ORIENTAL JOURNAL OF CHEMISTRY
An International Open Access, Peer Reviewed Research Journal
www.orientjchem.org
Est. 1984

ISSN: 0970-020 X
CODEN: OJCHEG
2022, Vol. 38, No.(5):
Pg. 1081-1093

Pigments in Ancient Manuscripts and Paintings Brought to Life by Raman Spectroscopy: A Short Review

CHHANDASI GUHAROY SARKAR*

Department of Chemistry, Hooghly Mohsin College, Chinsurah, Hooghly, West Bengal, India.
*Corresponding author E-mail: chhandasi_guharoy@yahoo.co.in

http://dx.doi.org/10.13005/ojc/380501

(Received: August 29, 2022; Accepted: October 17, 2022)

ABSTRACT

The current review focusses on the importance of Raman spectroscopy in identification of pigments in ancient manuscripts and panel and canvas paintings. The major advantage of Raman spectroscopy is its non-destructive nature and its capacity of *In situ* analysis. The present paper discusses the pigments detected in different artworks, their chemical compositions and corresponding Raman bands. It highlights the fact that the establishment of the pigment palette of an artwork provides valuable information regarding degradation products and mechanisms which helps in conservation efforts. It also aids in understanding the authenticity of any specimen. Raman spectroscopy has transcended the boundary of cultural history and has been able to throw light on ancient trade routes, thus exhibiting its significance in the general historical study of a region. The article refers to publications during the period 1995-2022 in order to portray the versatility of the utilization of Raman spectroscopy in the stated arena.

Keywords: Raman spectroscopy, Pigments, Manuscripts, Panel and canvas paintings.

INTRODUCTION

In the past four decades Raman spectroscopy has emerged as the most notable instrumentation method in the field of art, archaeology and heritage architecture.[1-6] In addition to its other numerous applications,[7,8] it has obtained widespread implementations in the identification of pigments, dyes and binders in paintings, wall-arts, frescoes and manuscripts, study of archaeological sites, analysis of gemstones, glass, fibres, papers, ceramics, pottery, ink and various other substances.[9-18] Raman spectroscopy was discovered by Sir C. V. Raman in 1928,[19] but its extensive employment in art and archaeology began with the appearance of Molecular Optical Laser Examiner (MOLE) Raman microprobe in 1975.[20] The first reported application of Raman spectroscopy to archaeological relics and artworks was by Guineau in 1984,[21,22] following which a host of papers were published on the topic. The introduction of powerful laser sources[1,10] and charge coupled device (CCD) detectors[10,23] has made Raman spectroscopy a recognized and routine technique in archaeometry and in the examination of historical materials. The use of portable Raman spectroscopy started in the early 2000.[10,24-27] With the advance of technology, more sophisticated instruments, viz., Raman-mapping,[28,29] LIBS (laser-induced breakdown spectroscopy)-Raman,[30] surface enhanced Raman spectroscopy (SERS),[10,31-33] tip enhanced Raman-spectroscopy (TERS)[23] emerged that sparked rapid progress in the field of cultural science, with Raman spectroscopy being used consistently by the researchers.

Raman spectroscopy has various advantages,[1,32-40] in particular, its non-destructive and non-invasive character and its ability of *In situ* inspection of objects, without any mechanical or chemical pre-treatments. It is a comprehensive technique for detailed compositional analysis of inorganic as well as organic materials. Raman spectroscopy has an edge over many other instrumental methodologies as water being a weak Raman scatterer, it allows spectroscopy of hydrated samples. In addition, its high molecular specificity, high sensitivity (ppm range), high spectral (≤ 1 cm^{-1}) and spatial resolution ($\leq 1\,\mu$m) and availability of a range of laser excitation sources have made it indispensable in the toolbox of the cultural and heritage scientists. However, the major drawback of the procedure is the fluorescence emission that makes the spectral studies relatively tough. Recently, Spatially Offset Raman Spectroscopy (SORS)[41,42] has been developed to explore the stratigraphy of layered artefacts. It is an important methodology to interpret the chemical compositions of subsurface pigments that are covered by turbid surface layers. The process also reduces the fluorescence of the top layer to a great extent. Raman spectroscopy in combination with other analytical techniques like gas chromatography-mass spectrometry, scanning electron microscopy, X-ray diffraction etc. offered a major impetus in the exploration of all types of art objects.

The establishment of an in-depth portfolio for any piece of artefact is important for several reasons. Firstly, it determines the time period of the artwork by probing into the materials and techniques of the specimen and also ascribes its authenticity. Secondly, it examines the degradation products and mechanisms of the art pieces. All these cumulatively furnishes essential information that helps in conservation and restoration of the art objects. A thorough search of the literature disclosed countless and diverse implementation of Raman spectroscopy in the arena of cultural science. The current article presents a short review on analysis of pigments in manuscripts and panel and canvas paintings by Raman spectroscopy, highlighting the pigments detected along with their chemical compositions and corresponding Raman bands. Furthermore, it also concentrates on the significance and uniqueness of each report from the viewpoint of the analytical methodology as well as the artistic discovery.

DISCUSSION

Chemical Analysis of Artworks and Artefacts-Historical Background

Till date, there is very little documentary evidence of the history of scientific evaluation of artefacts. One of the earliest reports of chemical analysis of pigments found in art objects, viz., pottery, glass and ceramics was provided by Rene-Antoine Ferchault de Réaumur[43] in France in a series of publications between 1716 and 1739. Later in 1815, in the United Kingdom, Sir Humphry Davy[44] published his findings on pigments of some wall painting fragments from Pompeii in the 'Philosophical Transactions of the Royal Society'. Further accounts of chemical analyses of ancient pottery were put forward by A. Salvetat[45] during the period 1857-1877. However, all these investigations were highly destructive. Even in 1922, Eccles & Rackham,[46] while inspecting the chemical compositions of English, Welsh, Chinese and Continental porcelains in the Victoria & Albert Museum's collection, had no other option but to destroy priceless specimens to achieve their goal. A great development occurred with the advent of X-ray Fluorescence (XRF)[47] instruments in the 1960s and this period can be considered to herald the true onset of archaeometry. Cultural and heritage science was further taken forward with the application of Raman spectroscopy as stated in the introduction.

Analysis of Pigments by Raman Spectroscopy

Pigments

Raman spectroscopy has been elegantly utilized in the characterization of pigments in numerous artworks and archaeological relics. The primary objective of the studies has been the detection of pigments and investigation of their compositions. However, another crucial target has been to contribute towards further development of the already established Raman spectral library of pigments. Such a database of organic as well as inorganic colours is essential for comparison and assignment of detected pigments in any art specimen. The ground-breaking publication of Bell *et al.,*[48] was the first step towards building of such a library. This has been followed by varied researches which all focussed on creating a substantial dataset of Raman spectra of natural, mineral and synthetic pigments.[48-62] A list of all the pigments discussed in this article along with their chemical compositions are presented in Table 1-Table 4. The structures of a few representative synthetic organic pigments are given in Fig. 1 while the structures of two representative natural organic pigments are shown in Figure 2.

