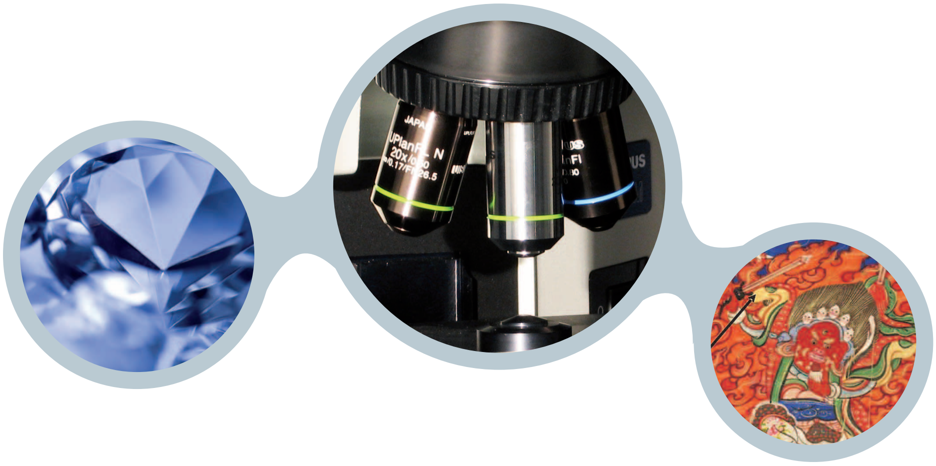

Application Note AN #518

Overcoming experimental challenges in Raman spectroscopy applied to art, archaeology and earth sciences

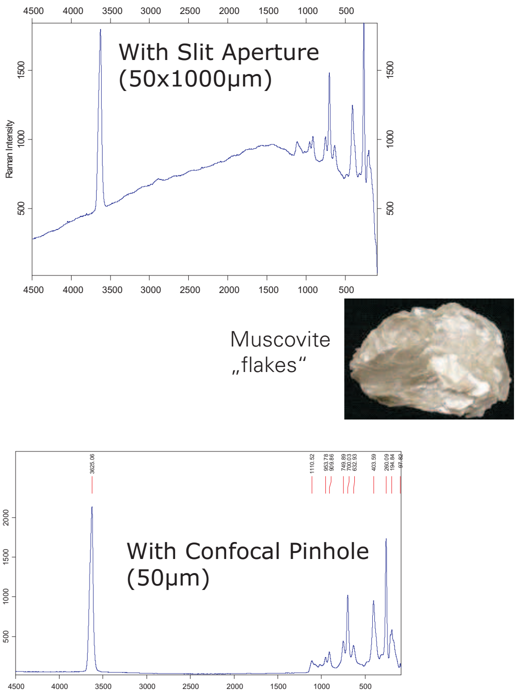

Fig. 1 Removing Fluorescence by Confocal Raman Microscopy

Introduction

Analytical techniques in art conservation include inspection with visible, polarized, UV and NIR light. Moreover, the use of micro X-ray fluorescence (XRF), energy dispersive X-ray analysis (EDS) and last but not least molecular spectroscopic methods such as IR and Raman micro spectroscopy are increasingly being used.

IR and Raman spectroscopy are powerful analytical techniques to detect, discriminate and identify material on a molecular level. In particular Raman spectroscopy offers some advantages when applied to art and archaeology as well as earth sciences, since it

- is non destructive,
- requires no contact,
- needs no sample preparation,
- is independent of environmental conditions,
- is suitable to be used for organic, inorganic as well as biological matter,
- can be used for depth profiling.

Raman micro spectroscopy combines high quality visible images with high laterally resolved molecular information. However, questions about the appropriate equipment i.e. choice of excitation wavelength are coming up when samples tend to fluoresce or heat. In order to minimize fluorescence the use of long wavelength excitation preferably in the near IR region is desirable. The choice of the suitable laser excitation is also driven by the fact that short wavelength excitation yields significantly better signal intensity assuming that side effects such as fluorescence are negligible. Sample handling of larger pieces of works of art are an issue too. Should a remote Raman probe or a confocal Raman microscope be used?

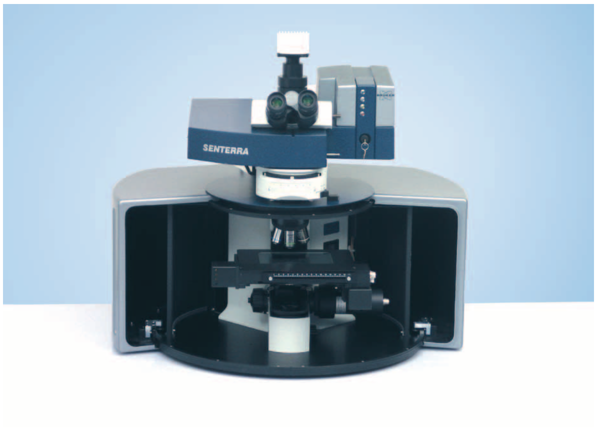

Fig. 2 Hybrid Technology - HYBRID Platform of Dispersive and FT-Raman Microscopy using up to four excitation wavelength 532nm, 633nm, 785nm and 1064nm

Discussion

Disturbing fluorescence can be avoided or reduced by

- quenching and using confocal Raman microscopy (fig. 1)
- use of techniques such as Shifted Excitation Raman Difference Spectroscopy [1]
- use of advanced data treatment such as "Concave Rubberband Correction" [2]
- selection of the appropriate excitation wavelength.

