

Advancements in Interfaced SEM and Raman Spectromicroscopy (μ RS)

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In recent years Raman spectromicroscopy (μ RS) has emerged as a powerful tool for chemical and phase characterization in materials science. It is a non-destructive vibrational technique probing the molecular structure with micron resolution and it can be used to analyze either very small samples or entire objects non-invasively. Owing to its non-destructive nature, it can be used in combination with other techniques, making the same sample reusable for subsequent analyses after μ RS has been performed.

A versatile non-destructive technique enabling *in situ* morphological characterization, elemental identification and structural analysis integrates μ RS with scanning electron microscopy (SEM) energy dispersive X-ray spectroscopy (EDS) in a 'hyphenated' SEM-EDS- μ RS system. Introduced for the first time in the late 80s¹, this system takes full advantage of the high spatial resolution offered by the SEM for non-destructive *in situ* nanoscale morphological and topographic mapping, and the atomic and molecular micro-probing of the EDS and μ RS for spatially resolved elemental characterization and structural analysis of materials on the same platform. These capabilities exceed what can be achieved when the Raman spectrometer is coupled with an optical microscope and when each instrument is used independently. However, one of the critical drawbacks of adding μ RS to such integrated systems (and probably the reason why they still haven't become widespread) is that the laser power for the μ RS (transferred through a fiber optic cable) is significantly reduced in the SEM configuration and reduces the Raman scattering generated by the samples. Nevertheless, there are three major areas of analysis when integrated SEM-EDS- μ RS system becomes indispensable. First is when the size of the feature to be probed with μ RS is a few microns or smaller and it is hard to identify it with the optical microscope, a traditional platform for μ RS. The second area is when dynamic studies may be necessary under variable conditions such as temperature and pressure. SEM temperature stages with different design are currently commercially available, as well, as alternating pressure systems through the use of variable/extended pressure or environmental SEMs. And finally, Surface Enhanced Raman Scattering (SERS) can be easily employed within the SEM chamber for the characterization of materials. SERS occurs by molecules adsorbed on, or in close proximity to the surface of certain nanostructured metal (normally silver or gold) substrates. It has been shown that the SERS signal exhibits up to eight orders of magnitude enhancement over the normal Raman signal.² The main predicament for nanostructured metal application to the sample surface lies on the difficulty of obtaining a uniform, thin and well adhered coating of nanoparticles and identifying the best area to perform the SERS measurement. SEM interfaced with a μ RS provides an ideal system to overcome this challenge by 1) evaluating the nanoparticles coverage/distribution on the sample and 2) locating suitable areas for successful and reproducible SERS analysis.³ Owing to the sensitivity enhancement, SERS can address the loss in laser intensity when it used on the SEM platform. Beside SERS can circumvent the fluorescence, the traditional Raman analysis can be frustrated by naturally fluorescent organic materials, or by fluorophores that have become incorporated into the sample from handling.

Here we show some of our recent results using the Nova 230 (FEI) variable pressure SEM, interfaced with the inVia (Renishaw) Raman system for the analysis of different samples, demonstrating the advancements of integrated SEM-EDS- μ RS system.

References:

- [1] M.Truchet, M.Delhaye, *J. Microsc. Spectrosc. Electron.* 1988; **13** (2), 167–175.
 [2] B.Sharma et al, *Materials Today*, 2012; **15**, 16.
 [3] S.V.Prikhodko et al, *J Raman Spectrosc* **46**, (2015) 632-635.

