## Validation of SERS Enhancement Factors in Micro and Macro configuration

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The huge signal enhancement that motivates the rapid spreading of Surface Enhanced Raman Scattering (SERS) in a wide range of applications is commonly quantified by measuring the SERS Enhancement Factor (EF).[1] The EF is defined as the ratio between the Raman cross-section of a test molecule measured under SERS and under normal Raman conditions and is normally measured in Micro Raman configuration. Macro Raman configuration, with a slit-like shaped laser spot, however, can provide a signal-to-noise ratio that is several tens of times larger than the conventional point focus of Micro Raman, being equal the laser intensities.[2] The increase in the signal to-noise ratio is due to the large spot used to illuminate the sample that overcompensate for the lower collection solid angle typical of a Macro, compared to a Micro, configuration. Therefore, Macro Raman can be advantageous over the Micro owing to a better signal-to-noise ratio and for investigating large area SERS substrates, e.g. in sensing or analytical applications: consider also that the use of compact portable Raman instruments in such area of application as the environmental and food chemistry and point-of-care tests occurs under conditions that are akin to a Macro Raman configuration.

We shall present here the validation of using Macro Raman to measure the SERS EFs, by comparing the values measured in the two configurations, on the same set of commercial substrates. In addition, a more general method to demonstrate that SERS EF can be equally well measured by Macro and Micro configurations will be presented.[3] Such method avoids the use of SERS substrates, normally subject to reproducibility and aging issues. We suggest using a parameter (R) proportional to the cross-section ratio of a silicon slab against that of a pure liquid (CCl<sub>4</sub>) as a reference to validate the measurement method. R has been determined in different setups at 514.5, 632.8 and 647.1 nm excitation wavelengths. Results confirmed the independence of R on the setup and showed that it can be measured with good reproducibility.[3]

## References

[1] Le Ru, E.C. Etchegoin, P.G. J. Phys. Chem. C 111, 13794 (2007).

[2] Ramsey, J. Ranganathan, S. McCreery, R. L. and Zhao, J. Appl. Spectrosc. 55, 767 (2001).

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