



Overcoming the Optical Focus Issues in Portable Raman Systems for Surface Enhanced Raman Scattering Analysis

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Current Technology Issues

The development of handheld and portable Raman system has brought the relatively unknown analytical technique into the main stream. Currently the majority of the available portable or handheld systems are based off of a closely related dispersive design. This design has its advantages due to the low power requirements, small size, and the resolution needed to identify a multitude of compounds. A characteristic of this basic design is that it only measures an extremely small fixed volume, which is sufficient when analyzing bulk pure substances. However, most of the portable and handheld applications today require high spectral resolution and a large laser interrogation area since most compounds and samples are mixtures or heterogeneous. Another issue is the tight laser focus needed for the efficient collection of the scattered Raman light. This tight focus increases the laser power density at the sample which creates intense heat buildup. This intense heat can be damaging to the sample, which can be easily observed on delicate SERS substrates, or it can be dangerous to the user and instrument if the samples are flammable or explosive.

The Solution

Snowy Range Instruments (SnRI) has overcome this hurdle with the Orbital Raster Sampling (ORS) available on it's bench top and handheld systems. With the conventional spectrometer designs a large interrogation area (large laser spot) requires a large aperture in the spectrometer to efficiently collect the laser light. This works against the requirement for high spectral resolution needed for spectral matching. This

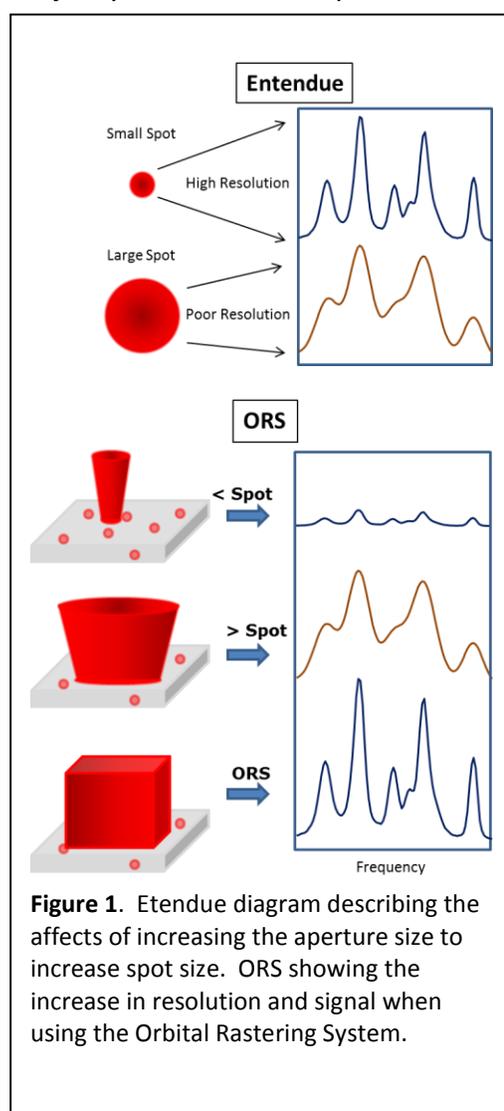


Figure 1. Etendue diagram describing the affects of increasing the aperture size to increase spot size. ORS showing the increase in resolution and signal when using the Orbital Rastering System.



important spectral effect is called etendue and etendue controls a spectrometer's sensitivity (light collection), resolution, and its interrogation area. This is illustrated in our etendue diagram, Figure 1.

The ORS advantage with a disperse target analyte on a solid SERS substrate is illustrated in Figure 1 ORS diagram. In a conventional spectrometer a tightly focused beam may produce high resolution, but it may also miss the SERS hotspots completely. A large beam in a conventional system would require a larger aperture and consequently a loss of resolution. Our unique sampling system produces the advantage of observing an increased number of the SERS hotspots while maintaining a high resolution for target species qualification.

Taking advantage of the large area interrogation is important when trying to identify difficult or non-homogeneous samples. One example is the analysis of surface enhanced Raman scattering (SERS) substrates. Surface enhanced Raman scattering is a Raman enhancing technique using nanoparticles or structures of coinage metals such as gold, silver or copper. Gold is the most common metal used due to its inert properties and resistivity to oxidation. SERS takes the Raman technique from a qualitative identification technique to a trace forensic detection technique. Solid SERS substrates, such as Klarite, are the most common commercially available substrate today. However the complex problem of applying the analyte to the surface and then finding the target analyte on a large area of 4 mm x 4 mm is difficult. The ability to quickly analyze the entire surface would push SERS technology into the main stream by making it more reproducible and easier to use.

