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A Decade of Raman Spectroscopy in Art and Archaeology

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1. Introduction

During the past decade, Raman spectroscopy has been increasingly applied for the analysis of objects of art and antiquities. Since the publication of the database of Raman spectra of pre-1850 pigments by Bell et al.,¹ the application of this technique in this field has grown exponentially. Although this database and the papers from several groups that appeared around the same time introduced many people to this research field, these were not the first applications of Raman microspectroscopy in art analysis. In 1979 Dhamelin-court et al.² described the coupling of a microscope to a Raman spectrometer and the application to the investigation of artifacts. In general, the first papers^{3,4} focused on instrumental improvements and explored the feasibility of the approach for the investigation of artifacts,^{5–7} centering mainly on pigment identification. Historically, in Raman spectroscopy, the major advances and novelty of applications have always been instrument driven.

The increasing importance of the Raman spectroscopic technique in the investigation of antiquities and art objects

is illustrated by the number of research papers that are published each year. Figure 1 shows the evolution of the published primary papers in this research field, based on a survey in the Web of Science. Despite the fact that older papers and journals are not always included in the Web of Science and that some groups tended to publish their results in local bulletins of their institutions, which are not included in the database, the trend is clear. This evolution is also reflected in the increased number of research groups that are publishing over time: in 1995 about 5 groups published research papers in this field, while in 2005 this number had risen to about 20. It should be remarked that the definition of a “research group” is quite arbitrary in this context, since often research projects are undertaken by combinations of different groups. Figure 1 also shows that there is an increasing interest in archaeometric research, but it is clear that Raman spectroscopy is becoming more important in this field. It has to be noted that the relative contribution of Raman spectroscopy in this field is an underestimation, since the papers in the subgroup were manually checked for their relevance, which was not done for the larger set. However, several relevant works give a general overview of interesting issues in archaeometry.^{8–11}

The increasing importance of this research field is also illustrated by the scientific conferences and sessions that have been dedicated to Raman spectroscopy and its applications to art and archaeology. Examples are the series of GeoRaman conferences that since the 1999 meeting have had a special session on this field and the FACSS conferences in 2002 and 2004. The first symposium totally dedicated to the application of Raman spectroscopy in art and archaeology was a very successful 1-day meeting held in the British Museum in November 2001. Later, more extended symposia followed in Ghent (Belgium, 2003) and Paris (France, 2005), and one is scheduled for Modena (Italy) in September 2007. These meetings have resulted in a special issue of *Journal of Raman Spectroscopy*.^{12,13} The first book dedicated to this topic, based on the meeting at the British Museum, was edited by H. G. M. Edwards and J. Chalmers and appeared in 2005.¹⁴ The Infrared and Raman Users Group (IRUG)

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Peter Vandenabeele works as a postdoctoral fellow at Ghent University, where he performs research in analytical Raman spectroscopy. The main fields of application are archaeometry, microbiology, pharmaceutical analysis, and geology. He authored or coauthored more than 30 peer-reviewed research papers on this subject as well as some chapters in books. He organized the International Conference on the application of Raman spectroscopy in art and archaeology in Ghent in September 2003.



Prof. Howell G. M. Edwards is professor in molecular spectroscopy at the University of Bradford. He has published more than 300 research papers and book chapters on Raman spectroscopy, in the domains of art and archaeology, forensics, astrobiology, etc. He organized several conference sessions on this subject and a dedicated meeting on Raman spectroscopy in art and archaeology in the British Museum.

organizes a biannual conference dedicated to this subject, and IRUG 7 was held in New York in 2006.

This literature review is focused on key issues and trends in Raman research in the field of art and archaeology during the past decade (1995 to summer 2006). Important topics include the construction of spectral libraries, the evolution in Raman instrumentation, pigment analysis, the identification of organic molecules, corrosion, ceramics and glass, the different types of research questions that have been posed, and the different types of art objects under investigation.

2. Spectral Libraries and Chemometrics

Raman spectroscopic materials identification is often based on the comparison of the Raman spectrum of the unknown substance with a spectral library of reference materials. One of the first spectral libraries to have been published is that from University College London,¹ which gives an overview of the Raman spectra of 56 inorganic pigments similar to those used before 1850. The first paper described Raman spectra recorded with HeNe (632.8 nm) and Ar⁺ (514.5 nm) lasers, while Burgio and Clark extended this database in a



Prof. Luc Moens is professor in analytical chemistry and vice-rector of Ghent University. His research concerns mass spectroscopy and Raman spectroscopy, often dedicated to archaeometry. The main topic of his research group is the development of analytical methods with application fields in biomedical, environmental, geological, archaeometrical, and industrial analysis.

