Application Note 410000004-A

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).

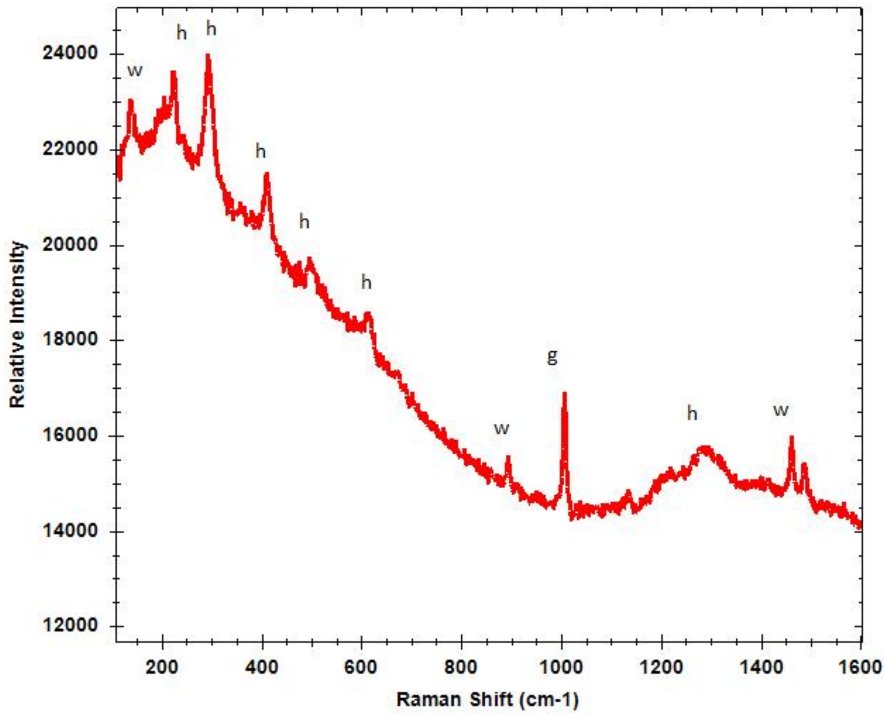

Figure 1. Raman spectrum of cave rock art measured in situ in daylight with peaks of the pigment haematite (h) and accretions of gypsum (g) and whewellite (w).

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.

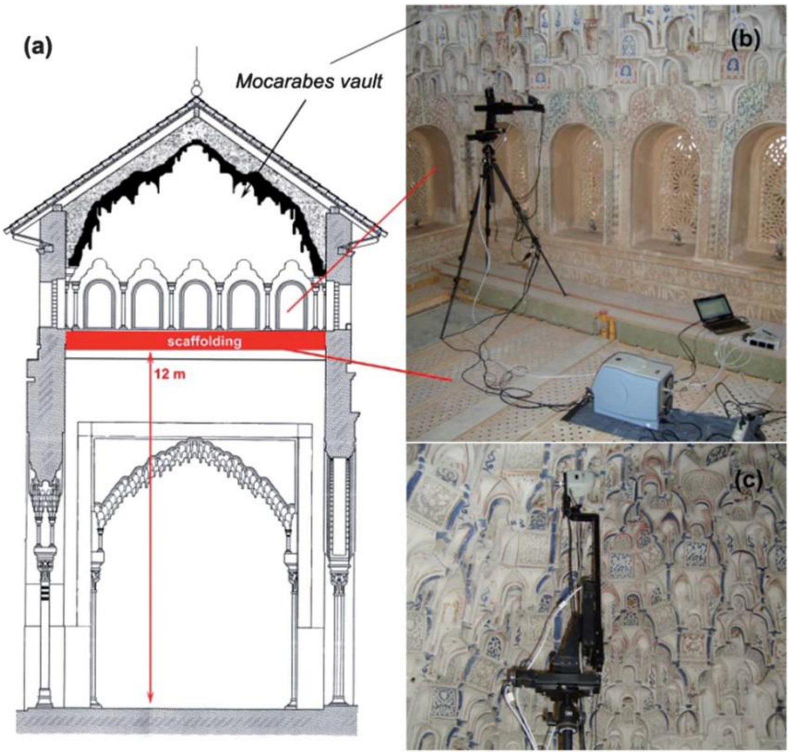

Figure 2. (a) Schematic of a vertical section of one vault in the Hall of the Kings with height of the scaffold holding instrumentation marked. (b) complete Raman instrument on top of the scaffolding and (c) details of the microscope probe on tripod. Reproduced from reference 2 with permission of The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