Table 1: Natural inorganic pigments- colour, chemical formulae and chemical names

Name of the Pigment	Name of the Mineral	Colour	Chemical Formula	Chemical Name
Vermillion	Cinnabar	Red	HgS	Mercuric sulphide
Red ochre	Hematite	Red	Fe_2O_3	Ferric oxide
Red lead	Minium	Red	Pb_3O_4	Lead tetroxide
Brown ochre	Goethite	Yellow to brown	α-$FeO(OH)$	Hydroxy oxo iron
Yellow ochre	Limonite	Yellow	$FeO(OH){\bullet}nH_2O$	Hydrated ferric oxide
Lead white	Hydrocerussite	White	$2PbCO_3.Pb(OH)_2$	Basic lead carbonate
-	Litharge	Red	PbO(Tetragonal)	Lead (II) oxide
-	Massicot	Yellow	PbO(Orthorhombic)	Lead (II) oxide
-	Orpiment	Yellow	As_2S_3	Arsenic (III)Sulphide
-	Realgar	Orange-red	α-As_4S_4	Arsenic sulphide
-	Pararealgar	Yellow	β-As_4S_4	Arsenic sulphide
-	Malachite	Green	$CuCO_3{\bullet}Cu(OH)_2$	Basic copper (II) carbonate
-	Antlerite	Green	$CuSO_4{\bullet}2Cu(OH)_2$	Dibasic copper (II) sulphate
-	Brochantite	Green	$CuSO_4{\bullet}3Cu(OH)_2$	Tribasic copper (II) sulphate
-	Langite	Green	$CuSO_4{\bullet}3Cu(OH)_2{\bullet}2H_2O$	Tribasic copper (II) sulphate dihydrate
-	Posnjakite	Green	$CuSO_4{\bullet}3Cu(OH)2{\bullet}H_2O$	Tribasic copper (II) sulphate monohydrate
-	Azurite	Blue	$2CuCO_3.Cu(OH)_2$	Basic dicopper (II) carbonate
-	Lazurite	Blue	$(Na,Ca)_8[(S,Cl,SO_4,OH)_2I(Al_6Si_6O_{24})]$	Sodium calcium aluminosilicate
-	Rutile	White	TiO_2	Titanium dioxide
-	Gypsum	White	$CaSO_4.2H_2O$	Calcium sulphate dihydrate
-	Calcite	White	$CaCO_3$	Calcium carbonate
-	Cerussite	White	$PbCO_3$	Lead carbonate
Bone white	-	White	$[Ca_5(PO_4)_3(OH)]$ and $CaCO_3$	Calcium hydroxyapatite and calcium carbonate
Barium white	-	White	$BaSO_4$	Barium sulphate
Chrome yellow orange	-	Orange-yellow	$PbO.PbCrO_4$	Basic lead chromate
Cadmium red	-	Red	$CdS. CdSe$	Cadmium sulfoselenide
Ultramarine blue	-	Blue	$Na_7Al_6Si_6O_{24}S_3$	Sodium aluminium silicate
Terre verte	-	Green	$K[(Al,Fe^{3+}),(Fe^{2+},Mg](AlSi_3,Si_4)O_{10}(OH)_2$	

Table 2: Synthetic inorganic pigments- colour, chemical formulae and chemical names

Name of the Pigment	Colour	Chemical Formula	Chemical Name
Zinc white	White	ZnO	Zinc oxide
Chrome yellow	Yellow	$PbCrO_4$	Lead chromate
Lead tin yellow I	Yellow	Pb_2SnO_4	Lead stannate
Prussian blue	Blue	$Fe_4[Fe(CN)_6]_3$	Ferric Ferrocyanide
Basic verdigris	Blue	$Cu(CH_3COO)_2{\bullet}Cu(OH)_2{\bullet}5H_2O$	Basic copper (II) acetate
Emerald green	Green	$3Cu(AsO_2)_2.Cu(CH_3COO)_2$	Copper (II) acetoarsenite

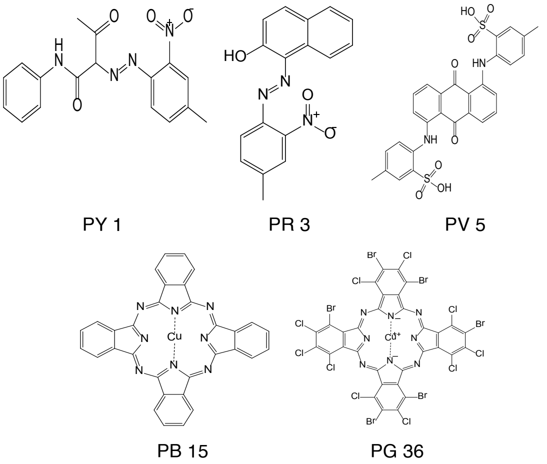
Table 3: Natural organic pigments- colour and chemical formulae

Name of the Pigment	Colour	Chemical Formula
Indigo	Blue	$C_{16}H_{10}N_2O_2$.
Carotenoids	Orange	$C_{40}H_{56}$
Carmine	Red	$C_{22}H_{20}O_{13}$

Table 4: Synthetic organic pigments- colour and chemical formulae

Name of the Pigment	Colour	Chemical Formula	
Phthalocyanine blue	Pigment Blue 15 (PB15)	Blue	$CuC_{32}H_{16}N_8$
Phthalocyanine blue RS	Pigment Blue 15:1 (PB15:1)	Red-blue	$CuC_{32}H_{16}N_8$
Phthalocyanine green BS	Pigment Green 7 (PG7)	Green-blue	$CuC_{32}HCl_{15}N_8$
Nitroso green	Pigment Green 8 (PG8)	Yellowish to bluish Green	$C_{30}H_{18}FeN_3NaO_6$
Phthalocyanine green YS	Pigment Green 36 (PG36)	Yellow-green	$C_{32}Br_6Cl_{10}CuN_8$
Arylide yellow or	Pigment Yellow 1 (PY1)	Reddish yellow	$C_{17}H_{16}N_4O_4$
Hansa Yellow	Pigment Yellow 3 (PY3)	Lemon yellow	$C_{16}H_{12}Cl_2N_4O_4$
	Pigment Yellow 74 (PY74)	Greenish-yellow	$C_{17}H_{16}N_4O_7$
Isoindole yellow	Pigment Yellow 109 (PY109)	Greenish to reddish yellow	$C_{23}H_8Cl_8N_4O_2$
Toluidine red	Pigment Red 3 (PR3)	Yellowish to bluish red	$C_{17}H_{13}N_3O_3$
Permanent red	Pigment Red 4 (PR4)	Yellowish red	$C_{16}H_{10}ClN_3O_3$
Alizarine violet	Pigment Violet 5 (PV5)	Violet	$C_{28}H_{22}N_2O_8S_2$

The efficacy of Raman spectroscopy in identification of pigments was highlighted by Gilbert *et al.,* in their publication on green pigments.[63] They emphatically stated that μ-Raman spectroscopy enabled them to detect green pigments other than malachite [$CuCO_3.Cu(OH)_2$] and verdigris [$Cu(CH_3COO)_2.Cu(OH)_2•5H_2O$], which were the only two ancient green pigments known till then. The group determined other copper pigments viz., antlerite [$CuSO_4.2Cu(OH)_2$], brochantite [$CuSO_4.3Cu(OH)_2$], langite [$CuSO_4.3Cu(OH)_2.2H_2O$] and posnjakite [$CuSO_4.3Cu(OH)_2.H_2O$], and also showed that copper sulphate mixed with other pigments created different shades of green. All the pigments depicted intense Raman bands in the region 966-988 cm^{-1} corresponding to the SO_4^{2-} group and above 3300 cm^{-1} denoting the -OH vibrations.


PY 1 PR 3 PV 5

PB 15 PG 36

Fig. 1. Representative structures of synthetic organic pigments

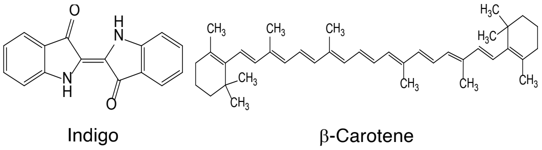

Indigo β-Carotene

Fig. 2. Representative structures of natural organic pigments

The following instances reveal the diversity in applications of Raman spectroscopy in the study of pigments in manuscripts and canvas and panel paintings.

