Comparison and characterization of pigments and dyes by Raman spectroscopy

Cheng-Huang Lin1,2 · Yuan-Feng Chang1

Received: 31 July 2021 / Accepted: 29 October 2021
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Abstract
This review provides a general understanding of Raman spectroscopy for use in the identification of pigments and dyes. The methodologies associated with a number of different related applications are also summarized. The first part of this review clarifies our basic knowledge regarding natural minerals and pigments. The second part discusses the fundamentals of currently used Raman spectroscopy, including surface-enhanced Raman scattering, μ-Raman spectroscopy, Raman imaging and spatially offset Raman spectroscopy. The third part focuses on recent applications, including the identification and analysis of various pigments and dyes that are used in paintings and related artworks. These studies show that Raman spectroscopy has great potential for use as a method for the rapid, non-destructive identification of such substances.

Keywords Pigments · Dyes · Raman spectroscopy · Non-destructive inspection

Introduction
Cultural relics and works of art are precious, and the rarity is due to their esthetic and historical significance. Therefore, the restoration and testing of cultural relics should be based on “non-destructive testing techniques” to minimize damage to cultural relics. As a non-destructive method of identification, Raman spectroscopy is one of the more convenient methods for the identification of pigments and dyes. Many natural minerals can be used as pigments when they are ground to fine powders. These include quartz (SiO2), bauxite (Al2O3), hematite (Fe2O3), magnetite (Fe3O4), pyrite (FeS2), marble (CaCO3), gypsum (CaSO4), cinnabar (HgS), galena (PbS), and barite (BaSO4). Raman spectroscopy is particularly suitable for the analysis of these types of inorganic pigments. Comparison and analysis characteristics of natural pigments can be roughly divided into several categories: (1) understanding the pigments and techniques that are used by artists, (2) researching the causes of the aging of paintings or pigments, and (3) improving inspection and processing methods/techniques, etc. These studies are interdisciplinary and include chemistry, physics and biology as well as art history and anthropology. Raman spectroscopy, including surface-enhanced Raman scattering (SERS), recently μ-Raman spectroscopy, Raman imaging and spatially offset Raman spectroscopy are frequently used for the identification of pigments/dyes in paintings [1–10]. A free online Raman spectra database has been reported by A. Mangone et al. [4]. As they describe, the “Pigments Checker Free Spectra Database” is an ongoing project with the goal of thoroughly characterizing each pigment in a collection with a series of spectroscopic and imaging techniques and to allow open access to the data. A Raman spectroscopic library of medieval pigments collected for five different wavelengths has also been reported by C. E. Nicholson, et al. [3]. Furthermore, the Infrared & Raman Users Group (http://www.irug.org) is a community that shares high-quality comparative reference spectral data, including IR and Raman reference spectra for the study of works of art, architecture, and archeological materials.

This review provides a general understanding of pigments/dyes, their characteristics and analysis by Raman spectroscopy and the characteristics of pigments and dyes are also described.
Raman spectroscopy can be used in non-destructive analyses and is undoubtedly one of the more appropriate methods for use in the identification of pigments and dyes. The spectral lines that are obtained are consistent, irrespective of the excitation wavelength of the laser, which is also an advantage of Raman spectroscopic methods. Although the Raman scattering light has intensified, the intensity of the fluorescence will also greatly increase. To avoid interference from fluorescence, lasers with longer wavelengths, such as green lasers of 532 nm or near-infrared lasers of 785 nm, are typically used as the excitation light source. In some case the use of the SERS (surface-enhanced Raman scattering) technique can be helpful in terms of reducing the interference of fluorescence [11]. Micro-Raman (μ-Raman) spectroscopy is the most extensively utilized type of Raman spectroscopy, which involves the pairing of an optical microscope with a Raman spectrometer. This coupling provides enormous power in sampling regions with high spatial resolution, in the order of 1 μm. On the other hand, Raman imaging is analogous to taking a photograph, in which spectral intensity values are collected simultaneously from the entire area of interest [8]. The Raman scattering light is filtered so that the intensity of just one narrow part of the spectrum is recorded on the detector whenever the laser illuminates a square or circular region on the sample. This method permits specific spectral information from different points to be obtained, leading to the formation of one-dimensional profiles, two-dimensional images, or three-dimensional rendered volumes [8]. Furthermore, spatially offset Raman spectroscopy is a spectroscopic technique that allows for the non-invasive chemical characterization of diffusely scattered materials, ranging from opaque plastics to biological tissues [6]. It has been explored for a range of applications, including objects of art.