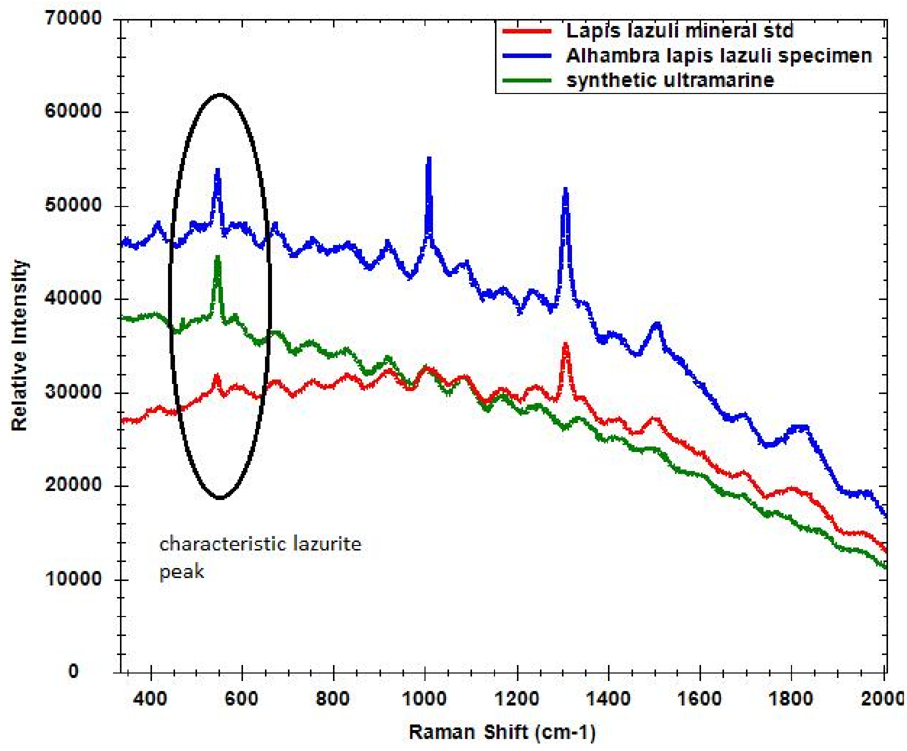

Figure 3. Raman spectra of blue pigments, all exhibiting characteristic lazurite peak at 548 cm-1.

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.