later publication, which included some organic materials examined using longer wavelength laser excitation (1064, 647.1, and 780 nm).¹⁵ This work is easily accessible through the Internet, and therefore, it forms a good starting point for people who are new in the field. Other extensive spectral libraries include e-VISART¹⁶ and the COLORAMAN project (<http://www.ct.infn.it/~arceo/>).¹⁷ The e-VISART database contains in addition infrared spectra relevant to the same artists' materials. Castro et al. give an overview of several databases that are available on the Internet¹⁶ which contain mostly reference spectra of mineral pigments. Several on-line databases are available, including those from LENS in Florence (Italy, <http://srv.chim.unifi.it/raman/>), the Dipartimento di Scienze della Terra in Siena (Italy, <http://www.dst.unisi.it/geofluids-lab/>), and D. Bersani from Parma (Italy, <http://www.fis.unipr.it/~bersani/raman/raman/spettri.htm>). The Web site of the Californian Institute of Technology contains an extensive database of Raman spectra of minerals (<http://minerals.gps.caltech.edu/files/raman/>), as well as links to other interesting spectral databases, such as those of Ens in Lyon (France, <http://www.ens-lyon.fr/LST/Raman/index.php>), of the RRUFF project in Arizona (USA, <http://rruff.geo.arizona.edu/rruff/>), and of the National Institute of Advanced Industrial Science and Technology (aist) in Nagoya (Japan, http://www.aist.go.jp/RIODB/rasmin/E_index.htm). The Infrared and Raman Users Group (IRUG, <http://www.irug.org/>) manages an extensive spectral library, containing mainly infrared spectra as well as some Raman data of artists' materials. These databases are usually focused on old materials, mainly pigments, while contemporary artists' materials have hitherto remained rather neglected; this can probably be ascribed to the significantly large number of organic synthetic dyes and pigments which have been synthesized and used in modern art work.

Apart from digital spectral libraries, some authors have published a series of papers with spectral data dedicated to specific types of materials.^{18,19} For example, the Raman spectra of a broad range of minerals have been published by R. Frost et al.,^{20–26} while the group of H.G.M. Edwards et al. has published several papers containing the FT-Raman spectra of biomaterials.^{27–38} Some papers also contain an overview of dispersive Raman spectra of specific groups of artists' materials which can be useful for their identification.^{39–41}

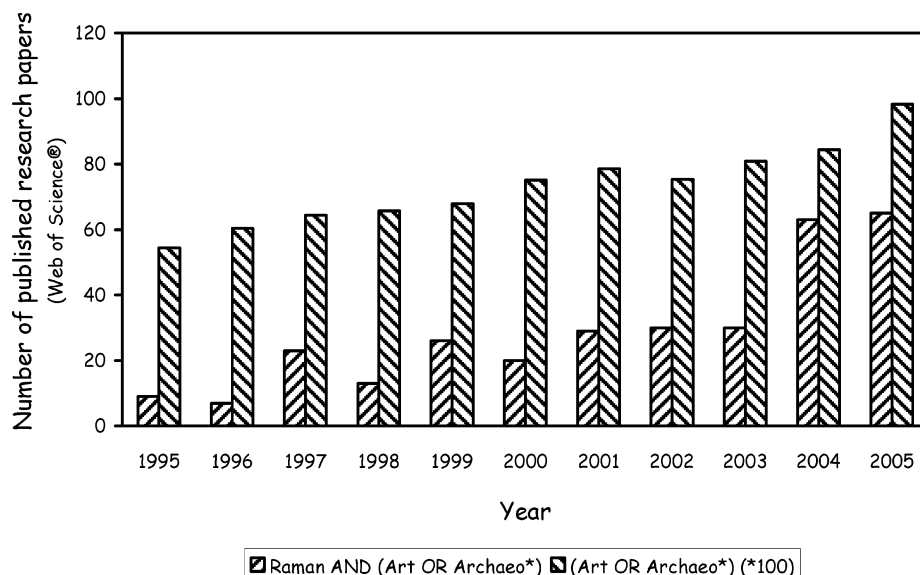


Figure 1. Evolution of the number of research papers on Raman spectroscopy in art and archaeology (1994–2005), after a survey on the Web of Science. The total number of research papers on art and archaeology is mentioned as well (number cited divided by 100).

The main obstacles to the comparison and merging of Raman spectral databases established in different laboratories are related to spectral differences caused by different laser wavelengths, inadequately described calibration routines adopted in these different laboratories, and the comparison between data reported in different data formats. The latter issue is perceived to be perhaps one of the major challenges to the construction of a unified Raman spectroscopic database in the near future, apart from the definition of high performance and rapid-searching algorithms.

In previous studies, chemometric methods have been applied to Raman spectroscopic data in the development of spectral searching algorithms. For instance, data reduction methods, such as principal components analysis (PCA), have been used as spectral searching algorithms for pigment identification^{42–44} while Ramos et al.⁴⁵ and Castanys Tutzó et al.⁴⁶ have applied the more complex fuzzy logic method⁴⁵ for pigment identification. FT-Raman spectra of ivories of different mammalian origins could also be distinguished from each other using chemometrics techniques.^{35,47} Several authors have used the PCA methodology in combination with derivative procedures to eliminate contributions from fluorescence emission backgrounds,^{48–51} while Bell et al. were able to identify the dyes of ancient Chinese papers by subtracting Raman spectra recorded with slightly different laser wavelengths^{52,53} and using a differential subtraction technique which effectively eliminated the fluorescence background signal. Wavelet transformations have also been used for this purpose.⁵⁴ Analysis of Variance (ANOVA) tests have been used to study paint layers of household paint flakes in a forensic context,^{50,55} and multivariate data processing methods have been used for the study of degradation processes and conservation states of artifacts,^{56,57} although much care should be taken in the interpretation of the latter results, as it is not straightforward to correlate the observed changes with the physical or molecular changes that occur during degradation.