**Raman spectral analysis of pigments and dyes**

**White pigments and dyes**

Kaolinite (Al₂Si₂O₅(OH)₄) or ground calcite (white lime; CaCO₃) can be ground to powder and used as a white pigment that can be mixed with water. These pigments are very important white/gray pigments, paints or building materials. Quicklime (calcium oxide, CaO), slaked lime (calcium hydroxide, Ca(OH)₂) and limestone (calcium carbonate, CaCO₃) are also pigments that were commonly used in the past. For example, some frescoes were painted using calcium hydroxide, and after the hydroxide is converted into calcium carbonate, they can be preserved for a very long period of time. Calcium carbonate has three isoforms: calcite, aragonite, and vaterite. Although the chemical composition is the same, the physical properties are quite different. Calcite (β-CaCO₃, calcite) is a rhombohedral structure of the hexagonal crystal system with two sets of intersecting rhombohedral cleavages; aragonite (λ-CaCO₃, aragonite) is an orthorhombic crystal system with only a parallel long axes. The cleavage is not obvious. For either form, the major vibrational modes arise from the –CO₃ molecule. Figure 1 (A) shows a schematic of a calcium carbonate (CaCO₃) crystal. The ionic radius of the CaCO₃ lattice is 100 pm (1 pm = 10⁻¹² m). Figure 1 (B) illustrates the six basic vibrational modes of CaCO₃ molecules. The vibrational modes of the molecule are represented by abbreviations. \( E_g (T) \) represents a mode in which the carbon atom does not move, while the three oxygen atoms move in the direction of the arrows. \( E_g (L) \) represents the mode in which the carbon atom does not move, two oxygen atoms move upward, and the third oxygen atom moves downward. The strongest vibrational mode is \( A_{1g} \) movement. For CaCO₃, the...
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wave number is 1085 cm\(^{-1}\). Some minerals show up to six similar vibrational modes. For example, CdCO\(_3\) (otavite), MnCO\(_3\) (rhodochrosite), FeCO\(_3\) (siderite), ZnCO\(_3\) (smithsonite), CoCO\(_3\) (spherocobaltite) and MgCO\(_3\) (magnesite) show the strongest \(A_{1g}\) modes at 1088, 1088, 1087, 1093, 1092 and 1094 cm\(^{-1}\), respectively [12, 16]. With information on the other five vibrational modes, these minerals can be distinguished from one another, although these metallic minerals are not often used as pigments. Figure 2 shows a comparison of the Raman spectra for eight types of pigments (spectra, a-h), all of which contain CaCO\(_3\). The former four pigments were obtained from minerals (A) and the latter four pigments were produced from animals (B). As can be seen, the vibrational modes of the –CO\(_3\) group can be observed in the spectra (\(E_g^\parallel (T)\), 154; \(E_g^\parallel (L)\), 280; \(E_g\), 712; \(A_{1g}\) 1085; \(E_g\) 1434; \(A_{1g}\) + \(E_g\) 1747 cm\(^{-1}\), respectively). These natural minerals also contain some fluorescent substances, which therefore results in the production of fluorescence bands in the Raman spectrograph. On the other hand, all four animal pigments also basically have the six –CO\(_3\) vibrational modes; however, because these pigments are derived from animals, their compositions are more complex than those of minerals. Shell white is a commonly used white pigment in China and Japan and usually made from oyster shells. The weak vibrational mode in 142 cm\(^{-1}\) indicates that it is different from a pigment derived from a mineral. In addition, a red fluorescence with a wavelength of ~633 nm was also observed. This could be due to some surface pigment in the oyster shell. Although pearl powder and coral powder are not common pigments, they are found in some Japanese paintings. They all produce peaks in Raman spectra, which correspond to \(A_{1g}\) group. As mentioned above, CaCO\(_3\) can exist in three polymorphs: calcite, aragonite, and vaterite. Polymorphs refer to substances with similar chemical compositions, but were formed under different conditions, resulting in crystals with different structures. Regarding pearl powder, which contains the same calcium carbonate structure, vibrational peaks with a wavenumber of 142 cm\(^{-1}\) were not observed, but vibrational peaks with wavenumbers of 180, 208, and 705 cm\(^{-1}\) were observed. The 712 cm\(^{-1}\) peak became indistinct. Coincidentally, these Raman spectral peaks can be used to appraise the authenticity of pearls. In the Raman spectrum of white coral, in addition to the expected vibrational modes of carbonates, peaks with wavenumbers of 1129 (s), 1517 (s), 2252 (w), and 2635 (w) were observed. In fact, the Raman spectra of carotenoids contain four vibrational bands in the ranges: 1480–1580 cm\(^{-1}\) (\(v_1\)), 1100–1200 cm\(^{-1}\) (\(v_2\)), and 1260–1290 cm\(^{-1}\) (\(v_3\)), which correspond to polyacetylene. The \(v_4\) band has been reported between 990 and 1018 cm\(^{-1}\), but is assigned to the in-plane

