APPLICATION NOTE

Raman micro-spectrometry for pigments analysis of works of art

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INTRODUCTION

For the restoration of the pictorial heritage, it is important to detail the materials used. This allows to place the work of art in a particular artistic context such as the nature or the weaving of a canvas, the use of a pigment.

Naked-eye, photographic or microscopic observations allow sometimes to describe the materials constituting the work of art.

Raman micro-spectrometry confirms and specifies data obtained by other means of analysis (UV fluorescence, false colors, chemical reagents).

Raman analysis is simple to implement and use. The observation obtained is quickly compared with the database previously established. The result then makes it possible to identify and discriminate the constituent materials of the work of art.

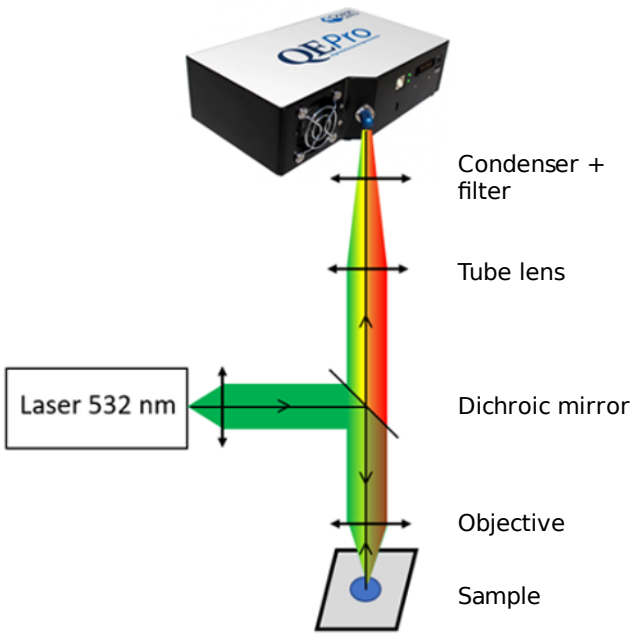


Figure 1: Schematic of the experimental setup

EQUIPMENTS

-Raman Spectrometer QE PRO 532nm

-Laser diode 532nm, 100mW

-Microscope Zeiss, epiplan neofluar objective

PIGMENTS ANALYSIS

Prior to start the Raman analysis of the work of art, it is necessary to constitute a bank of reference spectra. This spectral database will then be used to identify and discriminate pigments.

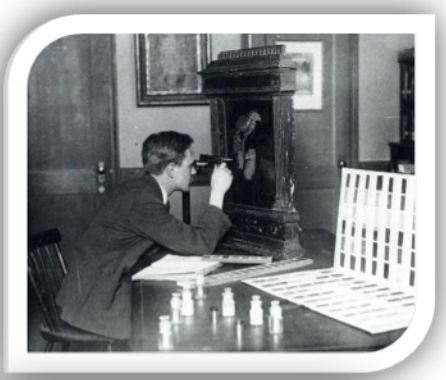


Figure 2. Daniel V. Thompson identifies pigments in the Fogg Museum's *Madona and Child* by Benozzo Gozzoli. Image : Harvard Art Museum Archives (1924)

Figure 3. The color chart shows red and brown pigments used as reference

Figure 4: Microscope

OPERATIVE PROCEDURE FOR THE CONSTITUTION OF THE SPECTRAL DATABASE

Each reference pigment is placed on a glass slide and then put under the Raman microscope.

As an exemple of discrimination, let's have a look at two pigments with the same chemical formula : Cinnabar and Vermilion. Cinnabar is a natural pigment, whereas Vermilion is an artificial pigment (Figure 5).

On the Vermilion, we can see the presence of peaks between 1000 et 1500 cm-1, not present on the Cinnabar. These two pigments have identical appearance but different spectral composition. So, they are well identifiable et discriminated.