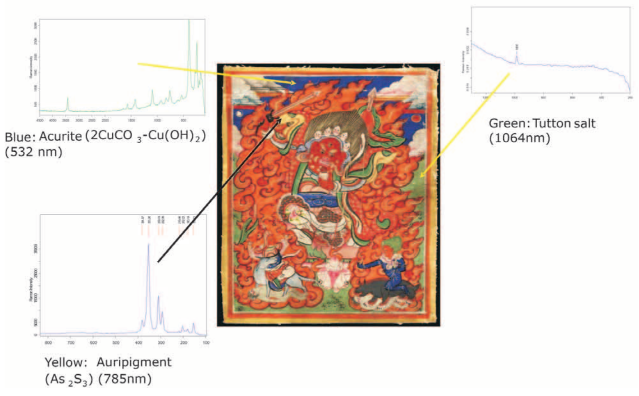

Fig. 3 Ancient Nepalese Painting (Thangka)

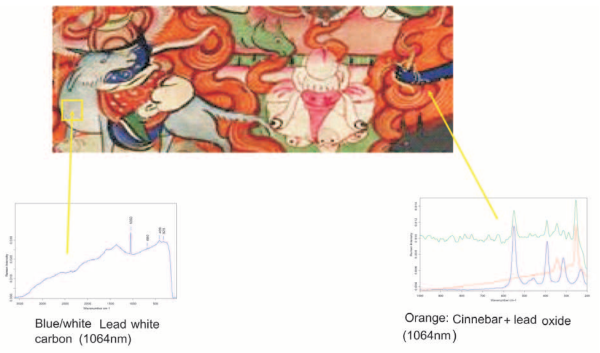

Fig. 4 Identifying mixed colors

By coupling dispersive with FT-Raman microscopy a broad variety of excitation sources ranging from 488nm to 1064nm (fig. 2) can be used. The selection of the appropriate wavelength is quite crucial to obtain fluorescence free and interpretable Raman spectra. Figures 3,4,5 are showing the Raman spectra recorded from an ancient nepalese painting (Thangka). The different dyes used for this painting are identified by using excitation lines ranging from the visible to the near infrared (1064nm). Whereas ancient dyes might tend to fluoresce not only because of aging effects, also modern dyes require analysis using visible to near IR (1064nm) excitation (fig. 6).

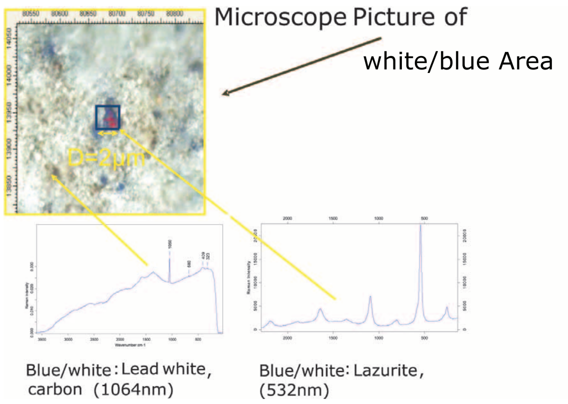

Fig. 5 Discrimination of Pigments using 532 nm, 1064 nm at high spatial resolution (100x objective)

For large objects of art a compact multi wavelength open-architecture confocal Raman microscope for material research related to the study and preservation of works of art has been designed (fig. 7). The open frame set up makes it possible to analyze large objects. Excitation lasers ranging from blue light to the near infrared (1064nm) provide analytical flexibility. Alternatively for objects which can not be moved a Raman video probe offers convenient access to wall paintings or other specimens which are difficult to reach.

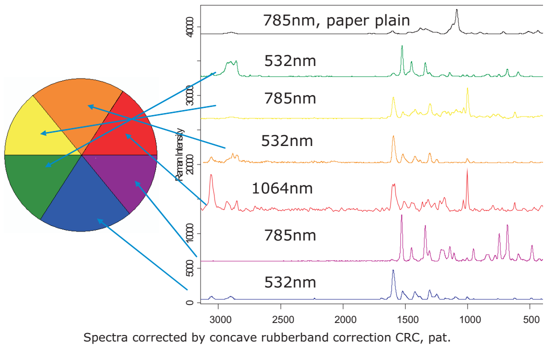

Fig. 6 RamanScopeIII In Situ Analysis of Laserjet Ink

Fig. 7 Open-Architecture Raman Microscope

Summary

It has been shown that the use of a broad variation of laser excitation wavelengths ranging from the visible to the near IR (1064nm) significantly enhances the probability to generate fluorescence free and interpretable Raman spectra. For large objects of art an open-architecture confocal Raman microscope facilitates the investigation considerably.

[1] Zhao J, Carrabba MM, Allen F Appl. Spectrosc. 2002; 56: 834

[2] Pierza M, Sawatzki J, Method and Device for Correcting a Spectrum, US Patent 7,359,815 B2

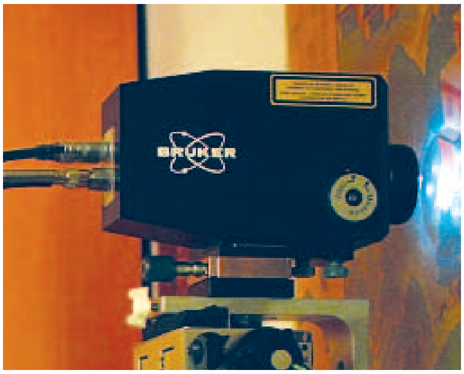

Fig. 8 Raman Video Probe

Acknowledgement: The authors would like to thank Prof. R. R. Ernst, ETH Zurich, Switzerland for courtesy of samples and photos of fig. 3,4,5,7,8

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