Scientific report - STM Claudia Conti

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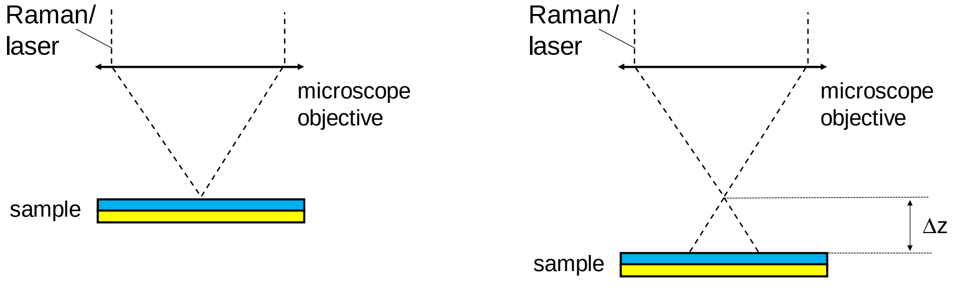
In the field of conservation of Cultural Heritage the knowledge of the composition of surface and subsurface layers is critically important to the adoption of an optimum approach to the preservation of concerned artwork. Although considerable advances have been made, recently, in non-destructive analysis of art - essential to preserving the integrity of such precious objects - one of the most critical issues is still largely outstanding: the detection of the chemical composition and distribution of substances located under the surface of artwork by non-invasive means. The research program aimed at contributing to this challenging issue by developing a new method, called micro-SORS, based on Raman Spectroscopy and able to obtain information about the distribution of materials inside painted multilayers, the elemental composition of subsurface pigments and the thickness of the layers with a resolution in the micrometer axial range, non-invasively and non-destructively.

In its basic form the micro-SORS relies on collecting at least two Raman spectra using confocal Raman microscope; first, with a sample in a conventional ‘imaged’ position and then, by moving the sample away from microscope objective by a ‘defocusing distance Δz’, to a ‘defocused’ position. The sample displacement away from the ‘imaged’ position causes the defocusing of both laser illumination and Raman collection zones on sample surface (see Fig. 1). The former measurement (the ‘imaged’ position) yields a spectrum dominated by the surface layer. The latter measurement (‘defocused’ position) yields a Raman spectrum which has a significantly higher degree of signal contribution from sublayers.



i) Imaged

ii) Defocused

Figure 1: Schematic of the defocused Raman measurements in micro-SORS analysis showing the sample in the ‘imaged’ and in a ‘defocused’ position implemented by displacing the sample away from microscope objective by displacement Δz from the original, ‘imaged’ position.

The research has been developed at the Rutherford Appleton Laboratory laboratories. During the first week the main steps have been the optimization of the laser deliver Raman collection zone dimensions, acquisition parameters, assessment of the separation of Raman collection signal zone from that of the laser illumination area and laser beam power. In particular the dependence of the micro-SORS results on the laser wavelength (we tried with 830 nm and 514 nm) has been investigated. In the second week, the efficacy of the method has been tested using both artificial samples and real art case studies. As for the artificial samples, disks of pigments mixed with resins have been prepared and analysed superimposing the disks on top of each other. Moreover, micrometric layers of varnishes have been considered. In both cases the results allowed to successfully obtain the composition and location of the two or three varnishes.

As for the real cases, small fragments were taken from the ***polychrome sculptures*** originate from prestigious devotional places called “Sacri Monti” built during the late fifteenth and seventeenth century in North Italy characterised by a series of chapels and kiosks containing wall paintings and terracotta or stucco sculptures representing the life of Christ. The fragments have been analysed both using micro-SORS (intact, without any preparation) and with conventional confocal Raman microscopy (in cross section). Here I report only one example as demonstration of the use of micro SORS: a small sample fragment was acquired from a blue mantle of Christ (see Fig. 2 a-b). Inspection using an optical microscope of sample cross section reveals the presence of three blue layers: the external one, approximately 20 µm thick containing well defined blue particles; the middle one consisting of a homogeneous light blue material being 20 µm thick; and the most deepest a 30 µm thick layer containing small blue particles. A conventional Raman microscopy carried out on the cross section in every single layer allowed to infer the composition of blue pigments; the external layer exhibits a very characteristic line of ultramarine blue with a marked Raman band at ~549 cm^{-1} assigned to the symmetric stretching mode of the S_3^- ions in a sodium alumino–silicate matrix. The middle layer consists of azurite, the basic copper(II) carbonate showing the most intense Raman band at 401 cm^{-1} and finally the blue particles of the third layer showing a characteristic signature of the iron(III) hexacyanoferrate(II) called Prussian blue.