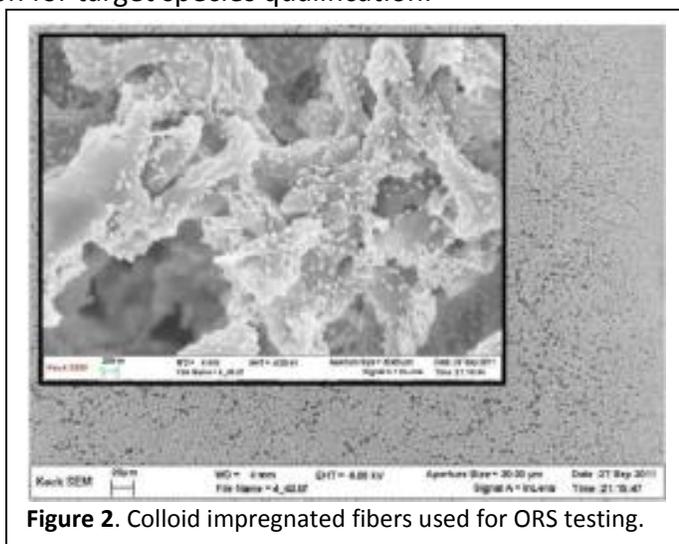


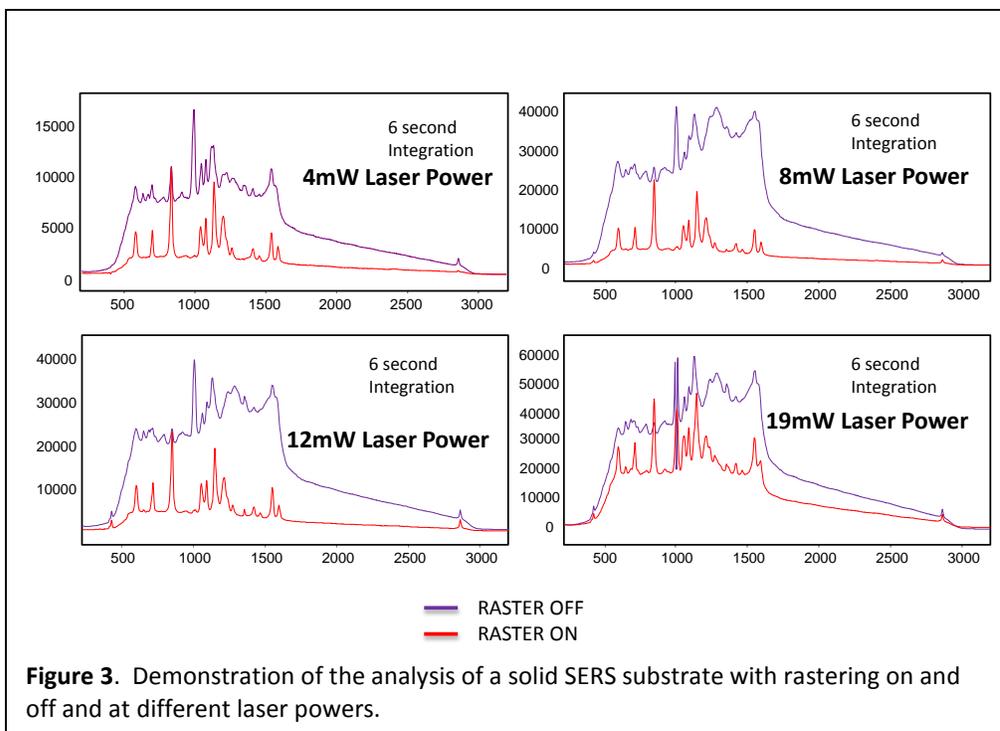
Figure 2. Colloid impregnated fibers used for ORS testing.

Experimental

An experiment was performed with the Sierra Series featuring ORS to demonstrate the reduction of the background and the overall increase of the collected Raman signal from a target analyte that is dispersed over a large area on a solid SERS substrate. The sample used is a SERS-active nanoparticle membrane which has been tagged with 2-Mercaptopyridine-N-Oxide, Figure 2. All spectra were taken on a dry membrane. The samples were placed on a glass slide ~3mm below the point and shoot laser aperture on the underside of the Sierra Series system. Different laser power settings were used in order to demonstrate the effects of the



raster function. For each different laser power and time combination, 3 spectra were taken with the raster on and three spectra (at different positions) were taken with the raster off. A reference (Laser OFF) was used for all spectra collected. What is shown in the Figure 3 is the



average of the three spectra. Figure 4 shows the Sierra Series 785 nm ORS bench top Raman system.

Results and Conclusion

The data shows that when the ORS is off a limited number of SERS active hotspots are interrogated and their spectrum is overwhelmed by the background caused by the surrounding substrate. On some occasions during the experiment the sample began to burn instantly when the raster was off, this is an undesired effect due to the irreversible damage to the sample due to high laser power density. The effects of high laser power can be observed in Figure 3. As the laser power increases from 4 mW to 19 mW with the raster off the background of the sample greatly increases due to the damage to the substrate cause by the laser. The Sierra Series with ORS overcomes the damage by reducing the average laser power while maintaining the high instantaneous power required for quality Raman collection thus reducing the observed



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The Peak of Spectroscopy



background. The ORS feature collectively reduced the background of the spectrum by averaging the SERS active hotspots which have a more intense Raman signature than the interference from the surrounding substrate. The development of a reproducible SERS substrate is an important goal in completing a SERS based analytical tool. However, without a reader that uses innovative technologies to prevail over issues with Raman instrumentation SERS applications will fail like many others have in the past. A reproducible SERS substrate in combination with the Sierra ORS system will provide a robust platform to create the different commercial applications needed for a SERS product to succeed. Snowy Range Instruments' Sierra Series Raman spectrometers are at the peak of spectroscopy.