Application Note AN R519

Usage of the Raman Video Probe for Pigment Studies

R.R.Ernst, ETH Zurich, Switzerland.

Introduction

The long-term goal of the project is the identification of pigments in ancient paintings, especially Tibetan thangkas, by non-destructive and in-situ Raman spectroscopy. Raman offers unique properties for this purpose. Because it is a reflective technique, it can be applied to an unprepared surface of a painting without causing any damage.

The first step towards non-destructive identification was the mounting of a SENTERRA II Raman microscope on a large gantry. This arrangement allows the study of paintings of up to 1.5 x 1 m. No samples have to be taken from the painting. The paintings must not even be unframed; the measurement is feasible through the covering glass. However, the paintings have to be moved to the SENTERRA II microscope and positioned horizontally on the table underneath the gantry.

Figure 1: Raman microscope SENTERRA II mounted on a

In numerous situations, it is not possible to move the paintings, and an investigation at the place of the painting is required. Typical situations are frescos in ancient buildings, paintings too heavy to be transported safely, and paintings that are too large for fitting underneath the microscope gantry. In such a situation, the usage of a mobile and flexible Raman Probe is indicated.

This brief report describes the first experiences with a Bruker Raman Video Probe that is remotely connected to a SENTERRA II Raman microscope via fiber optics. The Raman probe is mounted on a mount, consisting of a heavy Manfrotto tripod, equipped with wheels. To allow for reaching heights of up to 2.5 m, a quadratic 4 x 4 cm^2 Kanya rail profile of 110 cm length was added to the tripod. On the rail, a 70 cm side arm from a Sinar large-format camera system is mounted. (This side arm could easily be extended by further Sinar-system elements.) The camera sits on a Sinar P Front Standard that allows controlled movements in virtually all directions. The camera can easily be mounted and detached by a single winged screw.

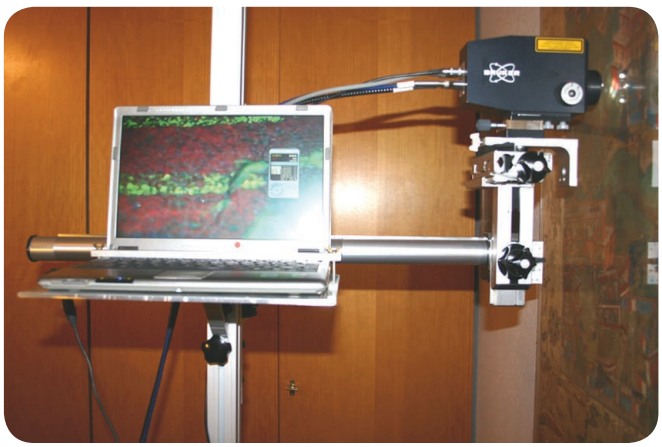


Figure 2: Raman Video Probe with laptop PC.

The Bruker Raman Video Probe is equipped with a video camera for monitoring the area under exploration. The computer display must be mounted in near proximity to the camera so that the focusing can be visually controlled. For this purpose, a platform has been added to the Kanya rail for carrying a Dell X1 laptop with a 12 inch screen.

The Raman Video Probe is connected via two glass-fiber cables of 30 m length to the SENTERRA II microscope for the laser excitation and for the analysis of the resulting Raman signals. This arrangement allows for truly "remote" measurements.

Figure 3: Raman Video Probe mounted on a tripod.

