Application Note 410000005-B

Portable Raman Instrumentation for SERS Applications

INTRODUCTION

Surface enhanced Raman spectroscopy (SERS) has attracted significant attention in recent years due to rising interest in trace level detection in the field for applications such as environmental safety, food safety, and homeland security. The worldwide number of SERS publications has jumped from approximately 3000 to 25,000 between the years 2000 and 2011[1]. The development of SERS technology is being driven by a need to overcome the technical barrier of the lower detection limit with Raman spectroscopy as well as the need for trace level detection of explosive compounds, chemical residuals, and biomedical diagnostics.

It is widely believed that surface enhancement mechanisms are mainly a result of either electromagnetic resonances between the collective oscillations of plasmons in metal particles and the incident optical field or chemical enhancement through the increase of molecule polarization after coupling with the metal surface[2]. With the advancements in nanotechnology, SERS technology has entered an era where SERS chips are made with highly controlled nanostructures on a substrate using metals such as gold or silver. Another type of SERS is solution-based that uses colloidal solutions of silver or gold particles.

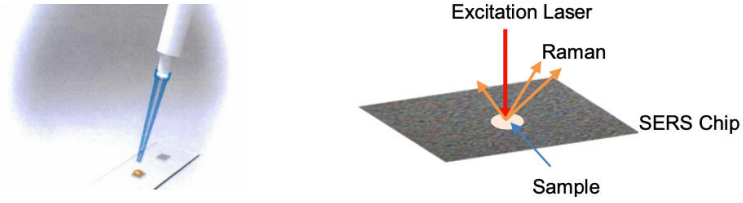

Figure 1. Illustration of a Raman Measurement Using a SERS Chip

For SERS developers or end users of SERS who are interested in a specific SERS application, the centerpiece of their experimental or technological platform must be a Raman setup that provides reliable lab grade performance and is affordable and portable, allowing them to tackle real world problems. The new generation of dispersive portable Raman spectrometers has brought SERS one step closer to real world applications. Due to the small area of the SERS substrate (~5x5 mm^2) where a tiny droplet of sample solution is deposited, accurate laser focusing on the surface is an essential requirement for the Raman instrumentation. While benchtop microscopic Raman systems meet this requirement, the fact that such instruments cannot be moved around hinders SERS developers from transferring their technologies to environments such as production lines, field testing or diagnostic locations where SERS analysis is intended to be carried out. The high cost of a benchtop micro-Raman also limits the adoption of SERS for real world applications.

The B&W Tek i-Raman Plus portable Raman system coupled with a BAC151 video microscope sampling accessory inside a BAC152 laser Class 1 enclosure is an ideal setup for SERS analysis. For solution-based SERS, if the measurement is conducted directly through the solution vial, the BCR100A Raman cuvette holder can be used with the i-Raman Plus.

RAMAN INSTRUMENTATION FOR SERS

High signal to noise ratio for best limit of detection

The B&W Tek i-Raman Plus features a back-thinned CCD detector with TE-cooling to -2 °C. Compared to a conventional front-illuminated CCD with a quantum efficiency at 50%, the back-thinned CCD quantum efficiency can reach up to 90%. Because of the low efficiency of the Raman phenomenon (10^{-8}), it is important that the electronic noise for the CCD detectors is at very low levels relative to the Raman signal. The TE-cooling of the CCD device effectively reduces the noise: dark noise halves for each 7 °C decrease in device temperature. The cooled detector in the i-Raman Plus allows for long integration times of up to 30 minutes. This greatly increases the detection limit and makes the low-light level applications such as SERS feasible. The 785 nm laser wavelength should be used for fluorescence reduction.

High resolution to resolve peaks of the substrate and the sample

For some SERS chips, there are intrinsic Raman peaks from the blank SERS surface. When the Raman peaks from the sample material are in the vicinity of the peaks from the blank SERS substrate, it is crucial that the sample Raman peaks can be separated from the peaks of the SERS chip. The spectral resolution for the i-Raman Plus 785S system is 4.5 cm^{-1}, which provides adequate resolving capability to differentiate two very closely positioned peaks. Figure 2 displays an example of two closely located peaks, with one peak (641 cm^{-1}) associated with the blank SERS and one peak (625 cm^{-1}) associated with the sample solution that is enhanced by SERS.

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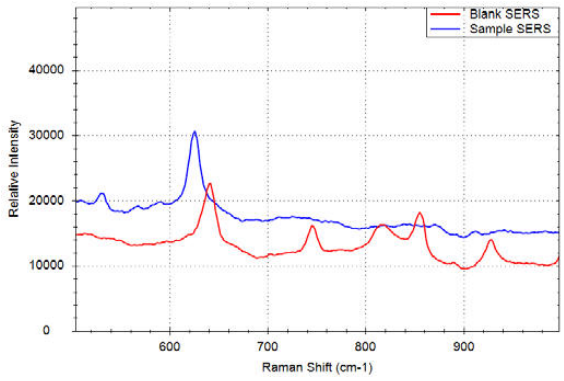

Figure 2. Raman Spectra of a blank SERS surface (red) and a sample material on SERS

RAMAN INSTRUMENTATION FOR SERS

Small laser beam size and accurate focusing control

Due to the fact that the SERS chips are often very small in size, small laser beam size and accurate laser focusing control are needed. The BAC151 video microscope sampling accessory coupled with the i-Raman Plus provides a laser beam size from 21 µm up to 210 µm when objective lenses with different magnifications are used. Table 1 displays the laser beam size and working distance when the objective lens magnification changes from 10x to 100x.

