

Raman Spectroscopy in Archaeological Studies

Chemical identification is an important part of the study of archaeological artefacts and artworks. This information can be obtained through nondestructive Raman analysis directly within the environment in which the artefacts are discovered. This information is extremely helpful in forming the basis of identifying pigments, dyes and paints used; thus indicating when and how a piece was made, giving insight into the time period of creation, and suggesting the authenticity of the object.

Raman spectroscopy can be used to measure lower frequency vibrations (than, for instance, FTIR) and this region below 500 cm^{-1} provides rich information for characterization of minerals and inorganic materials, such as pigments. By analyzing the Raman spectrum, we can also determine differences in polymorphic forms of pigments.

As Raman spectrometers have become smaller, the utility of Raman spectroscopy in archaeological investigations has increased. The instrument portability allows for on-site analysis without the need to remove samples and disrupt important archaeological sites. Portable Raman instruments such as the i-Raman® series are equipped with a fiber optic probe, which makes it easy to reach samples in different environments, even those that may be out of reach. The instrument portability and fiber optic probe can be used to measure samples of different shapes and sizes, without requiring sample preparation. The system laser power can be adjusted at 1% increments, allowing for use of low laser power (3 mW). Such versatility with the laser power control makes this system ideal in work with difficult samples such as dark pigments.

EXAMPLES

A recent study used portable Raman in the characterization of prehistoric paintings on the Abrigo de los Chaparros (Albalate del Arzobispo, Teruel) on the Iberian Peninsula[1]. The rock paintings were found in open-air shelters, making Raman measurements challenging due to sunlight and wind, as well as dust and crusts that have developed on the surface which can obscure the Raman signal of the

pigments. A flexible foam rubber cap (Carol's cap) was designed and utilized in the study to minimize these environmental interferences on the Raman spectra. A spectrum collected in daylight of finger dots in the cave is shown in **Figure 1**, where peaks of haematite (h) can be seen in addition to those attributed to crusts containing whewellite (w) and gypsum (g).



Figure 1. Raman spectrum of cave rock art measured in situ in daylight with peaks of the pigment haematite (h) and accretions of gypsum (g) and whewellite (w).

B&W Tek's portable Raman spectrometers are also being used in a comprehensive study of the materials used in the plasterwork in vaults of the Alhambra Hall of Kings, one of Spain's most important cultural sites[2,3]. This work which has been ongoing for several years is the study of the material in the plasterworks, focusing on the technologies in the application of the plasterworks and the decay they

have undergone over the centuries. **Figure 2** shows a schematic of the Hall of Kings indicating the location of the Raman instrument coupled to a microscope head on the scaffolding 12 m above ground, as well as pictures of the instrumentation and the video microscope with a motorized stage on a tripod mounting.



Figure 2. (a) Schematic of a vertical section of one vault in the Hall of the Kings with height of the scaffold holding instrumentation marked. (b) complete Raman instrument on top of the scaffolding and (c) details of the microscope probe on tripod. Reproduced from reference 2 with permission of The Royal Society of Chemistry.

Raman spectra were measured on the decorations of the stalactite vaults of the Alhambra without removing samples, thus maintaining the integrity of this important cultural heritage site while being able to study a larger area of the site. These decorations are built in gypsum and decorated in many colors reflecting the Islamic style. Different typical antiquity pigments have been identified, and from the details

of the spectra of lapis lazuli the geographic origin can also be identified. Blue is a predominant color in Islamic art, and originates from the mineral lazurite to form lapis lazuli pigment. **Figure 3** shows spectra of blue decorations in the vault and natural and synthetic blue pigments, all of which have the characteristic peak of the lazurite mineral at 548 cm^{-1} .



Figure 3. Raman spectra of blue pigments, all exhibiting characteristic lazurite peak at 548 cm⁻¹.

The pigments cinnabar and minium provide the red color in the vaults' decorations. These were found in different parts of the vaults, and appear to be used together in some decorative motifs. Spectra of the cinnabar were collected over the gypsum substrates. From the collected data, not only are the pigments

able to be identified, but also the degradation that they are undergoing. White coloring due to the degradation product calomel is present and detectable in the cinnabar Raman spectra as seen in **Figure 4**, which also include signal at 1009 cm⁻¹ from the gypsum over which the pigments are applied.