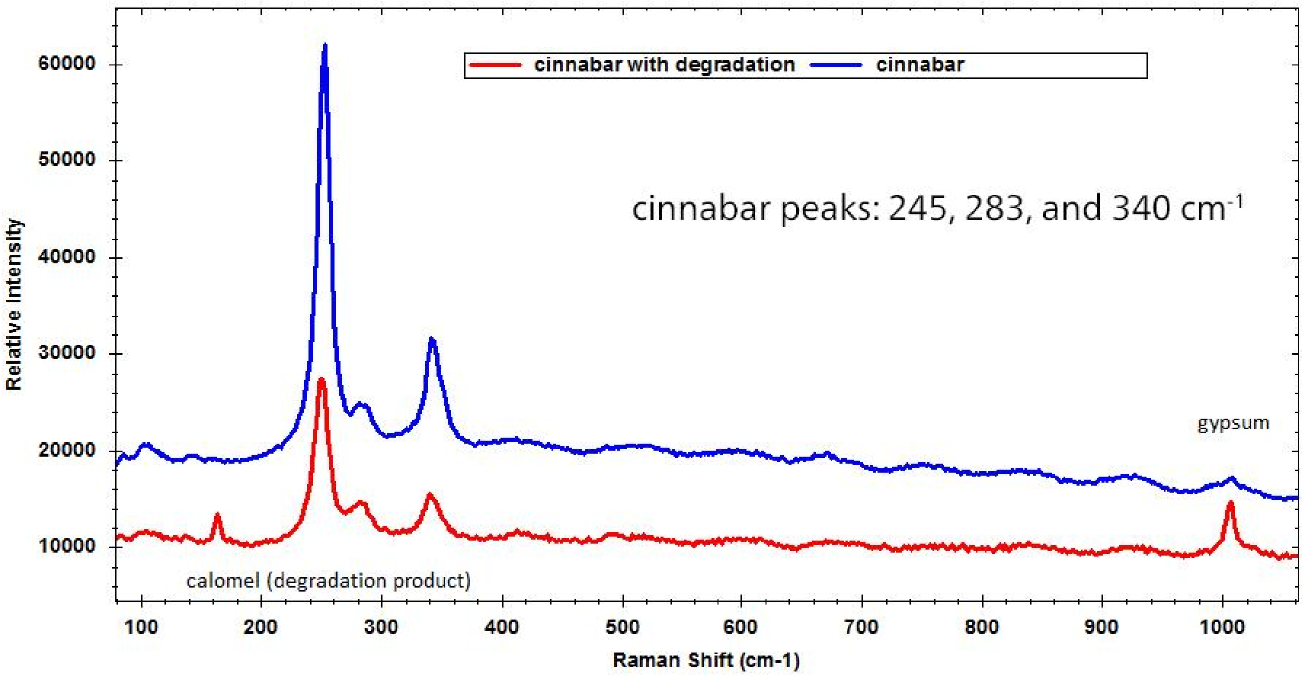

Figure 4. Raman spectra of cinnabar pigment in good condition, and showing signs of degradation.

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

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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

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CONFIGURATION

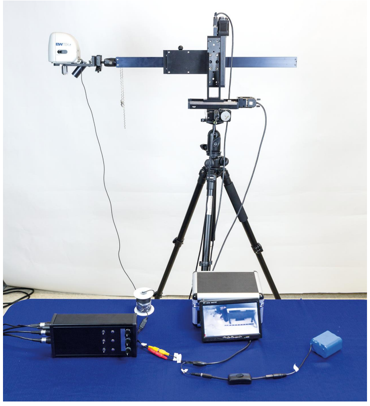
Spectromètre Raman portable i-Raman Plus 785H

L'i-Raman® Plus 785H appartient à notre série primée de spectromètres Raman portables « i-Raman », équipée de notre technologie de spectrométrie intelligente et innovante. Faisant appel à un détecteur à barrette CCD à haute efficacité quantique, avec refroidissement thermoélectrique et une gamme dynamique élevée, ce spectromètre Raman portable fournit des performances exceptionnelles avec un bruit réduit, même avec un temps d'intégration atteignant 30 minutes. Ainsi, les signaux Raman faibles peuvent aussi être mesurés.

Le i-Raman Plus 785H offre la combinaison exclusive d'une large gamme spectrale et d'une haute résolution avec des configurations autorisant des mesures de 65 cm^{-1} à 2800 cm^{-1}. Le faible encombrement et la légèreté de structure de ce système peu énergivore lui permettent d'effectuer partout des analyses Raman de qualité recherche. Équipé d'une sonde à fibre optique pour faciliter l'échantillonnage, l'i-Raman Plus peut être utilisé avec un support de cuvette, un microscope vidéo, une table de translation XYZ avec support de sonde ainsi qu'avec notre logiciel d'analyse à variantes multiples BWIQ® et le logiciel d'identification BWID®. Avec le i-Raman Plus, vous avez une solution Raman pérenne de haute fidelité pour l'analyse qualitative et quantitative.

Tête d'échantillonnage pour système Raman avec vidéomicroscope (785 nm)

Tete d'échantillonnage pour système Raman avec vidéomicroscope pour une utilisation avec les sondes Raman de B&W Tek en laboratoire ou dans l'industrie. Avec éclairage à LED coaxial pour une orientation sur la cible et caméra vidéo pour l'observation de l'échantillon. Compatible avec des objectifs de microscope standard. La sonde n'est pas fournie, elle est disponible séparément. La lentille d'objectif n'est pas fournie, elle est disponible séparément. Configuration 785 nm.



Potence manuelle pour le système d'échantillonnage vidéo Raman

La potence Raman portable possède un trépied léger, flexible et stable, qui donne à l'utilisateur la possibilité de fixer la tete du microscope BAC151x pour des mesures dans des zones d'accès difficile. La potence possède un positionnement de précision selon les axes XYZ manuel et s'adapte facilement aux divers environnements et locaux. Tete de microscope BAC151x non fournie. Adaptateur fourni.