Surface-enhanced Raman spectroscopy (SERS) for trace detection: measurement parameters

Stefan Müller*, Wenka Schweikert, Alexander Mendl, Frank Schnürer
Fraunhofer Institute for Chemical Technology ICT

In explosives detection, it is essential to detect the smallest traces quickly and reliably directly on site without time-consuming sample preparation. Beside other techniques like rapid testing kits, surface-enhanced Raman spectroscopy (SERS) is a very powerful tool to provide substance specific information. Especially the combination with handheld Raman systems is promising. But these systems have, due to the compact and robust setup, only a very reduced set of hardware. Therefore, the measurement parameters are usually fixed in such devices. In this work the relationships between the measurement parameters for a specific SERS substrate (gold on photo-etched GaN substrate [1]) and the analyte 1,2-bis-(4-pyridyl)-ethylene (BPE) were investigated, to find the optimum parameters of the SERS measurement for trace detection.

Comparing the SERS and the conventional Raman spectra (RS) of BPE, most peaks are shifted to higher wavelengths (Figure 1 and Table 1). This peak shift implies a SERS enhancement, which includes a chemical enhancement (charge transfer from the molecule to the metal).

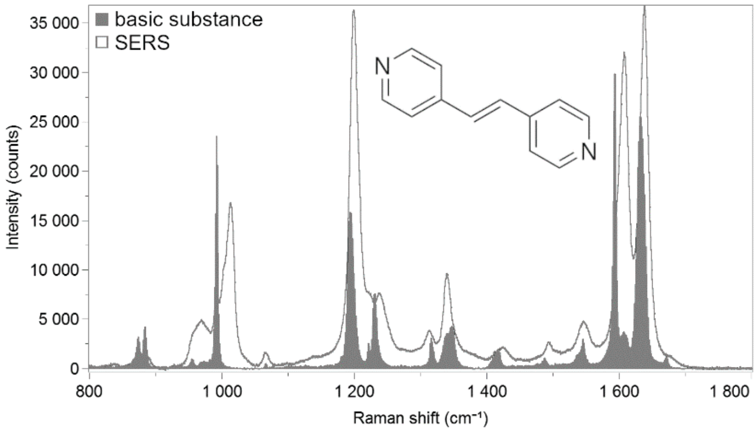

Figure 1: Raman spectra of BPE as powder and on a SERS substrate

Table 1: List of the frequencies and vibrations of the Raman spectra of BPE [2]

Peak in RS [cm^{-1}]	Peak in SERS [cm^{-1}]	Shift [cm^{-1}]	Vibration
1632	1638	+ 6	v C=C (ethylene stretch)
1594	1608	+ 14	v C=C/C=N (quinoidal modes coupled symmetrically)
1546	1546	0	v C=C/C=N (ring distortion via bond stretching)
1418	1424	+ 6	v C=C/C=N (ring distortions via asymmetric bond stretching)
1348	1339	- 9	v $C_{Ethylen}$-C_{Ring} (coupled to v C=C Ethylene)
1231	1237	+ 6	v C=C/C=N (Kekule vibrations coupled to v $C_{Ethylene}$-C_{Ring})
1194	1199	+ 5	δ C-H (ethylene)
992	1013	+ 21	v C=C/C=N Ring breathing

Using different excitation wavelengths different strengths of SERS enhancement can be observed. The best results were obtained with an excitation wavelength of 785 nm and 633 nm (Figure 2).

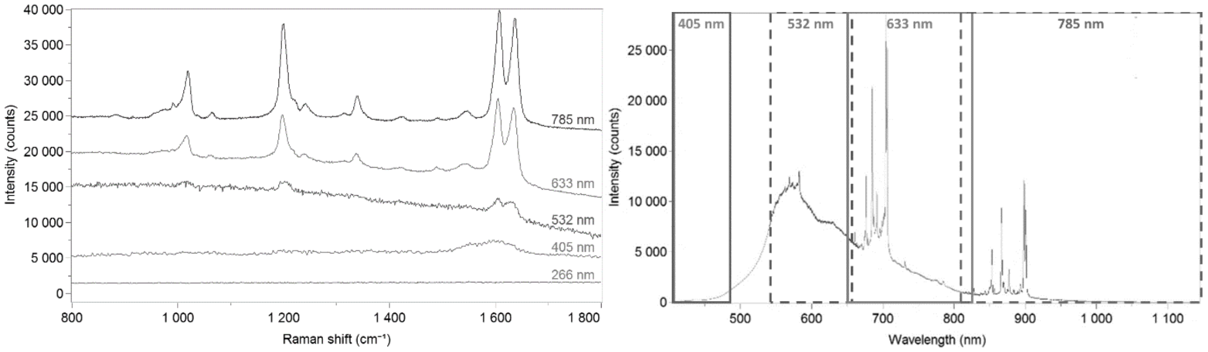

Figure 2: Raman spectra of BPE on SERS substrate with different excitation lasers (left) and the intensities of all lasers