**Fig. 2** Comparison of the Raman spectra for eight pigments, all of which contain CaCO\(_3\), which were obtained from minerals (A) or produced from animal sources (B), respectively

(A) CaCO\(_3\) from minerals

- \(E_g^\parallel (T)\), 154
- \(E_g^\parallel (L)\), 280
- \(E_g\), 712
- \(A_{1g}\) 1085
- \(E_g\) 1434
- \(A_{1g}\) + \(E_g\) 1747 cm\(^{-1}\)

(B) CaCO\(_3\) produced from animals

- Shell white
- Pearl powder
- White coral powder

![Raman spectra comparison](image-url)
rocking mode of the backbone –CH₃ groups [14]. These four peaks also appeared in the pink coral pigment and carbonate vibrational peaks, also observed with comparatively much lower intensities. If the pink coral pigment contains calcium, this indicates that it definitely contains calcium carbonate, even at relatively low amounts. Because red coral powder is extremely valuable, fake material composed of red marble powder is often found on this product. Another type of white pigment that is frequently used is white lead (basic lead carbonate, Pb(OH)₂·2PbCO₃). It had been used since ancient times and is the principal white pigment found in classical European oil paintings. In modern times, manufactured white pigments, such as zinc oxide (ZnO) and titanium white (TiO₂) have appeared in the market [15, 16]. Figure 3 shows Raman spectra of lead white, zinc white, titanium white and dolomite, respectively (spectra, a–d). It should be noted that lead white and dolomite show similar vibrational modes because of the –CO₃ group contained in its structure, but the vibrational modes are affected by the metal atoms (Pb or Mg). As a result, the strongest A₁g modes of lead white and dolomite are 1051 and 1099 cm⁻¹, respectively. Dolomite is also often found in white pigments. It can be used as a metallurgical flux, in refractory materials, building materials and ingredients for glass and ceramics. As a pigment in paint, zinc oxide is less opaque than titanium dioxide, but better than lithopone. Zinc oxide and titanium dioxide were first produced in 1834 and 1916, respectively. The former is suitable for glazing and drawing transparent cool colors and the latter is probably the most widely used white pigment that is now in use, since it is the brightest and most opaque of all white pigments and can cover all other whites. The so-called Chinese white is a special grade of zinc white, used as a pigment by artists, and is also the main ingredient of mineral makeup. Since lithopone (BaSO₄·ZnS) has good heat resistance, coating an object with a layer of this substance can improve its weather resistance. It is also a low-cost, white powder that does not transmit light easily, and its shading rate is second only to titanium dioxide. Lithopone is basically a mixture of gypsum and zinc sulfide, and, as expected, its Raman spectrum is similar to that of gypsum because it also contains an –SO₄ group. Raman spectra of different phases in the CaSO₄–H₂O system, including anhydrite (CaSO₄), bassanite (CaSO₄·1/2H₂O) and gypsum(CaSO₄·2H₂O) have been reported in detail [17, 18].