Figure 2c shows the results of defocusing measurement performed on this blue fragment. The Raman spectrum in the ‘imaged’ position is dominated by contribution from the top layer, lazurite, although traces of azurite and Prussian blue cannot be completely excluded. As the sample is displaced from its ‘imaged’ position, moved farther away from the microscope objective, the contribution of the most internal layer increases dramatically, while that of the middle layer is rather negligible, in line with expectations. The lack of information obtained from the middle layer can be explained by the relative weakness of Raman cross section of azurite compared with that of the other two pigments. The Raman intensity ratio of the spectra acquired at different defocusing distances Δz, considering the most intense bands of Prussian blue (2153 cm^{-1}) and lazurite (549 cm^{-1}), is shown in Fig. 2d. Even though lazurite persists up to the largest defocusing distance used, the band intensity ratio changes and the presence of Prussian blue as a separate (deeper) layer (rather than blended with lazurite in a single layer) is ascertained.

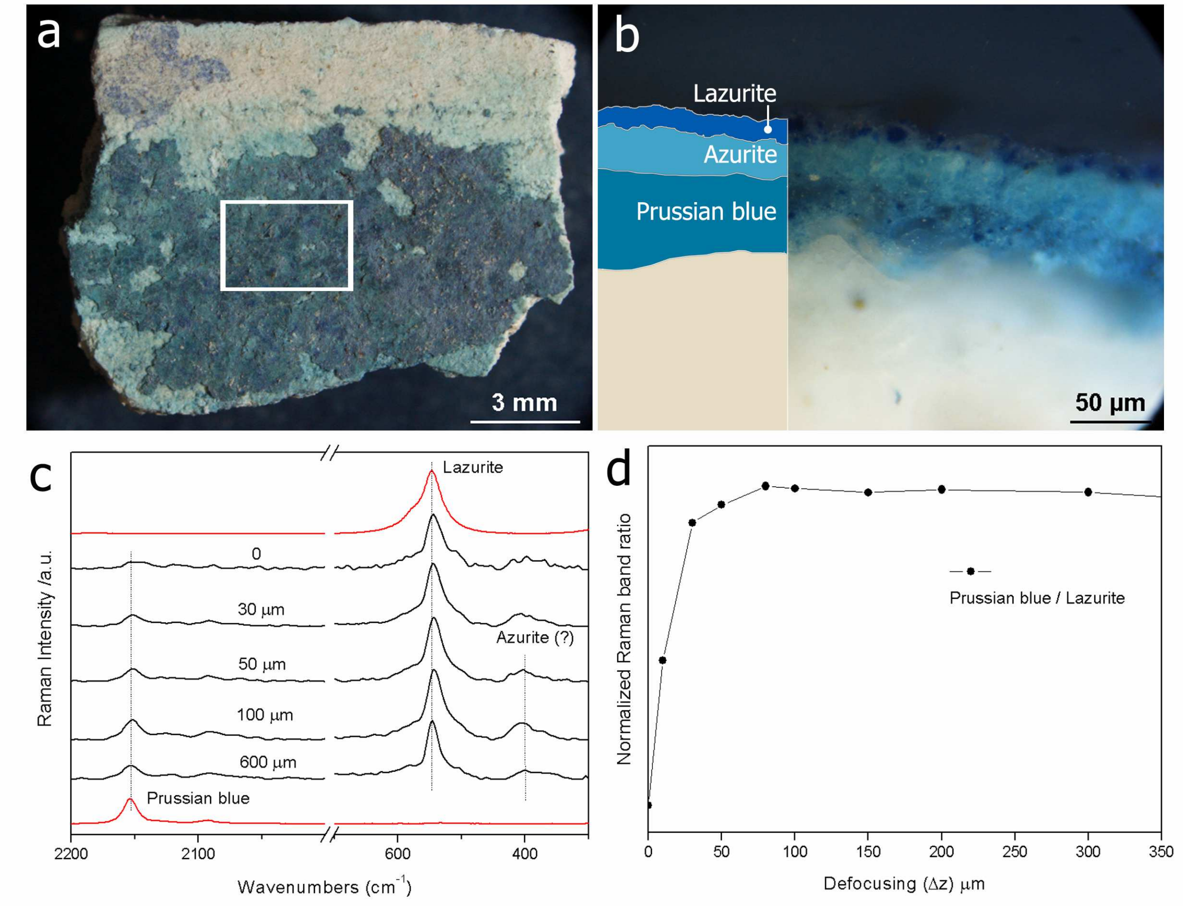


Fig.2: blue mantle sample: a) fragment image (white square indicates the area analysed with micro-SORS), b) optical image and scheme of the stratigraphy, c) The defocused spectra are shown for different distances from the imaged plane indicated next to each spectrum (0 = no defocusing (zero defocusing), i.e. sample position with sharply imaged sample surface). The spectra are offset for clarity. Note the line markers are for guidance of the eye to demonstrate the changing relative intensity of the lazurite and Prussian blue with the defocusing distances. d) Raman intensity ratio (Prussian blue/Lazurite) of the spectra acquired at different defocusing distances Δz.

In conclusion, several examples of noninvasive, non-destructive analysis of painted layers on painted sculptures and plasters using micro-SORS have been given revealing the chemical makeup of upmost layers. The limitations of the method include a high degree of absorption or fluorescence of probed layers and high heterogeneity of deposited pigments on sample surface. The technique expands the portfolio of available nondestructive analytical tools in Cultural Heritage and it has a potential to be developed into a portable non-destructive in situ analytical tool.

