Scientific report - STM Claudia Conti

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The program aimed at exploring the next phase of the research related to the development of a new non-destructive analytical method, called micro-SORS. In this new research phase the method has been tested when dealing with still unaddressed critical issues in the conservation of Cultural Heritage field. Micro-SORS has been developed for the first time in the Rutherford Appleton Laboratory (RAL) laboratories during my first Short Term Mobility program (November 2014). During the last 3 years a powerful contribute to the development of this technique has been given through the prolific collaboration between CNR ICVBC and RAL.

In its very essence, the method combines Spatially Offset Raman Spectroscopy (SORS), a related recently developed technique, with microscopy. This enables the analyst to resolve thin, micrometre scale stratified layers beyond the reach of confocal Raman microscopy and in a non-destructive way. The most basic variant of micro-SORS is defocusing micro-SORS, which can be practised without any modifications on conventional Raman microscopes and for this reason it is currently of the widest potential interest to the community. A related concept is full micro-SORS which is more effective but requires instrumental modifications involving hardware and/or software changes to include fully separated illumination and collection zones.

To date, micro-SORS has demonstrated its utility also in determining the overlayer depth, rejecting overlayer fluorescence and in two-dimensional mapping of hidden images or writing. It has been used to recover the subsurface composition of different materials in the polymer, paper, food and biomedical fields. In Cultural Heritage it has been successfully applied to real artworks to recover the deep molecular composition of painted stratigraphies spread on Renaissance terracotta sculptures and on plasters in a non-destructive way.

The research has been developed at the Rutherford Appleton Laboratory, using a dispersive Raman instrument (Renishaw) equipped with two excitation wavelengths (830 and 514 nm).
During the first week we explored the potential of a further variant of micro-SORS based on the internal offset of the laser illumination area. The software gives the option of moving the laser spot across the focal plane with “beam-steer” alignment mirrors. The mirrors allow to move the laser position from the centre of the lens focal point up to around 200 µm sideways, while the collection area remain in the same position for every measurements. The spectra acquired at different spatial offset should provide different “images” of the subsurface compounds. We carried out several tests with mock-up samples consisting of two or three micrometric overlapped on top of each other. The

comparison with measurements acquired in the same samples analyzed with defocusing and full micro-SORS variants highlighted a good contrast of the layers when analysed with beam steer as well (Figure 1a), although the major limitation concerns the objective magnification which can be used to obtain a meaningful spatial offset. In fact, just 5x objective provides 200 µm offset (which is the largest offset that could be introduced), while 20x or 50x allow very small movement of the laser. The drawback of using 5x objective is the large laser beam spot which has a rectangular profile 20x150 µm. Moreover, no Raman signal can be recovered from offset larger than 200 µm.
Internal offset has been tested on fluorescent samples as well, with very good outcomes: the fluorescent top layer is overcomed by the spatial offset, allowing to recover the subsurface signal (Figure 1b).