![Fig. 3 Comparison of the Raman spectra for four white pigments. Spectra a-d, Pb(OH)₂·2PbCO₃, ZnO, TiO₂, and CaMg(CO₃)₂, respectively](image)
Blue pigments and dyes

As a costly and rare blue pigment, the lapis lazuli has a long history of use. It was difficult to obtain blue pigments (ultramarine) that are ground from lapis lazuli, [19, 20] since the raw material is produced in Afghanistan. There is a blue pigment called Han blue (BaCuSi₄O₁₀) that has not been known until recently. Developed in ancient China, the so-called Chinese purple and Chinese blue, Han purple (BaCuSi₂O₆) and Han blue (BaCuSi₄O₁₀) were synthetic pigments (basic barium copper silicate) [21, 22]. Another early synthetic pigment was blue frit (Egyptian Blue, CaCuSi₄O₁₀), which was made by heating glass with a copper source. The ancient Egyptians had mastered some methods of making paint as early as the fourth century BC. They already knew how to use natural minerals, such as azurite (Cu₃(CO₃)₂(OH)₂), malachite (Cu₂CO₃(OH)₂) and cinnabar (HgS), by crushing them, and then washing the product with water to improve the purity of the pigments. Instead of lapis lazuli, malachite is widely distributed on the surface of the Earth and is a type of copper carbonate hydroxide mineral. Azurite often coexists with malachite, and can be used as copper ore to extract copper in large quantities [23]. After being ground into a powder, it can be used as a blue pigment, or even a glass-protected material [24]. Individual crystals are rare, but appear in the form of elongated to needle-like prisms. Therefore, in ancient times, blue pigments were produced from malachite or azurite, and green pigments were also obtained from malachite, or copper green (i.e., copper(II) acetate). Copper acetate reacts with arsenic trioxide to produce copper arsenate acetate, which was used as an insecticide and fungicide and is called Paris Green.

Figure 4 shows the Raman spectra of blue/green pigments obtained from malachite, respectively, as spectra (a) and (b). As can be seen, –CO₃ and –OH groups are found in both azurite (Cu₃(CO₃)₂(OH)₂) or malachite (Cu₂CO₃(OH)₂). This means that corresponding vibrational modes should be found in these spectra. In this case, the six –CO₃ vibrational modes are labeled with “arrow” symbols. The strongest A₁g modes of azurite and malachite are 1094 and 1096 cm⁻¹, respectively. The other modes are either too small to be identifiable, or they are overlapped by other peaks. These natural
minerals are all mixtures, which can also be seen from the photos in the insets. In the insets, spectra (a) and (b) show eight photos, randomly selected from various pigment powders, obtained by a CCD camera equipped on a microscope. It can be readily seen that some blue particles are present in the green pigment, and vice versa, i.e., some green particles are present in the blue pigment. In addition, there are particles of other colors, such as white, brown and black. These are probably quartz, iron oxide or other ingredients. Of course, it also depends on the origin of the ore.

In Taiwan (as well as in China), these pigments are usually separated into four portions based on the particle sizes. The large particles are darker in color, and the small particles are lighter. In Japan, these pigments are even divided into 10–12 grades, with different shades of color. When these pigments are ground into powder, there are still different particle sizes. When these pigments are added to water, the larger particles will sink to the bottom first, and the finer particles will sink more slowly. By using this principle, and repeating the steps several times, particles can be divided into many grades. After they dry, they are used as different shades of pigments. Although the pigments developed by these natural minerals have endured for a long time, moving the raw materials (stones) from the mountains to the place where they are processed is a difficult task. The pursuit of cheaper and more readily available blue pigment has always been something that painters and manufacturers have strived for. Prussian blue was the first modern synthetic pigment and it was frequently used in paintings, and was the traditional “blue” in blueprints and aizuri-e Japanese woodblock prints. A famous artwork that makes extensive use of Prussian blue, The Great Wave off Kanagawa by Hokusai, is characterized by its color. In 1870, the German chemist Adolf von Bayer reacted isatin and phosphorus trichloride and reduced the product, successfully producing indigo (C16H10N2O2). With the beauty of blue color, particularly indigo blue, the artwork of Hiroshige Utagawa was highly appreciated in Europe and America for the dynamic composition. This vivid blue is derived from the indigo plant and in Europe and America is called “Japan Blue” or “Hiroshige Blue”.