We prepared 1 imminent peer-review publication with the title: **Subsurface Analysis of Painted Sculptures and Plasters using Micrometre-Scale Spatially Offset Raman Spectroscopy (Micro-SORS).**

Due to the success obtained with real art cases, during the stay a strategic collaboration with Cambridge University to further advance the technology for applications in Cultural Heritage has also been established.

The further step has been the extention of the application of Micro-SORS from the area of Cultural Heritage to other important analytical problems involving chemically specific analysis on thin, ten's of micrometre scale layers. The method was applied successfully, for the first time, to resolve thin layers within polymers, wheat seeds and paper. All the layers were highly scattering and non transparent, beyond the reach of depth resolving power of conventional confocal Raman microscopy. Cross-sections of the samples were also analysed using conventional Raman microscopy to validate our non-invasive findings. The technique expands the portfolio of the available non-invasive chemically specific analytical tools to a range of important areas.
As an example, we report the results obtained with ***grains.*** The internal structure of the grain is depicted in Fig. 3. Different compounds have been detected with micro-SORS method: the Raman spectrum in the 'imaged' position is dominated by contribution from the top layer. As the sample is displaced from its 'imaged' position, moved farther away from the microscope objective, the contribution of the most internal layer increases dramatically, as shown in Fig. 4. We prepared 1 imminent peer-review publication with the title: **Non-invasive Analysis of Thin Diffusely Scattering Layers within Polymers, Wheat Seeds and Paper using Micro-Scale Spatially Offset Raman Spectroscopy (Micro-SORS).**

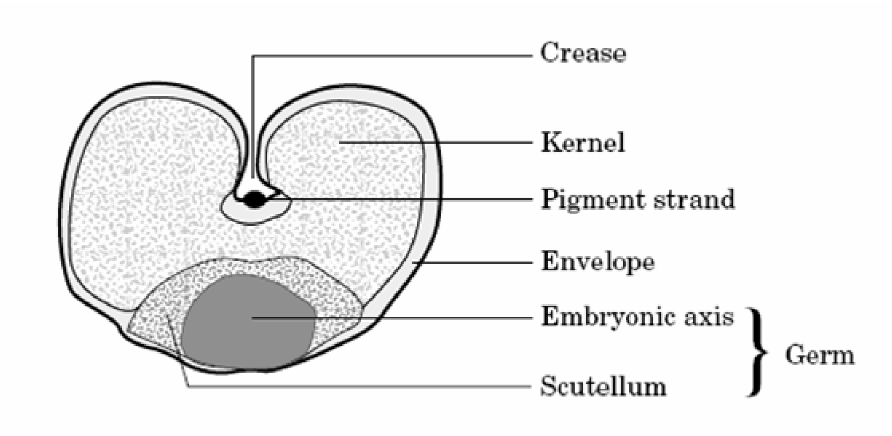


Fig.3: cross section of a grain.

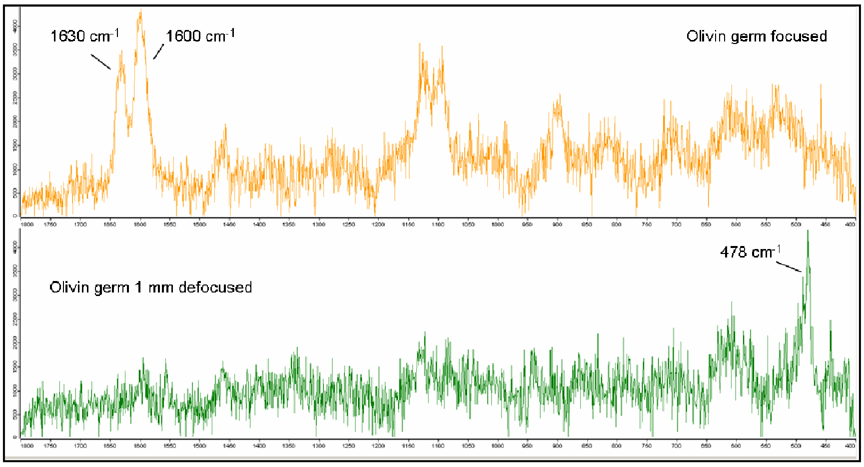


Fig.4: The defocused spectra are shown for the imaged plane (focused - yellow) and 1 mm distance from the imaged plane (green). The spectra are offset for clarity.

As a final step, we tried to develop Monte Carlo models to simulate the Raman photon migration in micron-size layers to provide deeper insight into the underlying mechanisms and to permit more effective optimisation of the method. Existing models developed at Rutherford Appleton Laboratory for conventional SORS has been adapted and optimised for micro-SORS. The preparation of further artificial samples suitable for the thickness studies has been planned.

Currently, we are looking at securing a large scale grant funding to maintain the gained momentum in order to further advance the newly developed Micro-SORS concept in a timely manner.

Credit: STFC/Stephen Kill

Prof. Pavel Matousek and Dr. Claudia Conti in the Raman spectroscopy RAL laboratory.