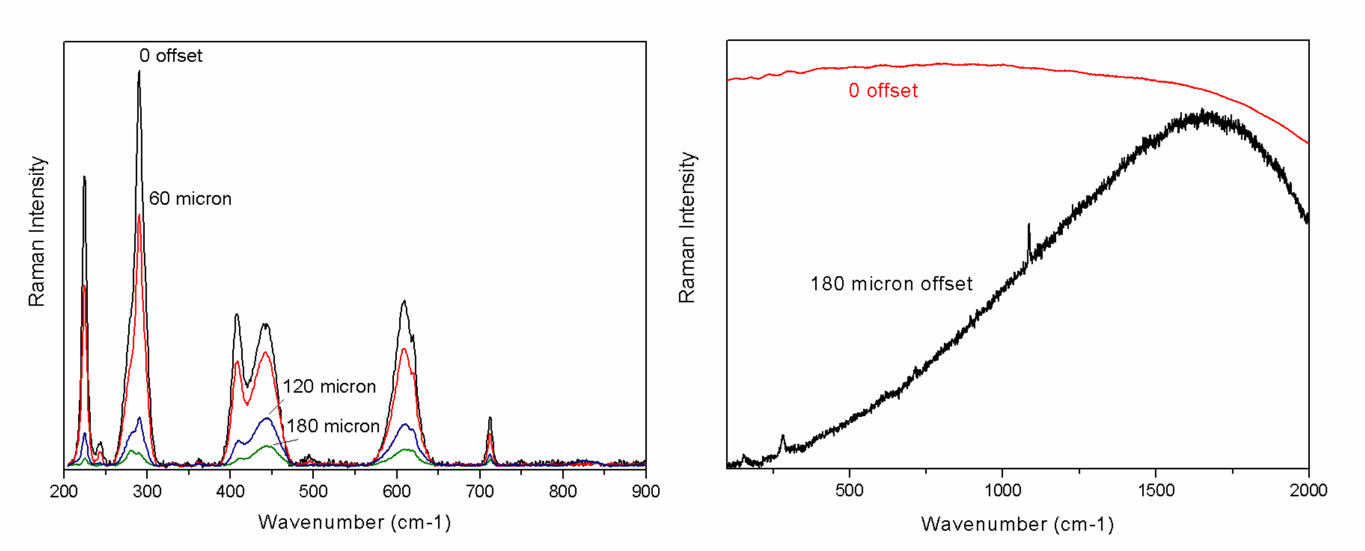

Figure 1: micro-SORS spectra acquired with internal offset; sequence of three layers painted system (a) and of top fluorescent sample (b).

During the second week we explored the potential of advanced <u>multivariate analyses</u> on spectra acquired in challenging situations in terms of layer thickness; in fact, the method has been optimized for thickness in the range 20-100 µm so far. The painted stratigraphies analysed with the internal spatial offset have very thin layers (a few micron each) and their discrimination with micro-SORS could be extremely tricky. Apparently, the micro-SORS sequence of spectra do not show any information about the bottom layers; the relative intensity ratio between the bands of two bottom thin layers does not change with visual inspection. Actually, a careful spectra treatment with PCA is very informative in presence of low Raman scattering cross section compounds, as zinc white pigment, in top position. On the contrary, when the thin layers are covered by good scatterers, like calcite, multivariate methods could not give additional information.

The third week has been devoted to explore the potential of micro-SORS to the <u>study of diffusion and penetration depth of conservation treatments applied to plasters or stuccoes</u>.

The aim is to develop a new protocol able to investigate the penetration depth achieved by the treatment in a non-destructive way. In particular, three gypsum samples have been treated with Paraloid B72, an acrylic resin. Each sample show a different penetration depth and diffusion inside the gypsum matrix. The experiments have been carried out using both internal offset and defocusing micro-SORS variants. The internal offset restricted the discrimination power of micro-SORS, while defocusing allowed to highlight small difference in the Paraloid intensity among the spectra acquired at different distances from the objective. To improve the contrast between gypsum and Paraloid signal, a spectral elaboration has been performed using the fitting procedure. In fig. 2 the Paraloid/gypsum ratio obtained by fitting has been plotted over the defocusing distances; sample 1, which is characterized by a shallower penetration depth shows a strong ratio decrease up to zero at 1.5 mm of defocusing distance. On the contrary, sample 3, involved in a deeper penetration depth, exhibits a non-zero ratio even at 2 mm of defocusing distance.

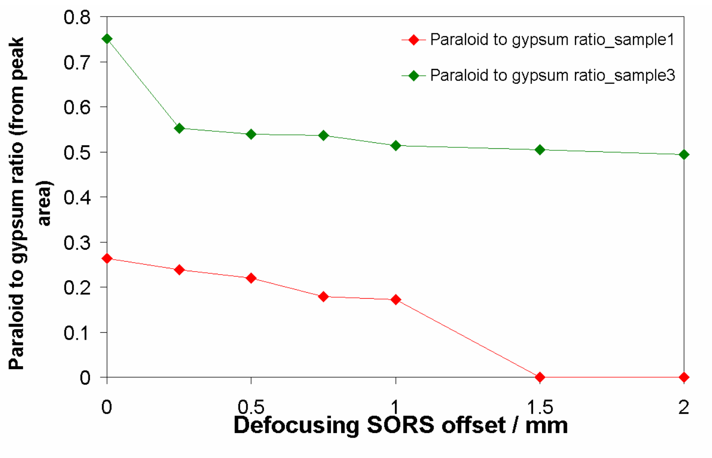

Figure 2: Paraloid/gypsum ratio achieved by fitting elaboration of defocusing micro-SORS spectra over the defocusing distances for sample 1 and 3.

During the three weeks I also had the opportunity to visit the conservation laboratories of The Bodleian Library in Oxford, The British Museum and The Victoria and Albert Museum in London. The aim of the visits was to establish strategic links and setting foundations for a new grant application to the Arts and Humanities Research Council (UK) for future collaborative research.

The STM project enabled us to maintain our established world scientific lead in this novel area of analytical science. Overall the outcome was an outstanding success and the stay is expected to result in at least 4 imminent peer-review publications, with more to follow.