

Introduction

Cultural heritage materials, such as paintings, books, documents, buildings, pottery, and monuments, are precious to society because they provide us with a snapshot of the practices and beliefs held by civilisations throughout different historical periods, which helps us understand better and map human development.

Humanity's high value on cultural heritage is a crucial driver of global tourism, reflected by the fact that in 2022, the international art and antiques market generated \$67.8 billion. To support this large market, the forensic study of cultural heritage materials allows for their authenticity to be determined and provides information about what techniques or materials were used in their creation. With historical context, this yields evidence about the period in which the materials were created and who could have made them. Forensic studies also enable the detection of forgery, which erodes trust in the preservation of heritage, can have severe socioeconomic consequences for the involved parties, and is a serious crime.

Raman spectroscopy is an established method for the molecular investigation of cultural heritage materials because it is non-destructive when used correctly, has exceptionally high molecular specificity and sensitivity, requires minimal sample preparation, and provides micron-range spatial resolution when coupled with confocal microscopy.¹ In this Application Note, the RM5 Confocal Raman Microscope, Figure 1, is used to identify different materials in cultural heritage artefacts.



Figure 1. Edinburgh Instruments RM5 Raman Microscope.

Materials and Methods

Raman spectroscopic measurements were performed on an Edinburgh Instruments RM5 Raman Microscope, equipped with 532 nm, 638 nm, and 785 nm lasers, a back-illuminated CCD detector, and a variable diameter confocal pinhole. These components can all be fully controlled using the Ramacle® software of the RM5 without disturbing the sample between measurements.

Rock Painting

The first artefact analysed was a multi-pigment flake extracted from a rock painting. Rock and cave paintings offer a window into the technological practices, societal structures, mythologies, and cognitive abilities of early human civilisations and, therefore, are of great interest to archaeologists and historians. When viewed under the microscope in brightfield mode, Figure 2a, the sample contained red, orange, white, and black pigments. The area of interest in the painting was analysed using a 785 nm laser, and the resulting spectra are shown in Figure 2b.

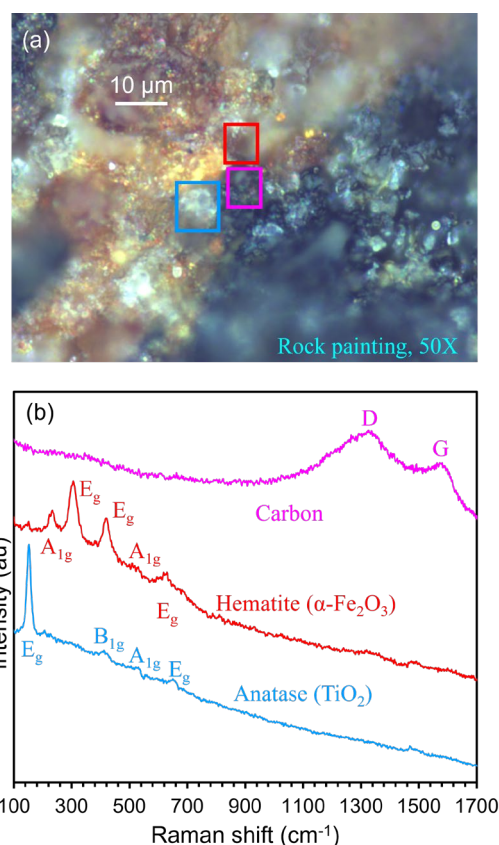


Figure 2. (a) Widefield image and (b) Raman analysis of a rock painting sample.

Unique spectral signatures were obtained from the framed regions on the rock painting. The pigment framed in pink contained a carbon-based colouring material, most likely prepared by charring wood and other plant-based matter. This assignment was made because of broad D and G bands ca. 1326 cm^{-1} and 1581 cm^{-1} , respectively, similar to carbonaceous materials such as graphene and graphite.² The prominence of the D band, associated with the crystalline disorder, in the spectrum suggests the carbon's amorphous structure.