It is to be expected that future research projects will focus on the extension of spectral libraries and that, apart from ancient inorganic pigments, organic molecules and modern synthetic artists' materials will necessarily be included. It is

also likely that spectral searching algorithms will be improved to assist the extraction of comparison data and that future efforts will be made to usefully merge existing databases and to improve the possibilities of the exchange of spectra recorded with different data formats.

3. Instrumentation

As stated earlier, many important landmarks in the evolution of Raman spectroscopy can be directly attributed to improvements in instrument technology; this certainly also applies in the case of Raman spectroscopy applied to art and archaeology. Several papers have stressed the confocal properties⁵⁸ of the micro-Raman instruments used in the investigations and the effective spatial resolutions thereby achieved in the experiments.^{59–61} Confocality refers to the ability to achieve high axial spatial resolution by the use of a confocal pinhole.^{2,62,63} Apart from this, most papers stress the nondestructive character of the micro-Raman spectroscopic technique, provided the laser power is kept sufficiently low.^{5,64,65} With the introduction of fiber optic instrumentation in this field,⁶⁶ the way was seen to be then open to the use of mobile Raman instrumentation for art analysis in museums and in the field.^{67,68}

In the literature, there is often some confusion when using the term “in situ investigation”. Strictly speaking, this refers to investigations where the instrument was transported to the location of the art object (e.g., museum, church, etc.) and, of course, this does not involve specimen sampling at all. Some papers misuse this term to mean “direct investigations of an artifact”, for which investigations no sampling was carried out, but which really necessitated the transportation of the artifact to the analytical laboratory. The term has also been misapplied to the Raman spectroscopic studies of specimens that have been taken during conservation procedures and for which no further sampling is required, an example of which is provided by the spectral characterization of a multiple layered paint fragment which has been mounted for analytical optical microscopy and for which further nondetachment is not necessary. Similarly, authors should be careful when describing “portable” equipment, when

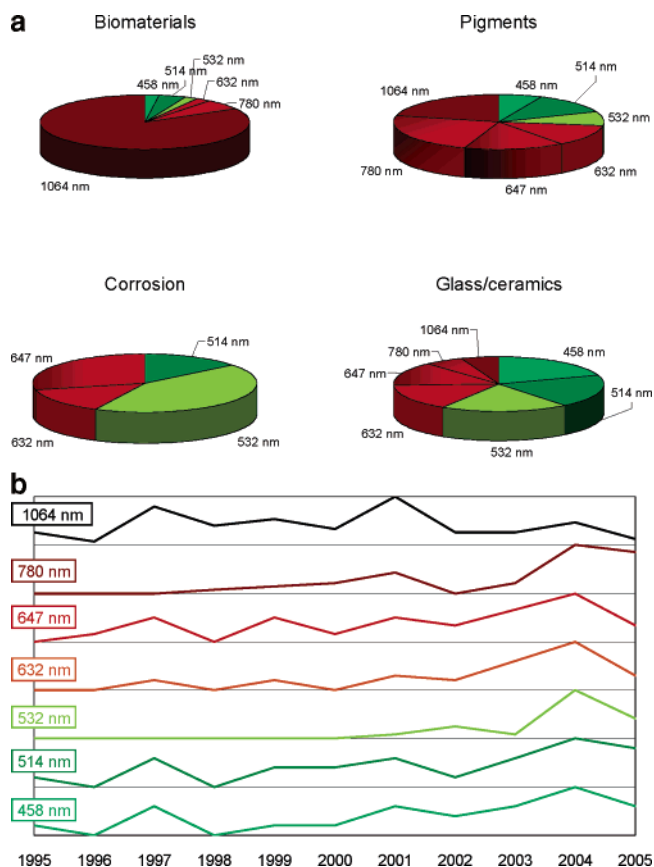


Figure 2. Use of different lasers as a function of their field of application and as a function of time.

normally “mobile” equipment would be a more correct description.

In situ investigations actually represent a difficult analytical challenge. There are the need to perform microinvestigations of complex samples, such as mixtures of pigments and an amorphous and often fluorescing organic binding medium, and the requirement to obtain as much information as possible from unique artifacts, which is de rigueur for all investigations in archaeometry. Complex chemical pathways such as degradation processes of biomaterials or interactions between inorganic and organic materials have to be considered as part of any analytical investigation portfolio in art and archaeology. Apart from these points, prevailing environmental conditions that apply during in situ investigations are often far removed from the ideal laboratory conditions; there is, in addition, an absolute need to work nondestructively with a large inhomogeneous object, a condition which is usually less stringently imposed when operating with a sample, and often, time and spatial restraints are applied.⁶⁹