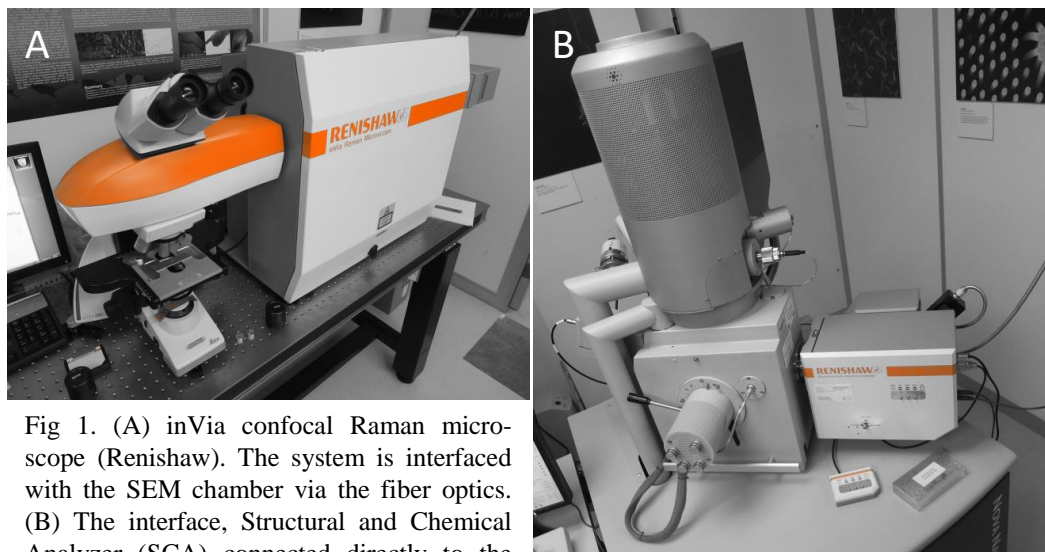


Fig 1. (A) inVia confocal Raman microscope (Renishaw). The system is interfaced with the SEM chamber via the fiber optics. (B) The interface, Structural and Chemical Analyzer (SCA) connected directly to the SEM chamber

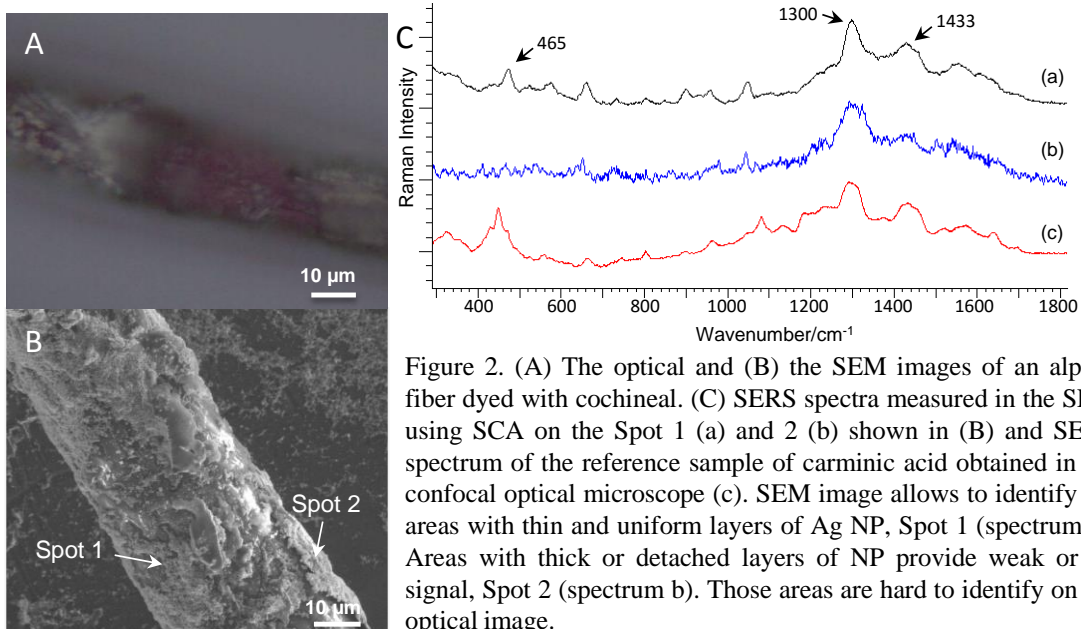


Figure 2. (A) The optical and (B) the SEM images of an alpaca fiber dyed with cochineal. (C) SERS spectra measured in the SEM using SCA on the Spot 1 (a) and 2 (b) shown in (B) and SERS spectrum of the reference sample of carminic acid obtained in the confocal optical microscope (c). SEM image allows to identify the areas with thin and uniform layers of Ag NP, Spot 1 (spectrum a). Areas with thick or detached layers of NP provide weak or no signal, Spot 2 (spectrum b). Those areas are hard to identify on the optical image.