Table 1: Laser spot size from BAC151

Objective lens magnification	Working distance (mm)	Laser beam spot size (µm)
10x	16	210
20x	12	105
50x	9.15	42
100x	3.2	21

Laser safety and blocking of ambient light interference

Because many types of SERS chips will generate specular reflective light when the excitation laser beam is directed onto the SERS surface, it is necessary to have an enclosure that can shield off the reflected laser beams and at the same time block interference from ambient light. For this, the BAC152 provides a laser Class 1 enclosure for laser safety and the necessary blocking of ambient light as well.

The B&W Tek i-Raman Plus portable Raman system coupled with a BAC151 video microscope sampling accessory inside a BAC152 laser Class 1 enclosure provides an ideal setup for SERS applications. The setup provides not only a high S/N ratio for best detection limit and high resolution to resolve peaks, but also the small and adjustable laser beam size along with accurate focusing control. Last but certainly not least, the laser Class 1 enclosure provides the necessary laser safety while at the same time eliminates ambient light interference.

FURTHER READING

Raman vs SERS... What's the Difference?

REFERENCES

1. B. Sharma, R.R. Frontiera, A.I. Henry, E. Ringe, and R.P. Van Duyne, Materials Today, 2012, 15(1-2), 16-25.
2. S. Botti, S. Almaviva, L. Cantarini, A. Palucci, A. Puiu and A. Rufoloni, J. Raman Spectroscopy, 2013, 44, 463–468.

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CONFIGURATION

i-Raman Plus 785S Portable Raman Spectrometer

The i-Raman® Plus 785S is part of our award-winning series of i-Raman portable Raman spectrometers powered by our innovative intelligent spectrometer technology. Using a high-quantum-efficiency CCD array detector with TE cooling and high dynamic range, this portable Raman spectrometer delivers excellent performance with low noise, even at integration times of up to 30 minutes, making it possible to measure weak Raman signals.

The i-Raman Plus 785S features the unique combination of wide spectral range and high resolution with configurations which allow measurements from 65 cm^{-1} to 3,350 cm^{-1}. The system's small footprint, lightweight design, and low power consumption ensure research-grade Raman analysis capabilities at any location. The i-Raman Plus is equipped with a fiber probe for easy sampling, and can be used with a cuvette holder, a video microscope, an XYZ positioning stage with a probe holder, as well as our proprietary BWIQ® multivariate analysis software and BWID® identification software. With the i-Raman Plus, you always have a high precision Raman solution for qualitative and quantitative analysis.

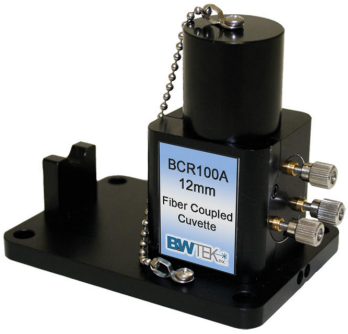
Raman Video Micro-Sampling System (785 nm)

Video microscope sampling system for use with B&W Tek's lab and industrial Raman probes. Includes a 20x objective at a working distance of 16 mm. Offers manual rough and fine adjustment on the X, Y, and Z-axes, coaxial LED illuminator for target alignment, video camera for sample observation, and is compatible with standard microscope objectives. Probe not included, available separately. 785 nm configuration.

BAC151C-785

Enclosure for Raman sampling system

Enclosure for Raman sampling system (i.e. microscope, probe holder) used to eliminate direct ocular and/or skin exposure from the laser emission. The enclosure is ergonomically designed to facilitate sample loading and system operation. For use with 532, 785 and 1064 nm wavelengths.



Raman Cuvette Holder for 9.5 mm measurement probe

The BCR100A Raman cuvette holder allows you to easily measure Raman spectrum of liquids and powders by attaching a Raman probe to the holder. This accessory part uses an internal mirror with a three-point precision locking mechanism for unmatched reproducibility, thereby increasing the Raman signal up to 3x higher than conventional cuvette holders. It is designed so that the probe shaft does not directly contact the cuvette and includes a light trap to reduce background fluorescence. The BCR100A is available in model versions for probes with a diameter of 9.5 mm or 12 mm and can be used with any standard cuvette of 12.5 mm x 12.5 mm outer diameter (1 cm path length) for sampling liquids or powders.