Manuscripts

As specified in the introduction, one of the earliest researches in heritage science using Raman spectroscopy was carried out by Guineau.[21,22] Interestingly, his work centred on ancient manuscript pigments. In the early 1990s, Best *et al.,* established that pigment grains of 1-2 μm in diameter could be studied by Raman spectroscopy.[64,65] One of their prominent projects involved the identification of pigments in a Skard copy of the Icelandic Jónsbók law code (1360 CE).[66] It showed the utilization of materials like bone white, cinnabar, orpiment, realgar, azurite and hematite. Cinnabar (the mineral form of the pigment vermillion) displayed intense Raman bands at 40 and 251 cm^{-1} and relatively weak ones at 281 and 340 cm^{-1}. Orpiment is an arsenic trisulphide (As_2S_3) mineral where As_2S_3 crystal has a monoclinic structure. It had distinctive bands at 352, 308, 290, 200, 152 and 134 cm^{-1} with two weak shoulders at 364 and 357 cm^{-1}. Realgar is also primarily an arsenic sulphide mineral differing from orpiment in the feature that it has a chemical formula α-As_4S_4 with monoclinic crystal system. Realgar exhibited medium intensity Raman vibrations at 231, 227 cm^{-1}. Azurite, which is a copper-based pigment manifested itself in two typical medium intensity

Raman bands at 408, 256 cm^{-1} with a shoulder at 251 cm^{-1}. Hematite is the mineral form of red ochre which is also known as red iron oxide in the literature. It has many variations viz., a lighter tone known as Venetian Red and a darker variety called Indian Red, or *Caput mortuum*. It was located by the very weak Raman signals at 406, 295, 290, 224 cm^{-1} with a shoulder at 295 cm^{-1}. Bone white is a white pigment which was prepared from Bone ash in the ancient times. Bone white was primarily composed of calcium hydroxyapatite and calcium carbonate. The Raman band corresponding to bone white was viewed at 965 cm^{-1}. Of special interest was the absence of lead pigments common in Europe at that time viz., lead white and red lead,[66] probably due to the absence of lead ores in Iceland.

Another important study of pigments with Raman spectroscopy was that of seven different Guttenberg bibles found in different parts of Europe. The King George III Bible consisted of pigments like vermilion, carbon black, azurite, lead tin yellow Type I, malachite, gypsum, calcite and lead white. Carter and her team put forward the palette of early Visigothic historiated documents (10th-mid 11th centuries)[67] which comprised of minium, cinnabar, orpiment, indigo and iron gall ink. It is fascinating to note that iron gall ink was used as a black pigment in these scripts rather than a writing medium. The writing medium was carbon black which presented a strong signal at 1578 cm^{-1} along with other relatively weaker bands. Iron gall ink was located by fingerprint peaks at 1478, 1341, 598 and 400 cm^{-1}. Minium, also known as red lead, is the natural form of lead tetroxide (Pb_3O_4). It presented a strong Raman signal at 122 cm^{-1} followed by medium to weak bands at 550, 390, 313, 225 and 151 cm^{-1}. Indigo is a plant-based natural organic pigment which expressed a characteristic strong Raman vibration at 1571 cm^{-1} assigned to the ν(C=C), ν(C=O) and ν(N–H) stretches. The work also demonstrated that Raman spectroscopy is a convenient tool in analysing admixture of pigments as it effectively revealed that the green pigment to be a mixture of orpiment and indigo, the orange colour being a mixture of orpiment and red lead while a light blue colour was produced by mixing calcite with indigo. A thorough scrutiny of several eastern manuscripts of the same period viz., Persian, Turkish, Chinese, Javanese and Korean manuscripts displayed similar colour palettes as that of the European ones, except some animal and plant products which were exclusive to the eastern scripts viz., Indian yellow ($MgC_{19}H_{16}O_{11}.5H_2O$).[68] Muralha *et al.,*[69] confirmed the pigment palette of four Persian scripts (16th-17th century) to be consisting of carbon-based black (with broad Raman bands at 1580 and 1325 cm^{-1}), indigo (with signature Raman peaks at 584, 1575, 599, and 546 cm^{-1}), malachite, lead white, lazurite, red lead, haematite, vermilion, orpiment, carmine, realgar and pararealgar. Malachite is a basic green copper carbonate pigment whose corresponding Raman bands occurred at 1086, 1051, 433, 354, 268, 217, 178, 155 cm^{-1}. Hydrocerussite or lead white is a basic lead carbonate [$2PbCO_3.Pb(OH)_2$], which depicted Raman peaks at 1052 and 1049 cm^{-1}. The blue mineral lazurite $[(Na,Ca)_8[(S,Cl,SO_4,OH)_2l(Al_6Si_6O_{24})]$ is a component of lapis-lazuli and it furnished strong bands at 548 and 1096 cm^{-1}, with weaker bands at 808, 583 and 259 cm^{-1}. The blue colour of the pigment appears due to the trapped sulphur radical anions. Carmine (with typical Raman bands at 1691, 1481, 1316, 1294, 1104, 1004 and 542 cm^{-1}) is an organic natural red pigment derived from cochineal, which is a red dye extracted from the dried bodies of certain female scale insects; carminic acid ($C_{22}H_{20}O_{13}$) being the main colorant of the pigment. Both realgar and pararealgar are the sulphides of arsenic (As_4S_4); realgar being the α-polymorph and pararealgar, the β-polymorph which originates when realgar is exposed to light. A synthetic green pigment known as emerald green was spotted by Raman spectroscopy with characteristic bands at 951, 539, 492, 371, 242, 217, and 154 cm^{-1}. This pigment was believed to be a result of subsequent retouching effects.

Cappa *et al.,*[70] elaborately discussed the pigments employed on parchments in the medieval period (8th-14th century), where they complimented Raman spectroscopy with X-ray fluorescence. The types of ink that were identified on the parchments included brownish black iron gall ink (tannic acid, ferric sulphate and Arabic gum as binder) for writing, red ink comprising of red iron oxide for writing as well as for decorations, blue/green ink (containing lapis lazuli and terra viridis) for ornamentations only. The illuminations showed the presence of pigments like vermilion, minium, hematite, orpiment and azurite. In addition, the Glagolitic documents exhibited the presence of lapis lazuli and malachite whereas the Greek and Latin codices displayed lead white and carbon black. Iron gall ink rendered two bands 1200 and 1550 cm^{-1}, designated to the C-O stretching vibrations of the ester and the carboxylic functionalities, respectively. Another broad band at around 550 cm^{-1} was allocated to the iron complex. Lapis lazuli is a rock i.e. it is an assemblage of more than one mineral viz., lazurite $[(Na,Ca)_8[(S,Cl,SO_4,OH)_2](Al_6Si_6O_{24})]$, calcite ($CaCO_3$), and pyrite ($FeS_2$) with occasional occurrence of diopside ($MgCaSi_2O_6$), amphibole ($A_{0-1}B_2C_5T_8O_{22}(OH,F,Cl)_2$, where A=Na, K;B=Na, Zn, Li, Ca, Mn, Fe^{2+}, Mg;C=Mg, Fe^{2+}, Mn, Al, Fe^{3+}, Ti, Zn, Cr; and T=Si, Al, Ti), feldspar ($KAlSi_3O_8$), and mica ($XY_{2-3}Z_4O_{10}(OH,F)_2$ with X=K, Na, Ba, Ca, Cs, (H_3O), (NH_4); Y=Al, Mg, Fe^{2+}, Li, Cr, Mn, V, Zn; and Z=Si, Al, Fe^{3+}, Be, Ti.). The actual pigment is known as ultramarine ($Na_7Al_6Si_6O_{24}S_3$) having a deep blue colour, which was manufactured by grinding lapis lazuli into a powder. The unique and bright blue colour is a result of the unpaired electron in the sulfur radical anions S^{3-}. Synthetic ultramarine began to be observed in the painting palettes of artists towards the beginning of the 19th century. Terre verte, also known as green earth or Verona green is an inorganic pigment acquired from the minerals celadonite $K(Mg,Fe^{2+})(Fe^{3+},Al)[Si_4O_{10}](OH)_2]$ and glauconite $[(K,Na)(Fe,Al,Mg)_2(Si,Al)_4O_{10}(OH)_2]$.