The spectrum of the pigment bordered in red, which contained intense bands at 233 cm^{-1} , 305 cm^{-1} , and 419 cm^{-1} , was assigned as hematite. This naturally occurring and abundant mineral contains alpha-phase iron oxide (Fe_2O_3) and is found in rocks and soil.³

The material bordered in blue was assigned as anatase, one of the five naturally occurring mineral forms of titanium dioxide (TiO_2) found in veins and cavities of igneous rocks.⁴ This was determined because the spectrum exhibited highly characteristic crystal lattice modes at 148 cm^{-1} , 401 cm^{-1} , 520 cm^{-1} , and 644 cm^{-1} . The orange pigment, not bordered in the painting, contained signatures from anatase and hematite.

Glass from Shipwreck

A glass bead was procured from the cargo of a merchant ship that sank in the Adriatic Sea in the 16th century. An artefact such as a glass bead is valuable to historians because it provides information about European manufacturing at the end of the Renaissance period, and the flow of such goods from Europe to international markets can be tracked. A cross-section of the glass bead was embedded within a block of epoxy resin with an exposed flat face, and this was examined using Raman spectroscopy, Figure 3.

The widefield image in Figure 3a shows that the bead is primarily made of green glass (a section of which is framed in gold), there are orange inclusions around the edges of the bead (framed in red), and it contains an internal curved strip of white glass (framed in blue). Raman spectra from each of these regions are shown in Figure 2b. The spectra from the red and gold-framed areas, which required excitation with 532 nm and 785 nm lasers, respectively, exhibit subtly different broad Raman bands characteristic of silicon-oxygen bond vibrations in soda lime silicate glass.

The spectrum of glass can be split into three regions: the low-frequency region, referred to as the bending massif ca. 500 cm^{-1} ; the medium-frequency region, ca. 800 cm^{-1} ; and the high-

frequency region, ca. 1100 cm^{-1} , which is called the stretching massif.^{5,6} These bands are information-rich. For example, the amount of silicon and the processing temperature of glass can be determined from the ratio of the area under the bending and stretching curves. Further, the relative intensities of each of the peaks that make up the stretching massif can be used to detect doping in the glass or to identify different types of bonds and, therefore, glass subtypes throughout the same sample.

In the area bordered in blue, a spectrum was obtained with a broad peak ca. 640 cm^{-1} . This was assigned as an inclusion consisting of cassiterite (SnO_2). SnO_2 imparts opacity to glass, enamels, and ceramics, giving the materials a cloudy white colour.^{6,7}

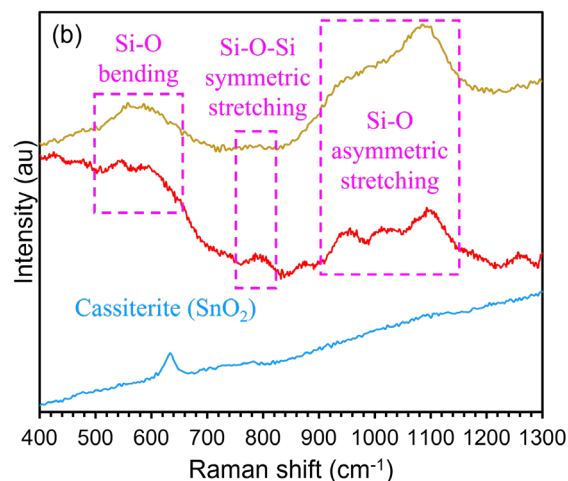
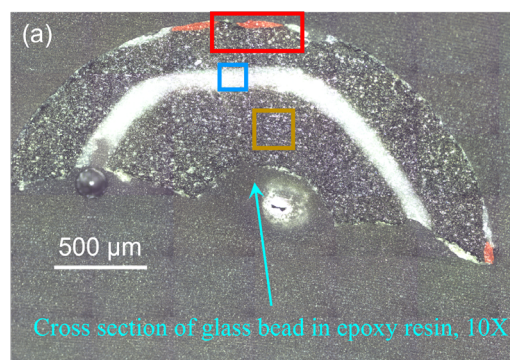


Figure 3. (a) Widefield image and (b) Raman analysis of glass bead.