Figure 2 illustrates the use of different lasers for specific Raman spectroscopic applications in the area of art and archaeology during the past decade. It is clear that the choice of the laser wavelength is related to the application; for example, when organic matter is being examined, FT-Raman instruments, operating with a Nd:YAG laser (1064 nm) in the near-infrared, are often preferred because of the improved rejection of fluorescence emission, while, for the examination of corrosion products or pottery fragments, green or blue lasers are selected because of the preferential sensitivity for the recording of mineral oxides and sulfides. Most pigment investigations are performed using a red laser. However, especially in pigment analysis, many authors still apply

several lasers for their Raman spectroscopic research to remove the likelihood of sample degradation being experienced with some systems.⁷⁰

When following the evolution of the number of published Raman research papers using a specific laser wavelength (Figure 2b), it is remarkable that the applications of most laser wavelengths are seen to be on the increase since 2004. This can be partially explained by the increase in the total number of research papers (Figure 1), although a problem arises from the adoption of multiple lasers in many studies now appearing. From these plots it is clear that the first published work using diode lasers (780–785 nm) only appeared in 1998 and that frequency-doubled Nd:YAG lasers (532 nm) in Raman spectroscopy of art and archaeological materials have only been used since 2001. These lasers seem to have now become very popular in this field. Solid-state lasers have the particular advantage over gas lasers in that they are less sensitive to shocks, which is important, for instance, when selecting a laser for mobile Raman equipment.

Another noted trend in the recent Raman spectroscopic analysis of artistic and archaeological objects is that research groups are now reporting the results of the combination of different analytical techniques. This evolution is self-evident, since the aim of archaeometrical research is to extract as much information as possible from a precious object while at the same time minimizing the damage. In most cases of artifacts that are being examined in the analytical laboratory, the release of the article from its museum or archival storage has only been achieved after prolonged consideration and granting of permission. Therefore, combined approaches, where complementary information can be obtained reasonably rapidly within a set time frame from the same sample or same spot on the artifact, are often used. Raman spectroscopy is often combined with an atomic or elemental analytical method, such as X-ray fluorescence spectroscopy or scanning electron microscopy. Examples of this approach are the investigation of mediaeval manuscripts⁷¹ and Egyptian burial masks⁷² by total-reflection X-ray fluorescence (TXRF) and Raman spectroscopy. The combination between proton-induced X-ray analysis (PIXE) and Raman spectroscopy has been illustrated by, among others, the analysis of Gustave Moreau's drawings,⁷³ a mediaeval altarpiece,⁷⁴ gemstones,⁷⁵ mediaeval frescoes,⁷⁶ a painting attributed to Botticelli,⁷⁷ stained glass windows,^{78–80} and a Mexican canvas painting.⁸¹ Raman spectroscopy has been combined with X-ray fluorescence (XRF) techniques during the investigation of ceramics,^{82,83} panel paintings,^{84,85} and wall paintings.⁸⁶ LIBS (laser induced breakdown spectroscopy) has been combined with Raman spectroscopy⁸⁷ for the examination of icons,^{82,83} painted plasters,⁸⁰ and polychromes on wood.^{90,91} Raman spectroscopy with GCMS⁹² and SEM/XRD combinations^{93,94} have also been reported. It is also interesting that the combination of the Raman and infrared spectroscopic techniques for the analysis of art and archaeological objects is rather rare.^{95,96}

4. Pigment Analysis

Pigment investigation is one of the most active research domains within art analysis using Raman spectroscopy.⁹⁷ The identification of pigments in artworks can provide information on the date of manufacture of the object or can help to decide on future restoration actions. This can also be useful to expose forgeries.⁹⁸ The Raman spectroscopic analysis of manuscripts has been mainly concerned with the pigment

investigation of European mediaeval books or loose parchment leaves^{58,59,71,99–112} but also extends to other periods or regions (e.g. Iceland,¹¹³ Persia,^{114,115} China,⁵² Japan,¹¹⁶ or Java, Thailand, Korea, China, and Uighur¹¹⁷). Some publications go beyond the identification of the pigments but try to find relations between manuscript decorators and scriptoria¹¹⁸ or try to differentiate between painters¹¹⁹ and give an overview of the use of a specific class of pigments over a wider period or region.¹²⁰

Whereas several papers have been published on the pigment analysis of manuscripts, the application of the technique has widened toward other types of artifacts, such as antique polychrome objects,^{72,90,121–128} canvas and panel paintings,^{40,42,66,81,84,129–132} minerals,^{133,134} rock paintings,^{135–144} or wall paintings.^{76,145–166} Although there seems to be no obvious reason, relatively few research papers have been published on the investigation of panel or canvas easel paintings.

Several papers have been published on the pigment analysis of works on paper, such as lithographs,^{167–172} drawings,^{73,173} and wallpapers.^{174–176} These investigations usually have to be performed with special care, since these artifacts are extremely vulnerable to damage. Bicchieri et al. examined degraded papers with several nondestructive spectroscopic techniques, including Raman spectroscopy.¹⁷⁷ Chaplin et al. used Raman spectroscopy for the investigation of old Hawaiian postage stamps.¹⁷⁸ Others have tried to extend the technique to the investigation of modern and contemporary artists' materials, but since literally thousands of organic synthetic pigments are available in the art world, the identification is frequently hampered by the lack of a sufficiently comprehensive database. However, some successful attempts have been made to record the Raman spectra of synthetic pigments.^{40,42}