Figure 5 shows the Raman spectra of blue pigments/dyes: spectra (a)-(c) for ultramarine, Prussian blue (Fe₃[Fe(CN)₆]₃) and synthetic indigo (C₁₆H₁₀N₂O₂), respectively. Ultramarine is the noble color that symbolizes the Virgin Mary and is usually reserved for the most important paintings, such as the blue robe of the Virgin Mary by Gérard David. Non-destructive analysis of indigo dye in biological and textile samples and theoretical and experimental investigations regarding this dye have been reported [25–27]. Natural indigo extracted from the indigo plant is one of the earliest and most popular vat dyestuffs [27]. It has finer particles and a high transparency and is often used when drawing leaves in Chinese paintings. Sometimes, it can be adjusted to green by adding Garcinia. In the early twentieth century, phthalocyanine (C₃₂H₁₈N₈), a synthetic metallo-organic pigment, was prepared for use as an inexpensive synthetic blue dye. Phthalocyanine blue pigment is a chemical pigment that only appeared later. Phthalo blue 23,050 is a member of the class of phthalocyanines. It is a bright, crystalline, synthetic blue pigment from the group of phthalocyanine dyes. Its brilliant blue is frequently used in paints and dyes and, for this reason, some commercial indigo dyes have been replaced by phthalo blue 23,050. Furthermore, the synthesis of a blue pigment, the so-called YinMn Blue (Yin₁ₓMnₓO₃), was reported [28, 29]. This is an inorganic blue pigment that was discovered accidentally. Its color can be changed by adjusting the proportion of manganese ions Mn⁴⁺ in the preparation which is responsible for the intense blue color. It has stable chemical properties, is non-toxic and does not fade. Compared with its competing ultramarine and Prussian blue, it is more durable and retains its bright color in oil and water for longer periods of time.

**Green pigments and dyes**

Besides malachite, other minerals that can be used as green pigments include emerald green, Be₃Al₅(SiO₄)₆[OH]₆ [30, 31] turquoise, CuAl₆[PO₄]₄(OH)₆·4H₂O, and chrysocolla (Cu, Al)₂H₂Si₂O₅(OH)₄·nH₂O. Some differences in emerald green minerals that were obtained from nine gem-mining regions have been identified by Raman micro-spectroscopy. Patina was a favorite paint used by early Italian oil painters, but under many conditions its color turns to brown. Cobalt green is a green inorganic pigment composed of cobalt oxide and zinc oxide. It has a high resistance to light and can be dissolved in concentrated acid, but is insoluble in alkali. However, its transparency is not high and it is sparingly soluble. As a result, it is not popular with most artists. Modern cobalt green is composed of a combination of cobalt oxide and chromium oxide or titanium dioxide, which is much stronger than the traditional cobalt green in terms of light resistance. Cadmium green, a composite green, is a blend of cadmium yellow and phthalocyanine green. Cadmium yellow and phthalocyanine blue are both excellent pigments, and the light fastness and tinting power of cadmium green are also very good. Viridian and chromium oxide green (Cr₂O₃) are also common green pigments. The tinting strength and vividness of the color are slightly weaker, but the color is suitable for expressing the green of woods and plants, and can be used as olive green. Finally, phthalocyanine green G is a synthetic green pigment from the group of phthalocyanine dyes. It has many commercial names and the composition of phthalocyanine green is similar to phthalocyanine blue, mainly copper phthalocyanine, which is a non-toxic organic pigment. It is also very good in terms of light fastness and tinting power, and it is an important dark green pigment.
Red pigments and dyes