Statues and Sculptures

Material from the face and hand of a figure depicting Saint Anthony of Padua, the patron saint of lost articles, were obtained and analysed to determine the pigments used by the sculptor. Religious icons, works of art used to represent sacred symbols and personages, are common in Roman Catholic and

Eastern Orthodox Churches. Statues and paintings of icons are found regularly in churches and cathedrals as a form of prayer. The spectroscopic study of religious icons is of significant interest to historians because it can be used to date the work, provides them with a better understanding of the evolution of painting techniques and can reveal later artistic modifications, all of which are helpful for restoration purposes.⁸ The Raman analysis of the materials in the icon is shown in Figure 4.

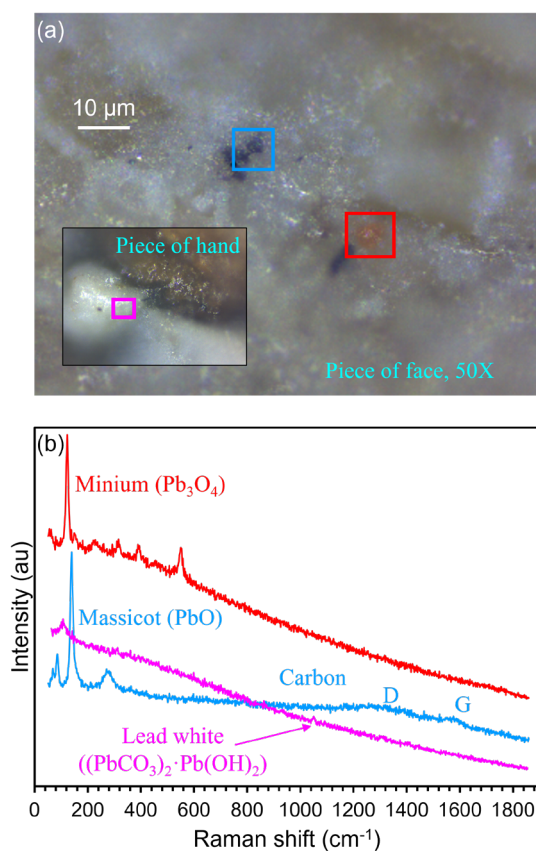


Figure 4. (a) Widefield image and (b) Raman analysis of pieces from the religious icon.

Various lead-based pigments were detected, and their location and corresponding spectra are shown in Figure 4. Lead-based paints were historically very popular because of their bright appearance, durability, and corrosion resistance, but their associated toxicity has led to diminished use. The orange pigment on the material taken from the face of the icon, bordered in red, was identified as minium, also known as red lead (Pb_3O_4). The spectrum of the pigment exhibited highly characteristic bands at 120 cm^{-1} and 549 cm^{-1} .⁹ The use of red lead can be traced back to at least the Middle Ages, where it was often preferred to the similarly coloured pigment

vermillion, made from powdered mineral cinnabar (HgS), because it was easier to prepare and less expensive.

The darker pigment from the face of the icon, bordered in blue, produced a Raman spectrum that indicated a mixture of two different materials. The D and G bands of a carbon-based material were detected, as were Raman signatures of the yellow pigment massicot (PbO) at 142 cm^{-1} and 285 cm^{-1} , another lead-based pigment that can be tracked back to antiquity.¹⁰

The white painted region on the material taken from the hand of the figure exhibited a small but consistently observed peak at 1050 cm^{-1} , which was assigned to the pigment lead white ($(\text{PbCO}_3)_2\cdot\text{Pb}(\text{OH})_2$).¹¹ It is one of the most common white pigments in paintings and murals, and it was even used historically as a cosmetic. The first recordings of the synthesis of the pigment can be dated back to the 4th Century BCE.¹²

Conclusion

In this Application Note, an Edinburgh Instruments RM5 Confocal Raman Microscope was used to analyse and identify materials in different cultural heritage samples. Raman microscopy is an excellent technique for the molecular investigation of cultural heritage materials because it is non-destructive, highly specific, sensitive, requires minimal sample preparation, can analyse very small samples, and provides micron-range spatial resolution.

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