One of the interesting controversies to emerge in the art and archaeology field from the past decade using Raman spectroscopy was the investigation of the Vinland map. This map depicts northern Europe and the North-American coast. If authentic, this map would prove that the Norse knew of the existence of this continent before the arrival of Columbus—which would strongly alter our idea of history. Radiocarbon dating of this map revealed a date of the parchment (not the ink) between 1411 and 1468 (95% confidence interval),¹⁷⁹ but statistical corrections have been made which suggest a narrower date range of between 1404 and 1440 AD (95.4% confidence interval).¹⁸⁰ However, anatase (TiO₂) was identified on certain locations associated with the ink lines on the map,^{181–183} which was also confirmed with Raman spectroscopy.^{184,185} Anatase is considered to be a synthetic pigment, which has been produced only since the early 20th century.¹⁸⁶ The anatase particles are seen to be homogeneous in size, which is indicative of a synthetic ground pigment, giving a modern date for the map. The conclusion that the Vinland map is modern^{187–189} is strongly contested.^{190–192} The identification of anatase in the ink is one of the main arguments to say that this is a modern map; however, recent evidence has emerged that titanium white was used not only from the early 20th century but that it had been found in early Roman and Chinese pigments.^{18,193} The fact remains, however, that the shape, color, and narrow size distribution of the anatase particles in the ink on the Vinland map cannot be easily ascribed to a mediaeval mineral source.

Analytical techniques are often used to examine complex chemical reactions that have occurred over time. Degradation

processes, such as the darkening of hydroxycerussite (lead white, 2Pb(CO₃)·Pb(OH)₂) after exposure to H₂S gas, have been studied by IR spectroscopy¹⁹⁴ and Raman spectroscopy.¹⁹⁵ This degradation, with the resulting formation of black galena (PbS), has been observed on a 13th century manuscript.¹⁹⁶ Batonneau et al. have observed the oxidation of galena crystals under laser irradiation, resulting in the formation of PbO.¹⁹⁷ The laser-induced degradation of the black pigment plattnerite (PbO₂) and the red pigment minium (Pb₃O₄) to produce litharge (PbO, tetragonal) and massicot (PbO, orthorhombic) was examined using different laser wavelengths.¹⁹⁸

Several papers have reported on the formation of the yellow photodegradation product pararealgar (As₄S₄) from orange-red realgar (As₄S₄).¹⁹⁹ Since many pigment investigations have hitherto been performed using elemental techniques (e.g., SEM-EDX or XRF), it is not unlikely that many yellow As-containing areas have been misassigned as being the relatively common orpiment (As₂S₃). This point alone is compelling evidence for the adoption of molecular spectroscopic analytical techniques for the analysis of pigments in conjunction with the elemental techniques. Using Raman spectroscopy, pararealgar has been identified in antique Egyptian artifacts,^{72,200} mediaeval manuscripts,^{100,196} portrait miniatures,⁶⁵ panel paintings,^{129,130,201,202} and a Nepalese wall painting.¹⁴⁹ Banerjee et al. performed quantum chemical studies to investigate the transformation and to assign the vibrational spectroscopic bands,²⁰³ while Bonazzi et al. combined Raman spectroscopy with X-ray diffraction^{204,205} to study the transformation and the intermediate phase. One of the most important questions is whether the artists intended to use a yellow or an orange pigment. Moreover, if they applied a yellow pigment, were they aware of the difference between orpiment and pararealgar? Clark and Gibbs found evidence that at least in one mediaeval manuscript there was a hierarchical difference between the use of orpiment and pararealgar.¹⁹⁶ Eremin et al. studied the use of realgar and pararealgar in antique Egyptian sandals where the banded decoration using each pigment implied that the use was quite deliberate.¹²³

Although no obvious reason can be given, research papers reporting on the investigation of statues are quite rare. However, the Raman spectroscopic analysis of pigments applied to a 13th century polychrome stone statue of Santa Ana in Santa Maria la Real, Sasamon, Spain, has successfully identified the materials used.^{125,206} Moreover, this work provides the earliest example found by Raman spectroscopy of the use of mosaic gold pigment (SnS₂) in Europe. Micro-Raman spectroscopy has as well been applied for the investigation of the original paint layers on a polychrome Pieta sculpture.²⁰⁷ Different pigments could be identified, including vermilion (HgS) and lapis lazuli (Na_{8–10}Al₆Si₆O₂₄S_{2–4}), pigments derived from the minerals cinnabar and the semiprecious stone lazulite, respectively.