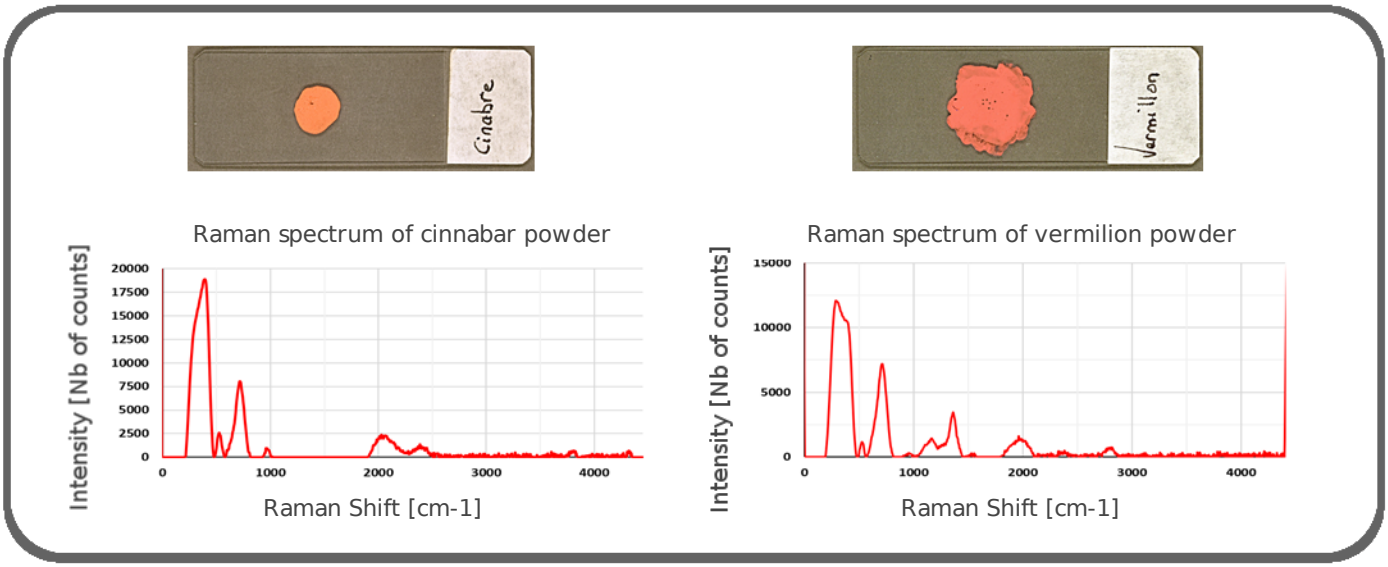


Figure 5. Example of discrimination between two pigments (Cinnabar and Vermilion)

STUDY OF A 17th CENTURY PAINTING

Raman test on the blue scarf with micro-samples

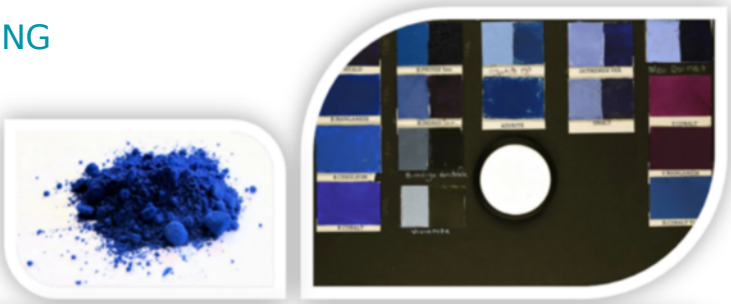


Figure 6. True ultramarine blue pigment (lazurite) comes from lapis lazuli. It is the blue pigment of reference for quality works of the 17th century

Figure 7: Color chart of old blue pigments (real ultramarine blue, smalt, lazurite, azurite, indigo, Prussian blue 1704)

Figure 8: Painting of Louis XIV

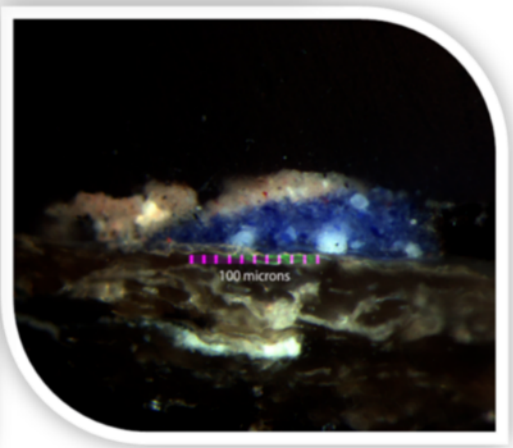
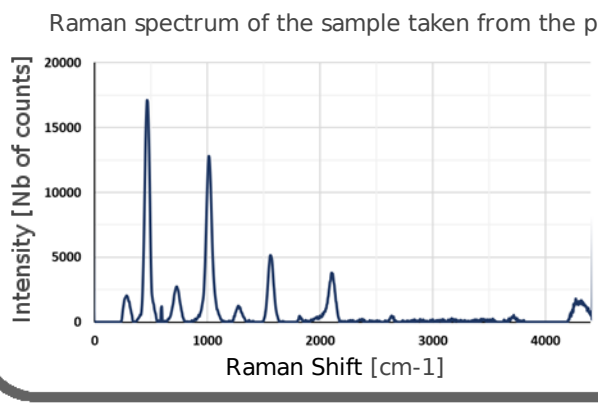


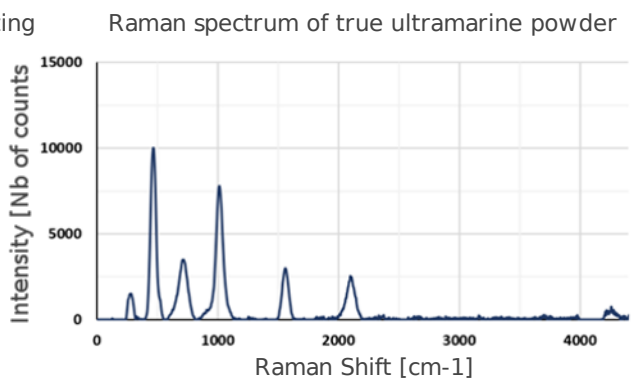
Figure 9: Micro-sample (Scale = 100µm)

However, in a painting, the pigments are not always pure. Moreover, they are linked by different mediums. These mediums, such as oil or gum arabic, generate strong fluorescence which drowns the Raman signal. It is therefore necessary, beforehand, to overexpose the test sample for a certain time without burning it to attenuate this fluorescence.

In order to isolate the pigment to be analyzed, it is often appropriate to make a micro-sampling (Figure 6). A sample of the blue scarf was therefore collected and compared to true ultramarine blue (Figure 10).

Figure 10 : Comparison of two pigments





Thus, the true ultramarine blue (lazurite) is comparable to the sample taken on the blue scarf. The scarf contains lazurite. In this work of restoration, it is possible to respond precisely to the need of the painting. Retouching, for example, can be done with this pigment.

In addition, identifying a pigment informs on the time of its use and makes it possible to date a work of art. Thanks to this analysis technique (among others), art experts and scientists authenticate a work and fight against counterfeiting.