Again, Burgio *et al.,*[40] reported the use of iron gall ink (crystalline form) not only as a writing medium but also as a pigment when they accomplished the task of constructing the pigment panorama of Italian codices of 12th-17th century by examining 174 manuscript cuttings and miniatures preserved in Victoria and Albert Museum. They documented the existence of pigments like lead white (1052, 1048 cm^{-1}), azurite (1095, 400, 247 cm^{-1}) indigo (1,575, 599, 546, 252 cm^{-1}), lazurite, (1096, 548 cm^{-1}) malachite (1,491, 433, 269 cm^{-1}), red lead (548, 390, 223 cm^{-1}), vermilion (343, 253 cm^{-1}), lead tin yellow type I (458, 294, 275, 198 cm^{-1}), carbon black (590, 345 cm^{-1}) and goethite (553, 390, 302 cm^{-1}) in the various folios. Goethite is composed of about 80-90% Fe_2O_3 and approximately 10% H_2O. Hematite is the dehydrated version of goethite while upon hydration, it becomes limonite. Lead-tin yellow is of two different types-lead-tin yellow type I (Pb_2SnO_4) and lead-tin yellow type II containing lead-tin oxide and silica (SiO_2).

Nastova *et al.,*[71] recorded the use of iron gall ink, carbon black as well as goethite for writing in Byzantine and post-Byzantine scripts of 10th-18th century along with the usual pigments of the time.

Another enthralling report was published by the same team, when they investigated two medieval old-Slavonic documents and compared their colour palette with those of medieval Western Europe.[72] The main pigments observed in the embellishments of the two scripts named “Vrutok four gospels” (13th-14th centuries) and “Benche four gospels” (16th century) were calcite, gypsum, lead white, yellow ochre, realgar, pararealgar, orpiment, vermillion, red lead, indigo, verdigris and malachite while a mixture of carbon and iron gall ink was utilized for writing. The last observation was markedly different from those of mediaeval Western manuscripts where usually only iron gall ink was employed for writing. Some other differences in the pigment palette were a) the use of indigo and yellow ochre mixture to achieve green colour in the old-Slavonic codices, whereas the same hue was obtained in Western Europe manuscripts by mixing indigo and orpiment; b) yellow ochre was applied as the underlayer to the green pigment in the old-Slavonic folios, but in the Western Europe ones lead white or lead tin yellow was employed for the same. The significance of the work also lies in the fact that the discovery of metallic copper as gold pigment on the cover of “Vrutok four gospels” was the first instance of detection of copper in use as a golden pigment. Calcite is the natural form of calcium carbonate which portrayed Raman peaks at 151, 279, 712, 1086 cm^{-1}. Gypsum is another white pigment which provided Raman vibrations at 414, 494, 1009, 1137 cm^{-1}. The Raman bands of pararealgar were viewed at 142, 182, 191, 220, 233, 272, 342 and 354 cm^{-1} while realgar portrayed Raman bands at 140, 180, 190, 218, 341 and 352 cm^{-1}. Limonite is the mineral form of yellow ochre. As mentioned earlier it is formed by hydration of hematite. The Raman bands corresponding to yellow ochre emerged around 298, 397, 478 and 556 cm^{-1}. Verdigris is a synthetic copper-based pigment which rendered distinct Raman vibrations at 202, 955, 1070, 1305, 1361, 1445, 1570, 2856–2937 cm^{-1}. The band at 1445 cm^{-1} corresponded to vibrations of the COO^- ion while the signals between 2856-2937 cm^{-1} was due to the stretching vibrations of the $-CH_3$ groups. However, along with verdigris, its degradation product moolooite ($CuC_2O_4.nH_2O$) was also discerned (with Raman bands at 142, 211, 558, 584, 832, 1305, 1487, 1515 and 1607 cm^{-1}).

Moolooite was probably the result of degradation of proteinaceous binders in verdigris.

Miguel *et al.,*[73] concentrated in ascertaining the products and the mechanism of red lead degradation in a medieval Portuguese manuscript, Lorvão Apocalypse (1189 CE), with the help of Raman microscopy (μ-Raman), micro-X-ray diffraction (μ-XRD) and micro-Fourier transform infrared spectroscopy (μ-FTIR). Raman procedure identified the pigments availed for the adornment of the folios to be vermilion (characterised by Raman bands at 343, 285 and 253 cm^{-1}), orpiment (characterised by Raman signals at 353, 309, 292, 154 cm^{-1}) and red lead (characterised by Raman vibrations 548, 390, 223, 149 and 122 cm^{-1}). It also clearly determined galena or lead (II) sulphide (PbS) as the degradation product of red lead. Two broad bands at 200 and 445 cm^{-1} represented galena. Moreover, a few bands were observed between 960 and 980 cm^{-1} which were indicative of lead sulfate ($PbSO_4$) evincing that galena had undergone laser-induced degradation. To elucidate the mechanism of degradation several experiments were conducted in the laboratory. Raman microscopic results of such simulations of the degradation of read lead proved beyond doubt that the degradation was a direct outcome of its reaction with orpiment as given in reaction (1).

$$2Pb_3O_4+As_2S_3 \longrightarrow 3PbS+(AsO_4)_2Pb_3 \qquad (1)$$

A similar observation was found in the inspection of fifteen Portuguese medieval codices (12-13th century) which exhibited the usage of vermillion, lazurite, red lead, lead white, orpiment, azurite and carbon-based black pigment.[74] All the pigments manifested Raman vibrations in the expected regions. In two of the manuscripts, there had been considerable darkening of the regions consisting of lead white due to the formation of galena, as a result of reaction with orpiment. Koochakzaei *et al.,*[75] checked the pigment palette of an Iranian codex of the Holy Quran (1795-1796 CE) associated to the early Qajar era with the help of Raman spectroscopy coupled with μ-XRF, SEM–EDS, FTIR spectroscopy and technical photography processes. Here again, the enthralling application of the cochineal-based pigment carmine was observed representing Raman bands at 1643, 1476, 1316, 1220 and 1104 cm^{-1}. The golden regions consisted of two types of materials-elemental gold and brass (an alloy of copper and zinc). The regions decorated with brass had developed a greenish tinge due to the formation of copper carboxylates $[Cu(RCOO)_2]$. These researches unambiguously evinced the importance of Raman spectroscopy in understanding the degradation process of pigments, thus furnishing valuable information towards the restoration of art objects.

It is intriguing to know that Raman spectroscopy has transcended the border of art history to throw light on other historical aspects of a region. In this respect the work of Brown and Clark[76] deserve special mention. They inspected the Lindisfarne Gospels produced around 715 CE to honour St. Cuthbert, who was bishop of Lindisfarne in Northumbria. Raman spectroscopy exhibited the existence of indigo, and there was no indication of lazurite. Indigo was characterized by a weak to medium overlapping triplet at 252, 264 and 277 cm^{-1}. In addition, a weak band at 1311 cm^{-1} [ν(C-C)], and a strong doublet at 1572/1584 cm^{-1} (ν(C=O), ν(C=C)] were also spotted. This was contrary to the earlier findings by light microscopy[77] which definitely suggested the usage of lazurite in the folios. Based on the discovery of lazurite in the Gospels, a trade route was believed to operate between Northumbria and the Badakhshan mines in Afghanistan, which was the sole source of lazurite at the time. However, this was proved to be erroneous when Raman spectroscopy proclaimed the complete absence of any lazurite in the Gospels.