5. Biomolecules

As seen in Figure 2a, most Raman investigations on biological molecules have been performed by using FT-Raman spectroscopy with Nd:YAG lasers (1064 nm). This is because most natural organic dyes, resins, gums, waxes, and textiles strongly fluoresce in the visible region, which overwhelms the Raman signal. Shifting the excitation wavelength to the near-infrared region can be helpful to avoid

this interference. However, for studying colored materials, such as pigments or dyes, authors advocate the selection of lasers operating in the visible in order to benefit from resonance effects. Dyes are also now being studied by surface enhanced Raman spectroscopy (SERS) or surface enhanced resonance Raman spectroscopy (SERRS).^{208–210} Dispersive Raman spectroscopy has been used to examine natural organic binding media and varnishes.³⁹ However, the identification of these materials on the artwork is often difficult, due to different treatments and mixtures possibly being used and to complications in the Raman spectra arising from the presence of materials resulting from materials degradation.^{211–213}

Several papers have reported the investigation of proteinaceous material with Raman spectroscopy. The Raman spectra of these materials are characterized by the presence of amide I ($\nu(\text{C}=\text{O})$) and amide III ($\delta(\text{CONH})$) bands at about 1650 and 1100 cm^{-1} , respectively. The exact positions of these bands reflect the secondary structure of the protein (that is the amount of α -helix, β -sheet, and random coil conformational structures). The skin of mummified bodies from hot deserts (Chiribaya^{214,215}) and ice deserts (Qilakitsoq,^{214,215} Ötztal^{214–216}) has been studied, and it was found that, although there is a significant difference in burial time and archaeological depositional environment, there is little difference noted spectroscopically between the protein degradation of the skins. A rare case of 1000-year-old penguin tissues, preserved in the Antarctic cold desert, has been studied,²¹⁷ from which it has been possible to note the differential degradation suffered by the keratotic proteins in the penguin fur, claws, skin, and feathers. Some differences observed in the Raman spectra of modern skin, hair, and nails are outlined in the literature,²¹⁸ while the comparison between the spectra of keratotic animal materials (horn, hoof, tortoise shell, and galalith)^{219,220} has been studied and a discrimination protocol reported which will assist in the identification of these materials in archaeological and museum artifacts. Edwards et al. examined historical specimens of human hair attributed to Victorian locomotive engineer Robert Stephenson and polymath Sir Isaac Newton,²²¹ and the extent of their preservation has been assessed. The molecular structure of the proteinaceous materials from parchment was studied by FT-Raman spectroscopy,^{37,222} from which spectroscopic signatures were noted that reflected the original processing technologies undertaken for the preparation of the skin surfaces. The Raman spectra of the proteinaceous fibers wool²²³ and *Bombyx mori* silk²²⁴ have been reported. In contrast to these animal fibers, plant fibers mainly consist of polysaccharides. Andreev et al.²²⁵ have published Raman spectra of some plants and historic textiles, while Edwards et al. have published a more elaborate overview of plant fibers and described the application of this technique for the study of degraded archaeological materials.^{30,33,226} A recent paper addressed the deterioration of a famous and unique historical linen relic, the fore-topsail of HMS Victory, Admiral Horatio Nelson's flagship at the Battle of Trafalgar in 1805, the result of which changed the face of Napoleonic Europe.²²⁷ The artificial deterioration of modern sailcloth simulated to match that of the Victory sail was analyzed by FT-Raman spectroscopy, and the extent of aging was compared with that of the genuine antique sailcloth to effect conservation and repair of the Victory sail—a major undertaking, due to some 90 holes and tears from battle damage and exposure to corrosive seawater, heat, and light.

Another group of biomaterials that have been intensively studied with FT-Raman spectroscopy are ivories. Ivory consists of collagen lamellae embedded in a carbonated hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{CO}_3)\cdot\text{H}_2\text{O}$) matrix.²²⁸ It is important to be able to differentiate between ivory artifacts and deliberate falsifications^{27,229,230} forensically, and the Raman bands of the protein as well as the inorganic matrix have been carefully assigned.²²⁸ It was demonstrated that it is possible to differentiate between ivories of different mammals on the basis of the Raman spectra,^{35,231} which is interesting from the art historical point of view as well as from the forensic point of view. Indeed, according to the Convention on the International Trade in Endangered Species of wild fauna and flora (CITES), the trade in Asian and African elephant ivory, as well as narwhal, sperm whale, wart hog, walrus, and hippopotamus tusk, is illegal, and therefore, it is important to be able to identify the ivory source to trace the route. It is also possible to differentiate between archaeological mammoth and elephant ivory,^{47,232} since biodeterioration has caused the degradation of the proteins in the former. This is often not just a matter of age of the specimen, however, since the actual depositional environment is critically important. Similarly, modern and archaeological human teeth were examined with FT-Raman spectroscopy.²³³

Several papers report on the application of Raman spectroscopy for the examination of plant exudates: resins and gums. The latter group are merely polysaccharides that are soluble or swell in water,³⁴ while the resins are of terpenoid origin and are insoluble in water. The possibilities of Raman spectroscopy for the examination of resins have been tested,^{28,31,234} and the applicability was evaluated with the examination of an archaeological tembaga^{235,236} and of organic remains in 2300-year-old Vietnamese jars.²³⁷ Papers have been published that focus on the typical Raman spectra of resins that have often been used as artists' materials, such as Dragon's blood,³² frankincense, and myrrh.²³⁸ Several papers have studied the fossilized resin amber^{36,239–245} and the semifossilized resin copal.²⁴⁶

