Quantitative measurements of waste water pollutants at very low concentration range using Surface Enhanced Raman Scattering, SERS.

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Laser Raman spectroscopy plays an increasing important role in nanobiotechnology and nanomaterials medicine and life science. Based on vibrational transitions, it has long been regarded as a valuable non destructive tool for the identification of chemical and biological samples as well as the elucidation of molecular structure. The problem appears when this technique is applied to the detection of very low concentration of analytes. Other methods are commonly used as HPLC or UV/Visible detection but they are time consuming and sample pre-treatment is normally required. Surface–Enhanced Raman spectroscopy (SERS) might be a more valuable detection method because it is a very sensitive technique that is manifested as an enhancement by many orders of magnitude of the intensity of Raman radiation by molecules in the immediate vicinity to nano-rough metal surfaces and nano-structured metal systems such as colloid clusters of noble metals[1]. When the localized surface plasmons of nanoscale roughness features on a silver or gold substrate are excited by visible or NIR light, strong electromagnetic fields are generated that increases the magnitude of the intensity of the inelastic scattering by orders of magnitude. It is in this way that SERS provides much better detection limits than Raman spectroscopy using standard Raman equipment.

According to the World Health Organization (WHO), the most dangerous threat for health of mankind emerging during the next years is polluted water. Under developed countries but also European countries already suffer from insufficient clean water supply. Many southern European countries will be affected due to increasing temperature and dryness caused by climatic changes so procure low quantities of fresh water by recycling of waste water should be the target. Water contaminated from industry and agriculture has to be efficiently treated to protect humans from being intoxicated with compounds or bacteria. It is well established in industrial wastewater treatment to use membranes for treatment of waste water containing high biodegradable organic compounds but are inefficient with respect to waters containing high amount of stress-inducing substances (olive oil industry), high colourity and low biodegradable organic compounds (textile industry).

In this context, to scrutinize the performance of pertinent membranes developed for the purification of relevant industrial wastewaters we have proceeded to a preliminary study applying quantitative SERS measurements of water solutions containing nanogram levels of Methylene Blue (methylthionine chloride), a heterocyclic aromatic dye used in the textile industry that causes severe central nervous system toxicity at plasma concentrations over 500 ng/mL[2]. We have utilized silver nanocolloids prepared according to modified Lee-Meisel method[3].

SERS measurements were based on the use of a "shaking cell"[4] in combination with the advantage of utilizing the right angle Raman light scattering collection geometry provided much higher sensitivity since this scattering geometry matches the scattering volume with the entrance slit of the spectrometer and improves the signal to noise ratio. The Raman spectra were excited with a water-cooled Ar^+ laser operating at 514.5 nm and were analyzed via a 64-cm focal length spectrometer (T-64000 JY - Horiba).

Representative SERS spectra from Methylene Blue at different concentrations are shown in Figure 1(A); the most intense Raman band centered at 1625 cm^{-1} is used for quantitative analysis by relating the peak intensity to concentration of Methylene Blue. Using Partial Least-Squares (PLS) analysis, a regression algorithm employing routines of the OPUS QUANT-2 Software (Bruker Optics) applied to a total of 11 spectra was used for quantitative analysis. Two ranks can be extracted, and the predicted versus known values of the concentration of the active agent for the 514.5 nm laser line shown in Fig. 1(B) allow for R^2 = 91% and RMSE = 15 ng/mL. For any practical purpose, these errors are in the same range as the threshold detection of Methylene Blue by the applied SERS method.

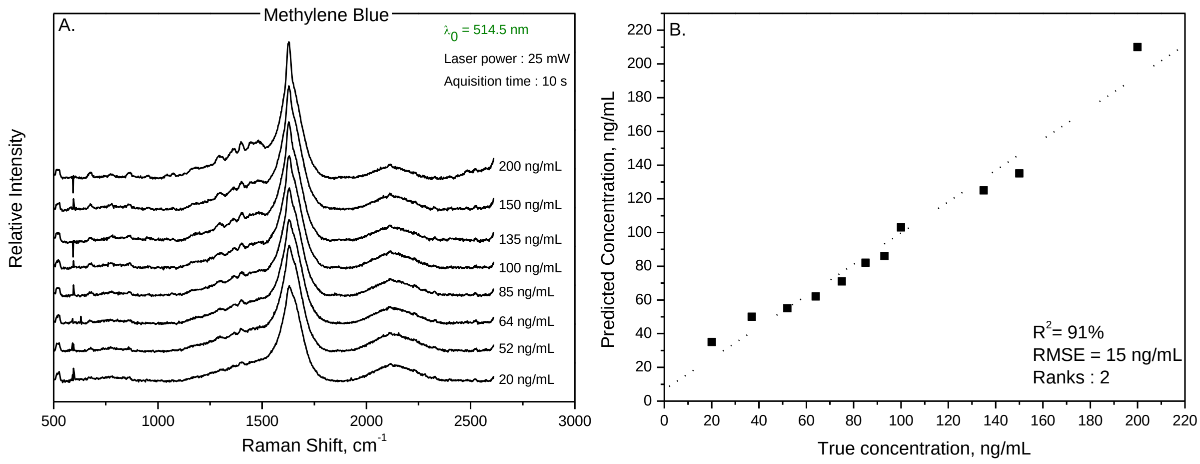

Figure 1. (A)Representative SERS spectra of methylene blue at different concentrations (left) and (B) The predicted correlated to the true values of Methylene Blue concentration quantitative results (right)

Future studies are oriented to test this nano-enhanced Raman scattering technique with a mixture of foulants from the textile industry. Similar quantitative SERS measurements at very low concentration level can be applied to test the efficiency of new nano-filtration membranes in the rejection of relevant low molecular weight organic pollutants in the cosmetics & pharmaceutical industry and in olive mill wastewaters, as well.

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References

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