Red pigments can be obtained from the original ores, such as red ochre, anhydrous Fe₂O₃, and the hydrated yellow ochre (Fe₂O₃·H₂O). Lead tetroxide (Pb₃O₄) was also a common source for red pigment and is known as lead red. Cinnabar (HgS) was the most common source ore for producing elemental mercury, and it was the historic source of the brilliant red or scarlet pigment termed vermilion and associated red mercury pigments [32]. HgS is dimorphic with two crystal forms, i.e., red and black forms. Red cinnabar (α-HgS) is the form in which mercury is most commonly found in nature and black metacinnabar (β-HgS) is less common in nature and has the zinc blende crystal structure. Vermilion was produced from cinnabar and has been used since ancient times as a powdered rouge. The ingredients of this pigment include mercury sulfide, and all mercury compounds are toxic. The purest cinnabar comes from China, hence the name “China Red”. The Raman spectra of vermilion (α-HgS; 39.7, 250.9 cm⁻¹) and metacinnabar (β-HgS; 37.8, 252.8 cm⁻¹) were reported by M. Radepont [33]. Some electrochemical evidence shows that elemental mercury is formed during the photodegradation/photodarkening of α-HgS [34]. Before that, it is generally in the form of β-HgS. However, even though vermilion pigment had been used since ancient times, the reason for why the color deteriorates and turns black remains a mystery to this day. Another ancient red pigment is red lead (Pb₃O₄). It is a bright red or orange solid and is used as a pigment as well as in the manufacture of batteries and rustproof primer paints.

Figure 6 shows Raman spectra of some red pigments (frame A, cinnabar; frame B, red lead), respectively; the photos show their colors and single particles of the red pigments. Jasper powder can be used as a dark red pigment. The common red color is due to iron(III) inclusions. It is an aggregate of microgranular quartz and/or chalcedony and other mineral phases and is an opaque, impure variety of silica, usually red, yellow, brown or green in color and rarely blue. Jasper can be highly polished and is used for items such as vases, seals, and snuff boxes.
Figure 7 shows the Raman spectra of a dark-red pigment made from Jasper (major component: quartz, as shown as spectrum (a); 202, 462 cm\(^{-1}\)). In fact, it was found that Jasper consisted of quartz (202, 462 cm\(^{-1}\)), dolomite (1099 cm\(^{-1}\)) and ferric oxide \((\text{Fe}_2\text{O}_3)\), as shown in spectra (b–d), respectively. The insets, in spectra (a–d), show four photos, randomly selected from some pigment powders. Some other unidentified spectra are not shown herein. In addition to inorganic pigments, with deep red color, alizarin \((\text{C}_{14}\text{H}_8\text{O}_4)\) is a pigment derived from the roots of plants of the madder genus and has been used throughout history as a prominent red dye, principally for dyeing textile fabrics. In 1869, it became the first natural dye to be produced synthetically. It is the main ingredient for manufacturing madder lake pigments, known to painters as Rose madder and Alizarin crimson. However, alizarin shows strong fluorescence bands, so that it is necessary to use SERS for its identification [35–37]. Figure 8 shows a comparison of normal Raman spectra obtained by the normal method (spectrum a) and SERS (spectrum b), respectively; in the case of SERS, alizarin was adsorbed on nano-Ag. A proposed mechanism for the adsorption of alizarin on Ag surfaces has been reported [38]. The most intense peaks are located at 1154, 1213, 1286, 1325 and 1480 cm\(^{-1}\). Such characterization of alizarin in archeological sites requires an experimental approach that avoids the destruction or perturbation of the artwork, since the SERS technique may provide useful information in terms of the chemical composition by using very small sample sizes and without the need for manipulation. Some pigments that were discovered at an archeological site in Messina, Italy have been analyzed by SERS [39]. Safflower red is extracted from the petals of *Carthamus tinctorius* L. and it is also a traditional natural dye with a brilliant red hue. The main coloring component of safflower red is carthamin \((\text{C}_{43}\text{H}_{42}\text{O}_{22})\). The use of Fourier transform-Raman and SERS analysis of safflower red-dyed washi paper was reported by M. V. Cañamares et al. [40]. The most intense peaks for safflower red are located at 1363, 1320, 1277 and 1159 cm\(^{-1}\) [41]. Carmine is also an important red pigment. It is produced from carminic acid \((\text{C}_{22}\text{H}_{20}\text{O}_{13})\), which is extracted from some scale insects, such as the cochinial scale and certain Porphyrophora species. Brightly dyed British uniforms were well known as redcoats, denoting British soldiers. Until the eighteenth century, the raw material of this pigment was obtained from insects and its production remains a trade secret to the day.
Fig. 7 Comparison of the Raman spectra of Jasper, quartz, dolomite and ferroic oxide, (a, b), respectively. The inset picture shows the color of a single particle of the pigment.