Attempts have been made to analyze natural organic dyes with Raman spectroscopy. Traditionally, these colorants are extracted from the artwork or pyrolyzed and analyzed by chromatographic means.²⁴⁷ Raman spectroscopy offers the advantage of noninvasive analysis, but fluorescence often hinders the investigations. Moreover, in its current stage, it seems that the discriminative capabilities of Raman spectroscopy are insufficient to differentiate between closely related dyes. Raman spectroscopy cannot at present achieve detection of very small amounts of dyes in an admixture. However, it still is possible to identify many dyes, in powder form and on textile fibers, by carrying out nondestructive investigations.^{52,248–250}

Several research groups have performed research on indigoid compounds. Indigo is extracted from the tropical *Indigofera* species or from *Isatis tinctoria* in more moderate climate regions. Von Bayer invented the synthetic product in 1880. In addition to these vegetable sources, bromoindigos can be extracted from *murex* shellfish and form the precious Tyrian purple dye. The different types of indigoid dyes have been extensively studied by Raman spectroscopy.^{8,251–253} By using Raman spectroscopy and linear discriminant analysis, it was possible to differentiate between natural and synthetic indigo samples,⁴⁹ although it is still an open question whether it would be possible to make this distinction for real samples. Maya blue is an intercalation product of indigo in a

palygorskite clay matrix and has been extensively studied by Raman spectroscopy.^{146,254} Shadi et al. have used SERRS to investigate indigo²⁵⁵ as well as alizarin and purpurin dyes.^{256,257} The organic dye brazilwood was studied extensively by using FT-Raman spectroscopy.^{38,258} The resonance Raman effect of carotenoids has been studied with different laser wavelengths^{259,260} and has been compared with that of linear polyenes.²⁶¹ The yellow carotenoid dye from saffron (*Crocus sativus* L.) has been studied with FT-Raman spectroscopy.^{262,263} The degradation and preservation of waterlogged archaeological wood has been examined by Raman spectroscopy,²⁶⁴ and acrylic consolidants in wooden objects could be identified.²⁶⁵

6. Corrosion

Raman spectroscopy is extremely well-suited for the investigation of corroded objects. Especially noteworthy is its ability to record molecular spectra with high spatial resolution. The technique allows the investigation of art objects directly and nondestructively, but it is even possible to examine embedded samples and to study the stratigraphy. Since Raman spectroscopy suffers little interference from water, it is possible to study electrochemical processes on electrode surfaces. Although the literature on Raman spectroscopy in corrosion science is quite extensive, the amount of papers on corroded artistic or archaeological objects is rather limited. This is quite surprising, since metals have been omnipresent in archaeological and historical objects since the Bronze Age. Most of these studies have discussed the corrosion of iron, copper, or lead objects.

The presence of corrosion products on historical objects is usually not considered as odious, although heavily corroded objects may lose their strength. A certain degree of patination is considered to contribute to the aesthetic value of the artifact and protects it to some extent against hazardous influences from the air. Therefore, conservators usually prefer not to remove the corrosion layers but rather try to preserve them and to prevent further corrosion.²⁶⁶ The corrosion products that are detected are usually minerals, on which several papers have been published.^{21,22,26,267–271} The study of corrosion products is often associated with pigment analysis. Indeed, similar materials are often retrieved, such as azurite ($2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$), malachite ($\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$), posnjakite ($\text{Cu}_4(\text{OH})_6\text{SO}_4 \cdot \text{H}_2\text{O}$), and brochantite ($\text{Cu}_4(\text{OH})_6\text{SO}_4$).^{120,272} In other studies, the discolored pigments on wall paintings^{146,273} could be identified as copper hydroxyl chlorides (atacamite ($\text{Cu}_2(\text{OH})_3\text{Cl}$), paratacamite ($(\text{Cu,Zn})_2(\text{OH})_3\text{Cl}$)), which are minerals that are also often retrieved during corrosion studies.²⁵

Trentelman et al. have extensively described the corrosion phenomena and their conservation treatment of bronze Chinese money trees.^{274,275} A pale blue corrosion product on different copper alloy artifacts was identified as being a copper formate or acetate.²⁷⁶ Formic or acetic acid vapors are thought to escape from the wooden showcases and cause this corrosion. Hayez et al. studied the corrosion products on artificial patinas.^{271,277} The patination of ancient lead supports from stained glass windows was examined in different locations over Europe.²⁷⁸ Different lead corrosion products were found, including, among others, cerussite (PbCO_3), hydrocerussite ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$), laurionite ($\text{PbO} \cdot \text{HCl}$), litharge (tetragonal PbO), anglesite (PbSO_4), and phosgenite ($\text{Pb}_2\text{CO}_3\text{Cl}_2$). Neff et al. elucidated the corrosion system for the corrosion of iron artifacts in soil^{279,281} by using

a combined approach of Raman spectroscopy, synchrotron micro-X-ray diffraction, scanning electron microscopy–energy dispersive X-ray analysis (SEM–EDX), and electron probe microanalysis (EPMA). The study of atmospheric corrosion of archaeological iron artifacts was also undertaken.²⁸⁰

7. Ceramics, Glasses, and Enamels

Ceramics, glasses, and enamels are silicate-containing materials that differ from each other in the amount of crystalline material that they contain.^{282–284} Ceramics are composite materials that consist of sintered grains. Some phases consist of the original compounds, but new phases can be formed during the sintering process. Ceramics consist of crystalline and amorphous phases. Glasses and enamels are fully melted during their synthesis. Whereas glasses are used without substrates, the term “enamel” is reserved for a glassy coating on a substrate. Natural (e.g., obsidians) and synthetic glasses can be distinguished. The difference between glaze (porcelain, stoneware, celadon) and glaçure (faience, earthenware) can be made on the grounds of the firing temperature achieved. Glazes are enamels on substrates that contain a lot of the glassy phase, whereas glaçure was fired at a lower temperature and covers porous material.