Figure 4. Raman spectra of cinnabar pigment in good condition, and showing signs of degradation.

Many of the gilded parts of the decorations have suffered from decay, and are not as widely present, so in situ analysis is often the only means of characterizing these limited (and often difficult to

access) sample regions[3]. Black area in the vaults near the gilding are consistent with tin oxides, suggesting that tin foil was used in place of gold in the gilding, perhaps during later restorations.

CONCLUSIONS

Portable Raman spectroscopy is an invaluable tool in the study of archaeological sites, allowing for in situ analysis which minimizes the impact of such studies on important cultural sites. The flexibility of the use of a fiber optic probe and tripod-mounted video microscope with a light weight instrument reduces the need for sampling, and increases the ability to make representative measurements over what can be very large sample areas. With laser power adjustable

to low levels, there is flexibility and control to work with difficult dark pigment samples. The information content of Raman spectroscopy is assisting in the understanding of the materials used in the construction and restoration of important archaeological sites, and in understanding the degradation that is occurring which should aid in preservation and restoration work.

ACKNOWLEDGEMENTS

The sharing of the research carried out by the groups whose work is highlighted here is gratefully appreciated. I would like to thank Prof. Antonio Hernanz of Universidad Nacional de Educacion a

Distancia in Madrid, Prof. Maria Jose Ayora Canada of the Universidad de Jaen, and Arturo Prudencio of Microbeam.

REFERENCES

1. "Spectroscopic characterisation of crusts interstratified with prehistoric paintings preserved in open-air rock art shelters", A. Hernanz et al, J. Raman Spectrosc., 2014 45(11), 1236-1243. doi 10.1002/jrs.4535
2. "In situ noninvasive Raman microspectroscopic investigation of polychrome plasterworks in the Alhambra", A. Dominguez-Vidal, M.J. de la Torre-Lopez, R. Rubio-Domene, M.J. Ayora-Canada, Analyst, 2012, 137(24), 5763-9. doi: 10.1039/c2an36027f.
3. "Gold in the Alhambra: study of materials, technologies, and decay processes on decorative gilded plasterwork", M.J. de la Torre-Lopez, A. Dominguez-Vidal, M.J. Campos-Sunol, R. Rubio-Domene, U. Schade and M.J. Ayora-Canada, J. Raman Spectrosc., 2014, 45(11), 1052-1058. doi 10.1002/jrs.4454

CONTACT

Metrohm Romania
Str. Emil Racoviță nr. 25
041753 București

office@metrohm.ro

CONFIGURATION



i-Raman Plus 785H Portable Raman Spectrometer

The i-Raman® Plus 785H is part of our award-winning series of i-Raman portable Raman spectrometers powered by our innovative intelligent spectrometer technology. Using a high-quantum-efficiency CCD array detector with TE cooling and high dynamic range, this portable Raman spectrometer delivers excellent performance with low noise, even at integration times of up to 30 minutes, making it possible to measure weak Raman signals.

The i-Raman Plus 785H features the unique combination of wide spectral range and high resolution with configurations which allow measurements from 65 cm^{-1} to $2,800\text{ cm}^{-1}$. The system's small footprint, lightweight design, and low power consumption ensure research-grade Raman analysis capabilities at any location. The i-Raman Plus is equipped with a fiber probe for easy sampling, and can be used with a cuvette holder, a video microscope, an XYZ positioning stage with a probe holder, as well as our proprietary BWIQ® multivariate analysis software and BWID® identification software. With the i-Raman Plus, you always have a high precision Raman solution for qualitative and quantitative analysis.



Raman Video Micro-Sampling Head (785 nm)

Video microscope sampling system head for use with B&W Tek's lab and industrial Raman probes. With coaxial LED illuminator for target alignment and video camera for sample observation. Compatible with standard microscope objectives. Probe not included, available separately. Objective lens not included, available separately. 785 nm configuration.