Measurement Procedure

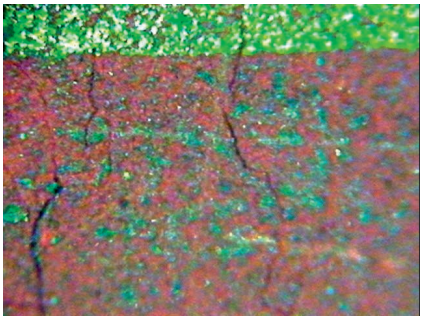
1. The measurement procedure begins with positioning the tripod, carrying the Raman Video Probe, in front of the object to be analyzed.
2. The laser output in the "Check Signal" mode is started at the Microscope. The laser spot serves in the "Measure" position of the Probe for localizing the exact sampling region on the painting.
3. The laser output is stopped again at the Microscope.
4. Via the computer display of the probe, the micro-region to be analyzed is selected in the "Video" position, and the focusing is done.
5. A photographic record is made.
6. The Raman Video Probe is put in the "Measure" position.
7. All the remaining activities are done at the SENTERRA II Microscope: Parameter selection, start of measurement, and analysis of the results.

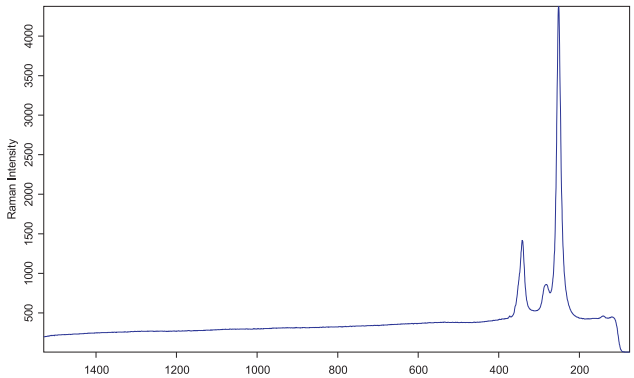
Measurement Results

For the first measurements, the Tibetan painting ET10, a display of the monasterial life in Derge, East Tibet, painted around 1770, has been selected. It is presently wall-mounted and relatively difficult to move. The painting is behind glass.

All Raman measurements are made with a Zeiss Epiplan Objective x10/0.20, No 442930.

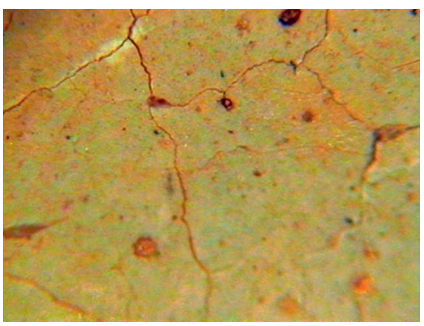
Area 1

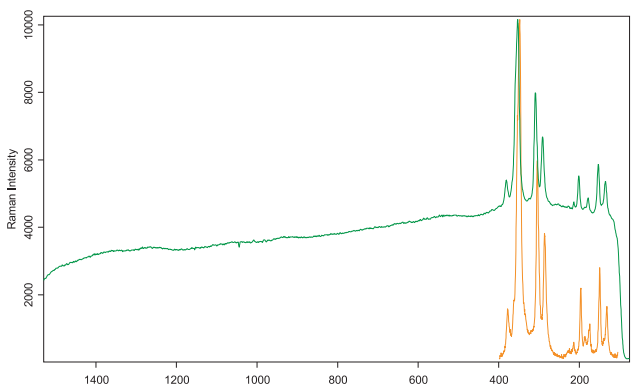




ET10: A red part of the painted wall of the monastery.
A superb cinnabar (HgS) spectrum is produced that renders identification certain. Maximum red laser power is applied. Integration time 4 s with 10 accumulations.

