabeele, P., Tate, J., Moens, L.: Non-destructive analysis of museum objects by fibre-optic Raman spectroscopy. Anal. Bioanal. Chem. **387**, 813–819 (2007b). https://doi.org/10.1007/s00216-006-0758-x

Vandenabeele, P., Christensen, M.C., Moens, L.: Analysis of South-Asian Shaman paintings at the national museum of Denmark. J. Raman Spectrosc. **39**, 1030–1034 (2008). https://doi.org/10.1002/jrs.1905

Vandenabeele, P., Garcia-Moreno, R., Mathis, F., Leterme, K., Van Elslande, E., Hocquet, F.-P., et al.: Multi-disciplinary investigation of the tomb of Menna (TT69), Theban Necropolis, Egypt. Spectrochim. Acta. Part A Mol. Biomol. Spectrosc. **73**, 546–552 (2009). https://doi.org/10.1016/j.saa.2008.07.028

Vandenabeele, P., Edwards, H.G.M., Jehlička, J.: The role of mobile instrumentation in novel applications of Raman spectroscopy: archaeometry, geosciences, and forensics. Chem. Soc. Rev. **43**, 2628 (2014). https://doi.org/10.1039/c3cs60263j

Vandenabeele, P., Conti, C., Rousaki, A., Moens, L., Realini, M., Matousek, P.: Development of a fiber-optics microspatially offset Raman spectroscopy sensor for probing layered materials. Anal. Chem. **89**, 9218–9223 (2017). https://doi.org/10.1021/acs.analchem.7b01978

Wehling, B., Vandenabeele, P., Moens, L., Klockenkämper, R., von Bohlen, A., Van Hooydonk, G., et al.: Investigation of pigments in medieval manuscripts by micro raman spectroscopy and total reflection X-ray fluorescence spectrometry. Microchim. Acta. **130**, 253–260 (1999). https://doi.org/10.1007/BF01242913

Zalaffi, M.S., Agostinelli, I., Karimian, N., Ugo, P.: Ag-nanostars for the sensitive SERS detection of dyes in artistic cross-sections – Madonna della Misericordia of the National Gallery of Parma: a case study. Heritage. **3**, 1344–1359 (2020). https://doi.org/10.3390/heritage3040074

Zoleo, A., Rossi, C., Poggi, G., Rossi, M., Meneghetti, M., Baglioni, P.: Spotting aged dyes on paper with SERS. Phys. Chem. Chem. Phys. **22**, 24070–24076 (2020). https://doi.org/10.1039/D0CP04099A