It may be mentioned at this point that although substantial work has been performed in this area till date, the work is rather scattered using disconnected specimens. There is a definite scope of further study to trace the evolution in the use of pigments in manuscripts over the ages and associating them to a definite era and region.

Panel and Canvas Paintings

Raman spectroscopy has extended the horizons of scientific analysis of paintings in a remarkable manner. It has been successfully utilized to describe the pigment palette of any artwork. Gutiérrez-Neira et al.,[38] spotted pigments like goethite, vermillion, hematite, azurite, carbon black, calcite, cerussite and hydrocerussite in the paintings of the famous Spanish Golden Age artist Diego Velázquez (1599-1660 CE). All the pigments expressed their usual Raman spectral vibrations.

Cerussite is a mineral containing anhydrous lead carbonate ($PbCO_3$) which depicted a conspicuous Raman peak at 1051 cm^{-1}. Again, Colomban and his team[78] detected the chief pigments to be lead white (with strong Raman bands at 1050 and 1054 cm^{-1}), calcite (with distinctive Raman band at 1086 cm^{-1}), litharge (with medium intensity Raman bands at 86, 139, 279 and 347 cm^{-1}), cinnabar (with weak Raman vibrations at 254, 284 and a strong one at 343 cm^{-1}), minium (with very strong bands at 122 and 551 cm^{-1}), azurite (with characteristics Raman vibrations at 400 and 1404 cm^{-1}) and lapis lazuli (with a very strong Raman band at 545 cm^{-1}) in a wood panel painting of 16th century by Raman spectroscopy. Litharge is the mineral form of lead oxide (PbO) where PbO is found in tetragonal crystal structure.

A beautiful example of the significance of Raman spectroscopy in the examination of painting pigments was provided by Edwards and his group.[79] The inspection of the Raman spectra of a supposed Renaissance canvas oil painting known as the "Malatesta" or “Full Length Portrait of a Gentleman”, disclosed the presence of cinnabar, carbon black, massicot, terre verte, gypsum, calcite and lead white- all pigments being consistent with Renaissance period. The Raman bands at 250, 285, 340 cm^{-1} signified the usage of cinnabar. The band at 140 cm^{-1} indicated the existence of massicot, while the signature signal of lead white could be seen at 1050 cm^{-1}, although very weak in intensity. Massicot is also a naturally occurring form of lead oxide (PbO), but it differs from litharge in the fact that it contains PbO in orthorhombic crystal structure. The appearance of chrome yellow (with Raman vibrations at 827, 374, 358, 324 cm^{-1}) in some regions was allocated to subsequent 19th century restorative efforts. Chrome yellow, also known as lead chromate, exists in nature as the mineral crocoite but the mineral ore itself was rarely availed as a pigment for paint. Synthetic chrome yellow began to emerge in the artists panorama in the early part of the nineteenth century. A fascinating observation in this painting was the appearance of three bands at 1520, 1157 and 1006 cm^{-1} designated to the C=C and C-C stretching vibrations of the polyisoprene unit of carotenoid. This could be explained by two possibilities- either, the pigment extracted from the natural sources was administered in the painting or it indicated the onset of degradative biological colonisation in this region of the specimen. Thus, Raman spectroscopy proved unambiguously the authenticity of a painting by definitely associating it with Renaissance period. Hibberts *et al.,*[80] reported a similar occurrence when they undertook Raman microscopic procedure of a supposed 15th century Renaissance oil painting on canvas depicting the crucifixion of Christ. The painting was in a very poor state when discovered and displayed no signs of restoration. Raman spectroscopy led to the identification of cinnabar, red lead, haematite, goethite, lead white, verdigris, azurite and *Caput mortuum*. The organic pigment carmine was also spotted in the painting. The picture palette was in accordance with the Renaissance period and so it proved beyond doubt that the work was executed during this time. Similarly, Raman spectroscopy of an oil painting “Young Woman Seated at a Virginals” evidenced the usage of vermilion, lead tin yellow Type I, green earth and lazurite-all pigments being typical of the artistic palette of Vermeer, thus helping to ascribe the painting to the Dutch painter Johannes Vermeer (1632-1675 CE).[81] Recently, in another similar attempt Raman spectra of an oil-sketch on a wooden panel presumed to be created by English artist John Constable[82] (1776-1837 CE) revealed predominantly the use of lapis lazuli, lead white, red lead and carbon black. All these pigments developed their fingerprint peaks in Raman spectroscopy. In addition, Prussian blue, chrome yellow and gypsum were also observed. Prussian blue is an iron complex having an intense blue colour whose Raman bands were seen at 2152, 2120, 2091, 279, 216 cm^{-1} while chrome yellow and gypsum generated signals at 838, 532 cm^{-1} and 1074 cm^{-1} respectively. All these pigments were already established to be part of Constable’s artistic panorama attributing the painting to Constable.

A very interesting application of Raman spectroscopy as a tool to evaluate the genuineness of any painting was found in a report of Saverwyns.[83] He spotted pigment anachronism i.e. locating pigments that were not in use at the time when the art specimens were executed, in six oil paintings (attributed to the period 1915-1918 CE) assumed to be by Liubov Popova (1889-1924 CE), one of the eminent exponents of the Russian avant-garde. Micro-Raman investigations of the six paintings revealed that the colour palette consisted of barium white, anatase and rutile variety of titanium dioxide, ultramarine, Prussian blue, cadmium red, hematite, carbon black along with many synthetic organic pigments. The organic synthetic pigments played a key role in recognizing the paintings as forgery. The synthetic organic blue pigment phthalocyanine blue (PB15), had been profusely used in all the paintings but it was introduced in the market in 1935. This has been located by the signature bands at 1528 cm^{-1} (allotted to the indole moiety), 682 cm^{-1} and in between 745-800 cm^{-1}. The vibration at 235 cm^{-1} was attributed to Cu-N bond. The green pigment phthalocyanine green (PG7) also employed abundantly, was prepared not before 1938. PG7 was determined by the fingerprint signals at 1533, 1442, 1387, 1337, 1280, 1209, 1081, 978, 955, 775, 742, 686 and 642 cm^{-1}. Another synthetic green pigment, PG8, was discovered in one painting but it had been commercially available since 1921. It displayed strong Raman vibrations at 447, 473, 498, 536, 637, 671, 756, 883, and 1354 cm^{-1}. A yellow pigment, PY74 (belonging to the class of arylide yellow or Hansa Yellow), which was marketed in 1957, was seen in three of the six paintings. PY74 was characterised by Raman bands at 1265 cm^{-1} ascribed to an amide III group, a relatively weaker amide I signal at 1670 cm^{-1} and vibrations at 828, 1331 and 1596 cm^{-1} designated to the stretching of the nitro groups. These four pigments played the pivotal role in concluding that the paintings were actually copies. The Raman vibrations of the inorganic pigments were not discussed in the article. However, titanium dioxide proved to be valuable in confirming pigment anachronism. Titanium dioxide has three natural crystallographic forms–anatase, brookite and rutile. Of these, anatase and rutile has been found in artists' palette. Rutile has tetragonal crystalline form whereas anatase is the metastable form of titanium dioxide also having a tetragonal crystal system. The rutile titanium dioxide, viewed in all the paintings, was commercially available in Europe from 1945, and therefore was unlikely to be present in the paintings under consideration.