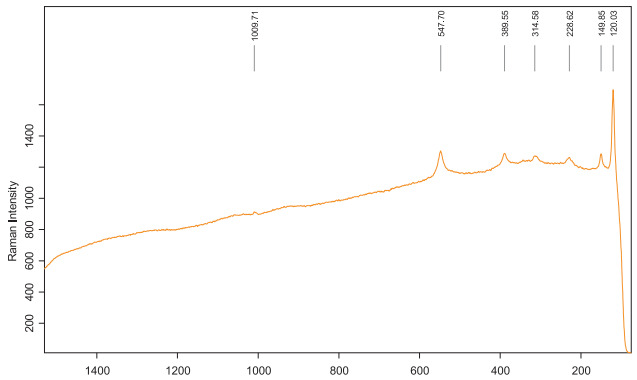
Area 2





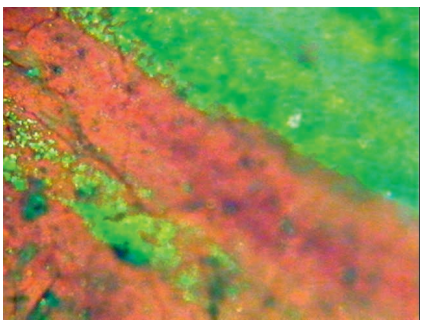
ET10: Yellow border of wall yields a beautiful orpiment (As_2S_3) spectrum!

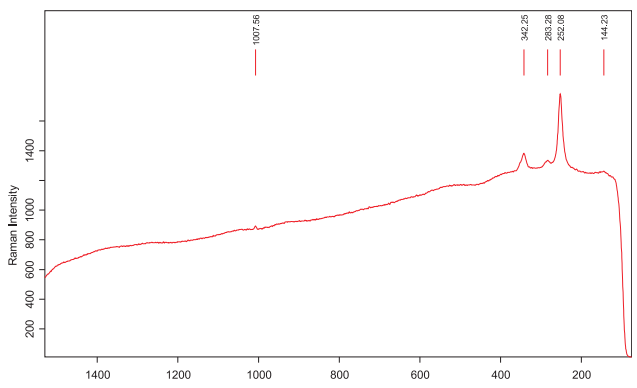
Area 3



ET10: The lower part of the master painter's cloth is a typical red lead spectrum. A weak gypsum line is also visible.

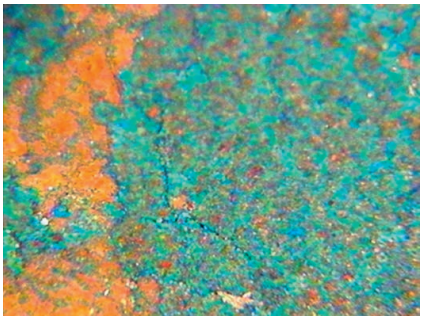
Area 4

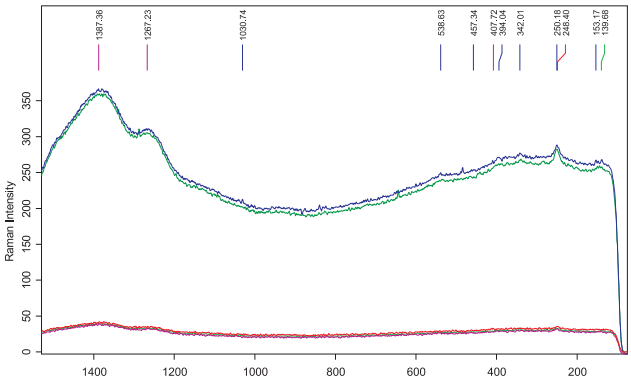




ET10: The master painter's vest consists of cinnabar and traces of gypsum and litharge (?).

Area 5





Blue part of monastery wall. Pigments are difficult to identify. Especially the blue is unclear. It could be azurite. There is certainly cinnabar present, possibly from a ground layer.

Conclusion

In many situations, the Bruker Raman Video Probe will prove to be of indispensable support for researchers, especially when examining frescos and large wall paintings.

Bruker Optik GmbH

Ettlingen · Deutschland
Phone +49 (7243) 504-2000
Fax +49 (7243) 504-2050
info@brukeroptics.de

Bruker Optics Inc.

Billerica, MA · USA
Phone +1 (978) 439-9899
Fax +1 (978) 663-9177
info@brukeroptics.com

Bruker Shanghai Ltd.

Shanghai · China
Phone +86 21 51720-890
Fax +86 21 51720-899
info.bopt.cn@bruker.com

www.bruker.com/optics