(A) Jasper
(B) Quartz
(C) Dolomite
(D) Ferric oxide

Fig. 8 Comparison of the normal spectra of alizarin (a) and SERS spectra of alizarin adsorbed on nano-Ag, respectively.

(A) Alizarin
(B) Alizarin + nano-Ag

Raman shift/cm$^{-1}$
Yellow pigments and dyes

Lead monoxide (PbO) is a yellow pigment that has been commonly used since ancient times. It was introduced into China from Persia in the Tang Dynasty and was used as a medicine. Its modern applications are mostly in lead-based industrial glass and industrial ceramics. The identification of lead pigments and their degradation products via the use of Raman spectroscopy has been reported [42]. Most realgar (As$_4$S$_4$) and orpiment (As$_2$S$_3$) dyes are produced together in low-temperature hydrothermal deposits and sulfur volcanic fumaroles, so orpiment is a symbiotic mineral of realgar, and there is a saying that the mineral is likened to a mandarin duck. They were significant items of trade in the ancient Roman Empire, where it was used as a paint pigment. Early occurrences of realgar as a pigment have been found in art works from Egypt, India, Central Asia, China and Japan. The yellow pigments that were most consumed in ancient China were gamboge (gambogic acid; C$_{38}$H$_{44}$O$_8$), orpiment (As$_2$S$_3$) and realgar (As$_4$S$_4$). In Fig. 9, spectra (a) and (b) show Raman spectra of realgar (As$_4$S$_4$) and orpiment (As$_2$S$_3$), respectively [43, 44]. The photos in the inset show that their color distribution is from yellow to orange. In contrast to inorganic pigments, Indian yellow was widely used in art, cloth dyeing, wall paintings and other products. It was noted for its intense luminance and was imported into Europe and well known from its use in Rajput–Mughal miniature paintings from the sixteenth to the nineteenth century. It is known that some artists, including Jan Vermeer, are thought to have used Indian yellow in his “A woman weighing gold”. Raman spectra of an authentic Indian yellow pigment sample from a private collection has been reported [45]. Another organic pigment is gamboge yellow, which is a partially transparent deep saffron to mustard-colored yellow pigment [46]. It is the traditional color used to dye Buddhist monks’ robes. Gutta gum is not a gum, but a resin. It is an exudate from Garcinia plants, and is highly appreciated for its yellow color. Gamboge usually contains about 70–80% yellow resin (gambogic acid, C$_{38}$H$_{44}$O$_8$ and C$_{29}$H$_{36}$O$_6$) and 15–25% water-soluble gum [47]. Although some background fluorescence can be observed, without using SERS, its Raman spectrum still can be seen, as shown in Fig. 10 (inset, a photo of gamboge pigment). The most intense peaks of safflower red are located at 1594, 1637, 1437 and 1250 cm$^{-1}$. Gamboge yellow is suited for the color of the yellow areas in the plumage of some birds and it was used as a yellow pigment as early as the eighth century in Asia and Japan and regularly imported to Europe in the seventeenth century.