A similar instance occurred in a putative Chagall (1887-1985 CE) painting named "*Nude woman reclining*".[84] The pastel painting is on cardboard and dated at 1910. The surface of the painting was examined at 15 sites by Raman microscopy and the chief pigments were- ultramarine blue, zinc white, phthalocyanine blue, PB15 (with characteristic bands being at 1528, 1452, 1338, 1305, 1220, 1140, 1106, 951, 746, 679, 591, 483 and 288 cm^{-1}), phthalocyanine green, PG7 (with distinctive bands at 1538, 1446, 1389, 1338, 1305, 1283, 1213, 1082, 978, 817, 775, 739, 684 and 642 cm^{-1}), and red and yellow iron oxides (FeO[OH] and Fe_2O_3 respectively). The bands at 608, 410, 291 and 224 cm^{-1} represented red iron oxide or hematite while the signals at 244 and 299 cm^{-1} indicated yellow iron oxide or goethite. Zinc white, chemically known as zinc oxide, was evinced by a conspicuous vibration at 438 cm^{-1}. Again, the phthalocyanine pigments proved chronological discrepancy as PB15 and PG7 were commercially accessible respectively since 1935 and 1938 as mentioned earlier, and therefore could not be present in a painting of 1910. The existence of phthalocyanine blue and phthalocyanine green in the oil painting on canvas 'Rebecca at the wall' (believed to be executed in the 18th century), assigned to a Neapolitan anonymous established the fact that the specimen had been retouched later.[85] The other pigments recognized were lead white, vermillion, amorphous carbon and chrome yellow orange. Chrome yellow orange ($PbO.PbCrO_4$) is a synthetic pigment that generated Raman bands at 343 and 828 cm^{-1}.

Vandenabeele *et al.*,[86] effectively applied fibre optics Fourier transform Raman spectroscopy in the interpretation of four different paintings with and without varnish coatings. 'Baby Elephant', a painting by Lucebert (1924–1994 CE), exhibited the rutile form of titanium dioxide (611 and 448 cm^{-1}) in the white areas. The red regions demonstrated the presence of azo pigments recognized as PR4 which is a β-Naphthol pigment having prominent Raman vibrations at 1600 cm^{-1} (allotted to the benzene quadrant stretch), 1400 cm^{-1} [ν(N=N)]], 1172 cm^{-1} [ν(C-N]) and 1157 cm^{-1} [δ(C–N)]. Another band at 1500 cm^{-1} was assigned to the azobenzene moiety. The green portions were due to another Hansa yellow class of pigment viz., PY3, possessing Raman signals at 1495, 1387, 1170 and 1159 cm^{-1}. Permanent white i.e., barium sulphate ($BaSO_4$) was recognized from the Raman vibrations at 987 [$\nu(SO_4^{2-})$], 462 and 453 cm^{-1}. The varnished painting 'La Toilette' by Edgar Degas (1834–1917 CE), the French impressionist painter, disclosed Permanent white, calcite ($CaCO_3$), and Prussian blue ($Fe_4[Fe(CN)_6]_3$). $BaSO_4$ was detected from its usual Raman signals while $CaCO_3$ manifested conspicuous bands at 1088 cm^{-1} (CO_3^- symmetric stretch) and 702 cm^{-1}. Prussian blue was deduced from the intense band at 2150 cm^{-1} due to the ν(C≡N) stretch. The painting 'La Mort d'un Esprit' by Giorgio de Chirico (1888–1978 CE) with a thick coat of varnish (≥1 mm) was also examined by FT Raman methodology. In spite of the varnish layer the red pigment vermilion was discovered, but with lower intensity than those obtained in the dispersive micro-Raman spectrum. The fourth painting scrutinized by the group was 'La Promenade du Monstre' on canvas by the Belgian surrealist painter Rene Magritte (1898–1967 CE). In spite of the varnish film, it revealed the existence of white lead and calcite which showed their typical Raman vibrations. The research, therefore, throws light on the fact that Raman spectroscopy can be employed to explore paintings keeping the varnish layer intact. This was a definite improvement over the micro-sampling method (Q-tip) where the paintings could only be scrutinized when the varnish had been taken off during restoration.

FT Raman spectroscopy was applied to great effect in the study of UV- and daylight fluorescent pigments by Boscacci *et al.,*[34] They employed a multi-analytical procedure comprising of FT Raman method, surface-enhanced Raman spectroscopy (SERS) and thin-layer chromatography. The fluorescent pigments belong to a class of 'special effect' pigments consisting of one or more fluorescent dyes in a medium of finely divided resins. These pigments absorb in the UV and visible range during daytime and emit at a higher wavelength in the visible region. This imparts a characteristic glow to the pigments.[87] These pigments have been used to good advantage by artists since 1950's. Two paintings named 'The Daily Neo-Mythology' and 'The Monster', on aluminium, belonging to the Italian pop artist Silvio Pasotti (1933-) were surveyed by Longoni *et al.,*[88] They utilized Raman spectroscopy, Fourier-transform infrared spectroscopy (FTIR), spectrofluorimetry with visible excitation and visible reflectance spectroscopy to look into the pigments present in the two artworks. The synthetic organic pigments present included phthalocyanine blue RS (PB15:1), phthalocyanine greens (PG7 and PG36), toluidine red (PR3), isoindole yellow (PY109), Hansa yellow (PY1) and anthraquinone (PV5). Phthalocyanine blue RS (PB15:1) is the α-form of phthalocyanine blue (PB15). Various inorganic pigments viz., the rutile variety of titanium dioxide, ultramarine blue, Prussian blue, barium sulphate and calcite were also located. All the pigments depicted fingerprint Raman signals viz., red β-naphthol demonstrated Raman bands at 793, 982, 1120, 1183, 1214, 1252, 1317, 1332, 1395, 1445, 1496, 1555, 1622 cm^{-1}, naphthol red showed prominent bands at 963, 1044, 1365, 1426, 1493, 1555, 1582 cm^{-1}, arylide yellow or Hansa yellow exhibited signature Raman vibrations at 789, 945, 997,1135, 1252, 1311, 1484, 1623 and Raman signals at 262 and 1400 cm-1 were attributed to anthraquinone. Of particular interest was the discovery of the fluorescent pigment rhodamine 6G in both the paintings by means of UV induced fluorescence and Vis-Raman spectroscopy. The Raman spectra displayed a relative maximum around 480nm, an intense fluorescence peak around 600nm and absorption bands at 530, 630 and 690nm. This work is one of the few instances of Raman spectroscopic study of fluorescent pigments in paintings to the best of our knowledge.

Raman spectroscopy also proved effective in the investigation of miniature paintings as demonstrated by Burgio *et al.,*[89] They complemented Raman microscopy with X-ray fluorescence technique in order to ascertain the pigment palette of eighteen miniature portraits of late 16th to early 17th century England. The principal pigments deduced included lead white, vermillion, red lead, indigo, azurite and amorphous carbon which all manifested their typical Raman spectra.

To summarise, the present review puts forward the importance of Raman spectroscopy in heritage science highlighting its applications in pigment studies of ancient manuscripts and panel and canvas paintings. The work discusses the pigments located in each art specimen along with their chemical compositions, degradation products and mechanisms and corresponding Raman bands. The article also elucidates the fact that the introduction of portable Raman instruments and other improved Raman techniques has proved essential in the investigations of various art objects. It throws light on the fact that Raman spectroscopy is a major analytical tool to establish the authenticity of an art work. The procedure also plays an important role in understanding not only the cultural history of a particular region but also its socio-political history. In conclusion, it may be suggested, that Raman spectroscopy has the potential to scrutinize the effects of various environmental factors including that of pollutants on pigments and dyes and this avenue may be traversed in future to have a better insight in case of more complex art specimens.

ACKNOWLEDGEMENT

The author thanks Department of Chemistry, Hooghly Mohsin College, Chinsurah, Hooghly, West Bengal, India.