The wavelengths 532 nm, 405 nm and 266 nm turned out to be unsuitable for analyte detection on this substrate. This is caused by two effects. First the metal of the SERS substrate must interact with the laser to induce the surface plasmons [3], second a high fluorescence can cover the signal of the Raman spectra. If the scattered light is plotted against the wavelength (Figure 2 left), the fluorescence peak is visible (increasing baseline). The highest fluorescence is in the region of the 532 nm laser. No fluorescence is visible at 405 nm and 785 nm. So it can be assumed, that the 405 nm laser does not induce surface plasmons on this SERS substrate and this is why no SERS enhancement is visible.

To develop a suitable measuring technique, the influence of the optical parameters regarding the measuring area must be considered. Figure 3 shows the measuring surface on the SERS substrate and the respective intensity of the BPE signal in relation to the optical magnification.

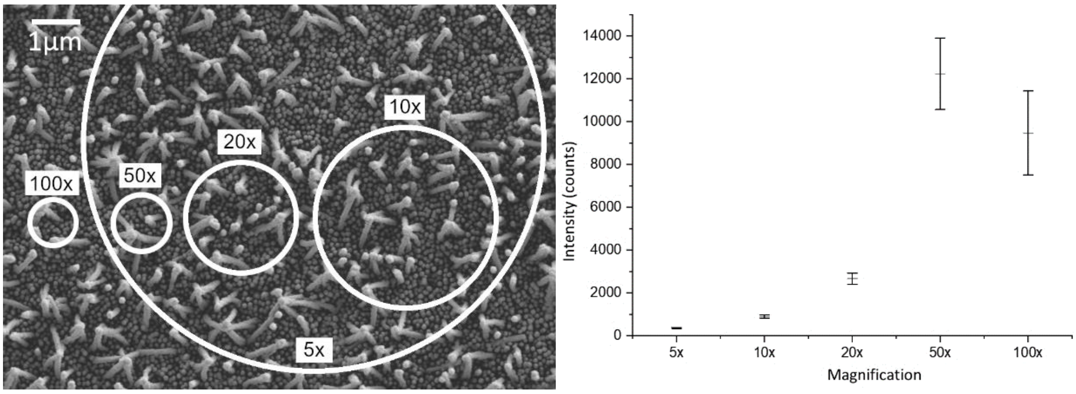

Figure 3: Measuring surface on a SEM image (left) and peak intensity @ 1608 cm^{-1} (right) at different magnification

The Raman signal is increasing with higher magnification up to 50x. Further magnification causes a reduced intensity of the Raman signal. Comparing the surface of the laser spot with the structure of the SERS substrate, the number of SERS-active hotspots is decreasing while the power density is increasing due to the higher focusing of the laser beam. Up to 50x the increasing of the power density is dominant, while the lower number of hotspots becomes important at higher magnification.

The influence of the laser wavelength and the optical magnification on the performance on a gold SERS substrate could be shown. We have shown that the measuring parameters plays an important role for the sensitivity. We have also found that these effects can vary significantly on different SERS substrates, e.g. the fluorescence for silver based SERS substrates (not shown here). Therefore, it is essential to match the Raman device with the SERS substrate, to develop successful onsite trace detection method using SERS.

Literature

[1] Bartosewicz, B., Andersson, P.O., Dzięcielewski, I., Jankiewicz, B., Weyher, J.L. (2019) Nanostructured GaN sensors for Surface Enhanced Raman Spectroscopy. Materials Science in Semiconductor Processing, 91, 97–101.

[2] Sprague-Klein, E.A., Negru, B., Madison, L.R., Coste, S.C., Rugg, B.K., Felts, A.M., McAnally, M.O., Banik, M., Apkarian, V.A., Wasielewski, M.R., Ratner, M.A., Seideman, T., Schatz, G.C., van Duyne, R.P. (2018) Photoinduced Plasmon-Driven Chemistry in trans-1,2-Bis(4-pyridyl)ethylene Gold Nanosphere Oligomers. Journal of the American Chemical Society, 140 (33), 10583–10592.

[3] Schlücker, S. (2014) Surface-enhanced raman spectroscopy: Concepts and chemical applications. Angewandte Chemie - International Edition, 53 (19), 4756–4795.