Obsidians are a type of natural volcanic glasses that are sometimes encountered in objects of art. Their elemental composition can be used to determine their provenance.^{285,286} Attempts were made to apply Raman spectroscopy for this issue,^{250,287} and the technique was used to study the formation history and the amount of water available during formation of these volcanic glasses.^{288,289}

Raman spectroscopic studies of ancient man-made glasses have often focused on their degradation,²⁹⁰ such as Raman studies on the glasses of the Pisa cathedral²⁹¹ and from the Valencian region.²⁹² Colomban attributed the coloration of stained glass to nanoparticles,²⁹³ while Edwards and Tait studied the pigments applied to the surface of mediaeval monastic painted glasses by Raman spectroscopy.²⁹⁴ Glasses used for the production of jewelry and mosaics (Ifriqiya, 1st century BD to 10th century AD) were studied by Colomban et al.²⁹⁵ The vitrification process of the rocks used in a vitrified fortress in France was studied by Smith and Vernioles.²⁹⁶

Several papers have been published by people studying red, blue, black, and white pigments on top of pottery fragments.^{80,297–304} Different types of enamels were studied, including Egyptian faience,³⁰⁵ French faïences,³⁰⁶ mediaeval glazed ceramics,³⁰⁷ postmediaeval glazed tiles,³⁰⁸ glazes of Iznik pottery³⁰⁹ and of Kütaş fritwares,³¹⁰ Medici and Meissen porcelain,^{311,312} Siennese majolica,⁸³ French sigillata ware,^{313,314} and a unique soft-paste porcelain plaque-mounted table.³¹⁵ The latter was considered important since it established a provenance for the porcelain manufacture to the Rockingham factory in the 1830s. Colomban et al. were able to differentiate between different types of antique enamels based on the Raman spectra of their bodies, glazes, and paintings.^{316,317} They also performed a thorough study of the glazing technique of mediaeval luster pottery and faience.³¹⁸ Chinese celadon shards were studied by Raman spectroscopy, in combination with XRF and XRD.⁸² Prehistoric Anasazi ceramics³¹⁹ and ancient Greek pottery³²⁰ were examined by Raman spectroscopy to study the mineralogical composition.

8. Minerals and Gemstones

During the past decade, Raman spectroscopy has often been applied as a powerful analytical technique in mineralogy and gemology. The technique has often been applied for the study of mineral inclusions, and from these examinations conclusions could be drawn about the geological genesis of the minerals. A complete overview of the use of Raman spectroscopy in these fields is out of the scope of this review paper. However, it is clear that certain aspects of mineralogy and gemology are comprised in the investigation of art objects. Many antique pigments are of mineral origin, and often precious stones were used in jewelry. Whereas for classical examinations of many gemstones they have to be removed from the art object, Raman spectroscopy is well suited for their nondestructive identification. By using fiber optics, the instrument can be set up in such a way that even gemstones in large objects can be easily identified.^{321,322} Apart from problems that may arise from accruing fluorescence, the discrimination between genuine and fake gemstones may seem straightforward,³²³ by comparison with spectra from an extended spectral library.¹⁹ However, good knowledge of common practices in gemstone treatment is required, since some treatments may obscure the gemstone Raman spectra. Kiefert et al.³²⁴ have described several examples of these treatments and their determination by Raman spectroscopy, including impregnated jadeite, dyed quartzite (to imitate jadeite), and artificially colored pearls.³²¹ Fissure fillers are often applied to improve the clarity of emeralds. This practice, which even has been described in Plinian times,³²⁴ consists of impregnating the gemstone with oils, glues, or resins. Recently, synthetic resins started to be used for this purpose. It was demonstrated that Raman spectroscopy could identify these fillers in the emeralds.³²⁵

9. Conclusions

This review reports on the applications of Raman spectroscopy in the investigation of archaeological and art objects. It gives an overview of the most important findings of the past decade. Raman spectroscopy is becoming increasingly important in art analysis, as seen by the number of papers that are published in this research field. Archaeometry is a challenging research field, where the purpose is the extraction of as much information as possible from fragile and unique artifacts. Raman spectroscopy is well-adapted for the non-destructive examination of molecular species with a good spatial resolution. The use of Raman spectral libraries is reviewed, the evolution of Raman instrumentation is discussed, and the potential toward mobile equipment for in situ investigations is discussed. Many papers have been published on pigment analysis of art objects. The controversy of the Vinland map is discussed, and several groups have studied pigment degradation. Many biomaterials have been examined using FT-Raman spectroscopy to avoid fluorescence emission. Other important research topics include the analysis of corrosion phenomena with Raman spectroscopy, the analysis of glass, glazes, and ceramics, and the study of minerals and gemstones.

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