REFERENCES

1. Casadio, F.; Daher, C.; Bellot-Gurlet, L. *Top. Curr. Chem.*, **2016**, *374*(62), 161-211.
2. Madariaga, J. M. *Anal. Methods.,* **2015**, *7*, 4848-4876.
3. Committee AMCTB. *Anal. Methods.,* **2015**, *7*, 4844-4847.
4. Casadio, F.; Van Duyne, R. P. *Analyst.,* **2013**, *138*, 7276–7278.
5. Vandenabeele, P.; Edwards, H. G.; Moens, L. *Chem. Rev.*, **2007**, *107*(3), 675-686.
6. Buckley, S. *Antiquity.*, **2015**, *80*, 733-734.
7. Soonmin, H. *Orient. J. Chem.*, **2019**, *35* (Special Issue 1), 1-7.
8. Vijayasekhar, J. *Orient. J. Chem.*, **2018**, *34*(5), 2671-2672.
9. Arlt, T.; Mahnke, H-E.; Siopi, T.; Menei, E.; Aibéo, C.; Pausewein, R-R.; Reiche, I.; Manke, I.; Lepper, V. *J. Cult. Herit.*, **2019**, *39*, 13–20.
10. Caggiani M. C, Colomban P. *Phys. Sci. Rev.,* **2018**, *3*, 7-24.
11. Edwards, H. *Encyclopedia of Spectroscopy and Spectrometry.*, **2013**, 2-17.
12. Pérez-Rodríguez, J. L.; Robador, M. D.; Centeno, M. A.; Siguenza, B.; Duran, A.; *Spectrochim. Acta-A: Mol. Biomol. Spectrosc.*, **2013**, *120*, 602-609.
13. Maguregui, M.; Knuutinen, U.; Martínez-Arkarazo, I.; Giakoumaki, A.; Castro, K.; Madariaga, J. M. *J. Raman Spectrosc.*, **2012**, *43*(11), 1747-1753.
14. Łydzba-Kopczyńska, B. I.; Gediga, B.; Chojcan, J.; Sachanbiński, M. *J. Raman Spectrosc.*, **2012**, *43*(11), 1839–1844.
15. Bersani. D.; Lottici. P. P. *Anal Bioanal. Chem.*, **2010**, *397*, 2631–2646.
16. Bellot-Gurlet, L.; Le Bourdonnec, F-X.; Poupeau, G.; Dubernet, S. J. Raman *Spectrosc.*, **2004**, *35*(89), 671–677.
17. Smith, G. D.; Clark, R. J. H. *J. Archaeol. Sci.*, **2004**, *31*, 1137–1160.
18. Clark, R. J. H. C. R. *Chim.*, **2002**, *5*, 7-20.
19. Raman, C. V. *Indian J. Phys.*, **1928**, *2*, 387-398.
20. Delhaye, M.; Dhamelincourt, P. *J. Raman Spectrosc.*, **1975**, *3*, 33–43.
21. Guineau, B. *J. Forensic Sci.*, **1984**, *29*, 471-485.
22. Guineau, B. *Stud. Conserv.*, **1984**, *29*, 35–41.
23. Centeno, S. A. *J. Raman Spectrosc.*, **2016**, *47*(1), 9-15.
24. Pozzi, F.; Basso, E.; Rizzo, A.; Cesaratto. A.; Tague, T. J. *J. Raman Spectrosc.*, **2019**, *50*, 861–872.
25. Madariaga, J.; Bersani, D.; Colomban, P. *J. Raman Spectrosc.*, **2012**, *43*, 1529-1535.
26. Gnyba, M.; Smulko, J. M.; Kwiatkowski, A. J.; Wierzba, P. *Bull. Pol. Acad. Sci. Tech. Sci.*, **2011**, *59*, 325-329.
27. Sakamoto, A.; Ochiai, S.; Higashiyama, H.; Masutani, K.; Kimura, J.; Koseto-Horyu, E.; Koseto-Horyu, E.; Tasumi, M. *J. Raman Spectrosc.*, **2011**, *43*(6), 787-791.
28. Pigorsch, E. *J. Raman Spectrosc.*, **2020**, *52*(1), 78–84.
29. Minčeva-Šukarova, B.; İssi, A.; Raškovska, A.; Grupče, O.; Tanevska, V.; Yaygıngöl, M.; Kara, A.; Colomban, P. *J. Raman Spectrosc.,* **2012**, *43*(6), 792-798.
30. Giakoumaki, A.; Osticioli, I.; Anglos, D. *Appl. Phys. A.,* **2006**, *83*, 537–541.
31. Langer, J.; de Aberasturi, D. J.; Aizpurua, J.; Alvarez-Puebla, R. A.; Auguié, B.; Baumberg, J. J.; Bazan, G. C.; Bell, S. E. J.; Boisen, A.; Brolo, A. G.; Choo, J.; Cialla-May, D.; Deckert, V.; Fabris, L.; Faulds, K.; de Abajo, F. J. G.; Goodacre, R.; Graham, D.; Haes, A. J.; Haynes, C. L.; Huck, C.; Itoh, T.; Käll, M.; Kneipp, J.; Kotov, N. A.; Kuang, H.; Le Ru, E. C.; Lee, H. K.; Li, J-F.; Ling, X. I.; Maier, S. A.; Mayerhöfer, T.; Moskovits, M.; Murakoshi, K.; Nam, J-W.; Nie, S.; Ozaki, Y.; Pastoriza-Santos, I.; Perez-Juste, J.; Popp, J.; Pucci, A.; Reich, S.; Ren, B.; Schatz, G. C.; Shegai, T.; Schlücker, S.; Tay, L-L.; Thomas, K. G.; Tian, Z-Q.; Van Duyne, R. P.; Vo-Dinh, T.; Wang, Y.; Willets, K. A.; Xu, C.; Xu, H.; Xu, Y.; Yamamoto, Y. S.; Zhao, B.; Liz-Marzán, L. M. *ACS Nano.*, **2020**, *14*(1), 28–117.