Purple pigments and dyes

Cobalt phosphate is an inorganic compound with the formula Co$_3$(PO$_4$)$_2$. It is a commercial inorganic pigment known as cobalt violet. After precipitating with a little phosphate solution, the cobalt salt solution has a beautiful purple color. Tyrian purple is a pigment made from mucus from snails of the oyster family and was originally used by the Phoenicians. Around 1200 BC, the Greeks inherited this process and continued to
produce until the fall of the Roman Empire in 1435. The production of this pigment is very time-consuming, and it has become a symbol of wealth and power. Murex is obtained from marine shellfish, which is widely distributed and especially abundant in tropical waters. The sub-gill glands of many types of Murex secrete a yellow mucus, which turns purple in the presence of light. The main chemical is 6,6'-dibromoindigo (C\(_{16}H_{8}Br_{2}N_{2}O_{2}\)). In 1856, W. H. Perkin, a British chemist, first discovered mauveine, an aniline dye that is also known as aniline purple and Perkin’s mauve. He was attempting to synthesize phytochemical quinine for the treatment of malaria, but his attempts led to the discovery of the first synthetic dyes. It also led to the production of many synthetic dyes and pigments. As a pioneer in the development of hundreds of synthetic dyes and pigments, such as azo and diazo compounds, these synthetic dyes led to the vigorous development of organic chemistry, including the systematic design of colorants. The development of organic chemistry has reduced our dependence on inorganic pigments. Quinacridone (C\(_{20}H_{12}N_{2}O_{2}\)) pigments are another orange, red and purple pigment with excellent fastness, bright shade and high tinting power after the appearance of phthalocyanine pigments. It is a polycyclic pigment and an organic pigment, with hues, such as magenta and scarlet, and is used in high-end oil paints.

**Black pigments**

Natural minerals were used as colorants since prehistoric times, in which black, red and white pigments were widely used pigments in ancient times. Charcoal or carbon black was used as a black pigment. Galena is one of the earliest minerals mined by mankind. People have used galena as cosmetics since the times of the ancient kingdom of Egypt. Galena (PbS) was used as a black pigment for many centuries, starting in antiquity, at least. Magnetite (Fe\(_{3}O_{4}\)) powder can also be used as a black pigment. However, when collecting its Raman spectrum, the laser power must be lowered; otherwise, the Raman spectrum of only Fe\(_{2}O_{3}\) is observed.

**Conclusion**

In this review, we summarize the characteristics of pigments and dyes based on Raman spectroscopy. This information may be of interest to readers who are interested in conservation science and related to artworks. Some basic knowledge, including recently developed Raman techniques, such as micro-Raman (μ-Raman) spectroscopy, Raman imaging and spatially offset Raman spectroscopy are discussed. The characteristics described herein are followed by white, blue, green, red, yellow and purple pigments or dyes. Some
applications are also described. Even though the present text is somewhat simple and concise, the material presented in this review will be very helpful to art beginners and art restoration workers when they deal with oil paintings, Japanese paintings, Chinese paintings, etc.

Acknowledgements This work was supported by grants from the Ministry of Culture of Taiwan under Contracts No. 110-Research-05 and the National Science Council of Taiwan under Contracts No. NSC 109-2113-M-003-006, respectively. The authors highly appreciate the cooperation of Miss. Pei-Wen Chien and Hui-Ting Chang in this review. They also wish to thank Prof. Way-Zen Lee (Department of Chemistry, NTNU), Prof. Hsiang-Lin Liu (Department of Physics, NTNU) and Prof. M. James Shyu (Department of Information Communications, CCU) for their many helpful suggestions.

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Cheng-Huang Lin received his PhD in 1994 from Kyushu University, Department of Applied Chemistry under the guidance of Prof. Totaro Imasaka. He then remained at that institution as a Research Assistant until 1996. Following this, he continued his research career as a postdoctoral fellow at Iowa State University in the USA. He returned to Taiwan in 1998, where he was appointed an Assistant Professor at Chaoyang University of Technology. Shortly after this, he was appointed an Assistant Professor at National Taiwan Normal University, where he was promoted to the rank of Professor in 2005. From 2021-, he moves to Department of Fine Arts. Now, his current research interests focus on conservation science,
especially on Asian cultural relics, based on Raman spectrometry and MALDI-TOFMS.

Yuan-Feng Chang received her PhD in Conservation Science from Tokyo University of the Arts in 1995. While studying in Tokyo, she studied Asian painting restoration at Handa Kyuseido which belong to ACNT. She joined Museum of Art, Boston, Conservation Dept. of Asian Painting (1997-2000). She then served as a consultant in the restoration project of the Dunhuang Mogao Grottoes at the Getty Museum. She returned to Taiwan in 2000, where she was appointed an Assistant Professor at National Tainan University of the Arts. After this, she was appointed an Associate Professor at National Taiwan Normal University, where she was promoted to the rank of Professor in 2015. From 2009 to now, she is the director of the Research Center for Conservation of Cultural Relics, National Taiwan Normal University.