32. Campanella, B.; Botti, J.; Cavaleri, T.; Cicogna. F.; Legnaioli. S.; Pagnotta, S.; Poggialini, F.; Poli, T.; Scalarone, D.; Palleschi, V. *Microchem. J.*, **2020**, *152*, 104292-104299.
33. Zalaffi, M. S.; Karimian, N.; Ugo, P. *J. Electrochem. Soc.*, **2020**, *167*, 037548-037555.
34. Boscacci, M.; Francone, S.; Galli, K.; Bruni, S. *J. Raman Spectrosc.*, **2020**, *51*(7), 1108-1117.
35. Chiriu, D.; Pisu, F. A.; Ricci, P. C.; Carbonaro C. M. *Materials (Basel).*, **2020**, *13*(11), 2456-2472.
36. Smith, E.; Dent, G. **2019**, John Wiley & Sons, New York.
37. Bersani, D.; Conti, C.; Matousek, P.; Pozzi, F.; Vandenabeele, P. *Anal. Methods.*, **2016**, *8*, 8395-8409.
38. Gutiérrez-Neira, P. C.; Agulló-Rueda, F.; Climent-Font, A.; Garrido, C. *Vib. Spectrosc.*, **2013**, *69*, 13-20.
39. Vandenabeele, P.; Moens, L. *J. Raman Spectrosc.*, **2012**, *43*(11), 1545-1550.
40. Burgio, L.; Clark, R.; Hark, R. *Proceedings of the National Academy of Sciences of the United States of America.*, **2010**, *107*, 5726-5731.
41. Chiriu, D.; Desogus, G.; Pisu, F. A.; Fiorino, D. R.; Grillo, S. M.; Ricci, P. C.; Carbonaro, C. M. *Microchem. J.*, **2020**, *153*, 104404-104412.
42. Vandenabeele, P.; Conti, C.; Rousaki, A.; Moens, L.; Realini, M.; Matousek, P. *Anal. Chem.*, **2017**, *89*, 9218–9223.
43. Colomban, P. *Arts.,* **2013**, *2*, 77–110.
44. Davy, H. *Philos. Trans. R. Soc.*, **1815**, *105*, 97–110.
45. Salvetat, L. A. *Paris: Malet-Bachelier.,* **1857**.
46. Eccles, H.; Rackham, B. South Kensington, UK: Victoria and Albert Museum Publishing, **1922**.
47. Hall, E T. *Archaeometry.,* **1960**, *3*, 29-37.
48. Bell, I. M.; Clark, R. J. H.; Gibbs, P. *J. Spectrochim. Acta A Mol Biomol Spectrosc.*, **1997**, *53*(12), 2159-2179.
49. Marucci, G.; Beeby, A.; Parker, A. W.; Nicholson, C. E. *Anal. Methods.,* **2018**, *10*, 1219-1236.
50. Tomasini, E. P.; Gómez, B.; Halac, E. B.; Reinoso, M.; Di Liscia, E. J.; Siracusano, G.; Maier, M. S. *Herit. Sci.*, **2015**, *3*, 19-26.
51. Fremout, W.; Saverwyns, S. *J. Raman Spectros.*, **2012**, *43*(11), 1536-1544.
52. Scherrer, N. C.; Stefan, Z.; Francoise, D.; Annette, F.; Renate, K.; *Spectrochim Acta A Mol Biomol Spectrosc.*, **2009**, *73*(3), 505-524.
53. Lahlil, S.; Lebon, M.; Beck, L.; Rousselière, H.; Vignaud, C.; Reiche, I.; Menu, M.; Paillet, P.; Plassard, F. *J. Raman Spectrosc.*, **2012**, *43*(11), 1637-1643.
54. Tomasini, E. P.; Halac, E. B.; Reinoso, M.; Di Liscia, E. J.; Maier, M. S. *J. Raman Spectrosc.*, **2012**, *43*(11), 1671-1675.
55. Casadio, F.; Bezur, A.; Fiedler, I.; Muir, K.; Trad, T.; Maccagnola, S. *J. Raman Spectrosc.*, **2012**, *43*(11), 1761-1771.
56. Defeyt, C.; Vandenabeele, P.; Gilbert, B.; Van Pevenage, J.; Cloots, R.; Strivay, D. *J. Raman Spectrosc.*, **2012**, *43*(11), 1772-1780.
57. Fremout, W.; Saverwyns, S. *J. Raman Spectrosc.*, **2012**, *43*(11), 1536-1544.
58. Colombini, A.; Kaifas, D. *E-Preservation Sc.*, **2010**, *7*, 14-21.
59. Castro, K.; Pérez-Alonso, M.; Rodríguez-Laso, M. D.; Fernández, L. A.; Madariaga, J. M. *Anal. Bioanal. Chem.*, **2005**, *382*, 248-258.
60. Bouchard, M.; Smith, D. C. *Spectrochim. Acta A Mol Biomol Spectrosc.*, **2003**, *59*(10), 2247-2266.
61. Burgio, L.; Clark, R. *J. Spectrochim Acta A Mol Biomol Spectrosc.*, **2001**, *57*(7), 1491-1521.
62. Clark, R. J. H.; Cridland, L.; Kariuki, B. M.; Harris, K. D. M.; Withnall, R. *J. Chem. Soc. Dalton Trans.*, **1995**, 2577-2582.
63. Gilbert, B.; Denoël, S.; Weber, G.; Allart, D. *Analyst.,* **2003**, *128*, 1213-1217.
64. Best, S. P.; Clark, R. J. H.; Withnall, R. *Endeavour, New Series.,* **1992**, *16*, 66-73.
65. Best, S. P.; Clark, R. J. H.; Daniels, M. A. M.; Withnall, R. *Chem. in Britain.,* **1993**, 118-122.
66. Best, S. P.; Clark, R. J. H.; Daniels, M. A. M.; Porter, C. A.; Withnall, R. *Stud. Conserv.*, **1995**, *40*(1), 31–40.
67. Carter, E. A.; Pérez, F. R.; García, J.; Edwards, H. G. *Philos. Trans. Royal Soc.*, **2016**, 374.
68. Clark, R. J. H. London, UK: Christopher Ingold Laboratories, University College London., **2003**, *162.*
69. Muralha, S.; Burgio, L.; Clark, R. *Spectrochim. Acta A Mol Biomol Spectrosc.*, **2012**, *92*, 21-28.
70. Cappa, F.; Fruehmann, B.; Schreiner, M. Ed (s): Lazzara, G.; Fakhrullin, R. *Nanotechnologies and Nanomaterials for Diagnostic, Conservation and Restoration of Cultural Heritage.*, **2019**, 127-147.
71. Nastova I.; Grupče, O.; Minčeva-Šukarova, B.; Ozcatal, M.; Mojsoska, L. *Vib. Spectrosc.*, **2013**, *68*, 11-19.

72. Nastova, I.; Grupce, O.; Minčeva-Šukarova, B.; Turan, S; Yaygingol, M.; Ozcatal, M.; Martinovska, V.; Jakovlevska-Spirovska, Z. *J. Raman Spectrosc.*, **2012**, *43*(11), 1729-1736.
73. Miguel, C.; Claro, A.; Goncalves, A. P.; Muralha, V. S. F.; Melo, M. J. *J. Raman Spectrosc.*, **2009**, *40*(12), 1966-1973.
74. Muralha, V. S. F.; Miguel, C.; Melo MJ. *J. Raman Spectrosc.*, **2012**, *43*(11), 1737-1746.
75. Koochakzaei, A.; Gharetapeh, S. A.; Bidgoli, B. *J. Herit. Sci.*, **2022**, *10*, 1-16.
76. Brown, K.; Clark, R. *J. Raman Spectrosc.*, **2004**, *35*(1), 4-12.
77. Roosen-Runge, H.; Werner, A. E. A.; in Kendrick TD, (Ed.), Oltun and Lausanne, Switzerland., **1960**, *1*, 261-295.
78. Stanzani, E.; Bersani, D.; Lottici, P. P.; Colomban, P. *Vib. Spectrosc.*, **2016**, *85*, 62-70.
79. Edwards, H.; Vandenabeele, P.; Benoy, T. *J. Spectrochim. Acta A Mol Biomol Spectrosc.*, **2014**, *137C*, 45-49.
80. Hibberts, S.; Edwards, H.; Abdel-Ghani, M.; Vandenabeele, P. *Philos. Trans. Royal Soc.*, **2016**, 374.
81. Burgio, L.; Clark, R. J. H.; Sheldon, L.; Smith, G. D. *Anal. Chem.*, **2005**, *77*(5), 1261–1267.
82. Surtees, A. P. H.; Telford, R.; Edwards, H. G. M.; Benoy, T. J. *J. Raman Spectrosc.*, **2021**, *52*(12), 2228-2223.
83. Saverwyns, S. *J. Raman Spectrosc.*, **2010**, *41*(11), 1525-1532.
84. Chaplin, T. D.; Clark, R. *J. H. Appl. Phys. A.,* **2016**, *122*, 144-148.
85. Cazzanelli, E.; Platania, E.; Santo, G.; Fasanella, A.; Castriota, M. *J. Raman Spectrosc.*, **2012**, *43*(1), 1694-1698.
86. Vandenabeele, P.; Verpoort, F.; Moens, L. *J. Raman Spectrosc.*, **2001**, *32*(4), 263-269.
87. Ismael, R.; Schwander, H.; Hendrix, P. Ullmann's Encyclopedia of Industrial Chemistry., **2013**.
88. Longoni, M.; Cicala, N.; Guglielmi, V.; Poldi, G.; Bruni, S. *Heritage.,* **2022**, *5*, 42-60.
89. Burgio, L.; Cesaratto, A.; Derbyshire, A. *J. Raman Spectrosc.*, **2012**, *43*(11), 1713-1721.