Development of a technique for studying trimethylamine oxide solutions using planar SERS structures

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Abstract

Trimethylamine oxide (TMAO), one of the components of the blood, is a marker of the risk of cardiovascular disease. Optimization of the method for studying TMAO by Raman spectroscopy, as the fastest analytical method, is an important task today. In this work, we study the effect of treatment with HCl solutions and boiling isopropanol vapor on SERS structures based on metal-dielectric mirror and Ag nanoparticle layers on the Raman spectra of the TMAO. The influence of the methods of deposition of the analyte on the substrate on the quality of the Raman spectra was studied. TMAO solution with concentrations of 10 mM was used as an analyte in the work.

Experimental

In this work, a planar structure based on a silver mirror with a layer of Ag nanoparticles was used as an SERS substrate (Fig. 1). The metal and dielectric layers were fabricated by vacuum thermal and electron beam evaporation, respectively. To obtain nanoparticles of the required size and remove impurities from the metal, the structure underwent atmospheric annealing at 400 C for 10 minutes.

The substrates were treated by keeping them in a 3.5% acid solution and then washing them in deionized water, or by keeping them in boiling isopropyl alcohol vapor.

Freshly prepared solutions of TMAO 10 mM were used as an analyte. Anail was applied using a dispenser in drops of 4 µl, or by soaking in a solution. After application, the analyte was dried in a fume hood at room temperature.

The study was carried out on an inVia confocal microscope from Renishaw with the following parameters: wavelengths of 532 and 785 nm; laser power 5 mW; light spot diameter 4 µm; spectrum accumulation time 60 s.

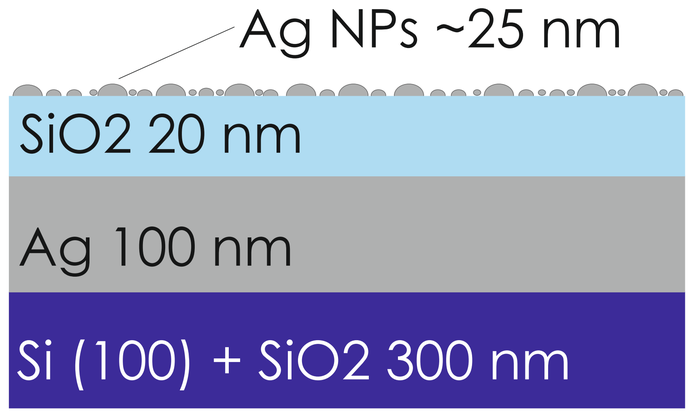

Figure 1 - SERS substrate sceme

Results

The influence of the duration of the soaking of the untreated substrates in the solution showed that the most rational is the exposure of the sample for 30 minutes. Increasing the exposure time to 60 minutes (in 2 time) increases the intensity of the spectrum by only 18%. It should be noting that the soaking of the samples made it possible to distribute the analyte much more uniformly than when applied by a drop.

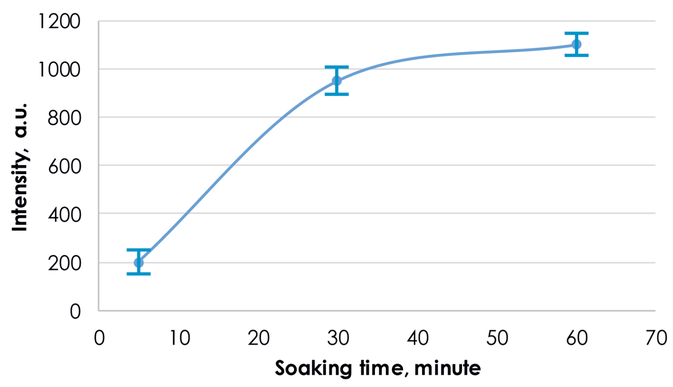

Figure 2 - Dependence of the intensity of the 760 cm^{-1} peak on the soaking time, wavelength 532 nm

The study of the influence of the treatment time on the intensity of the spectrum showed that the optimal time for holding the substrate in the acid solution is from 15 to 30 seconds. A further increase in the treatment time of the substrate leads to a rapid decrease in the intensity.

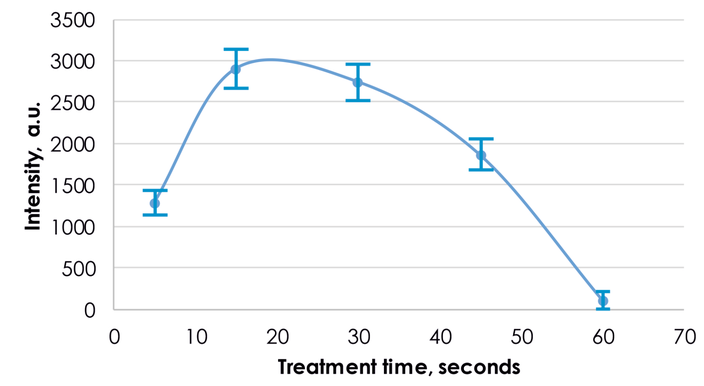

Figure 4 - Dependence of the intensity of the 760 cm^{-1} peak on the treatment time, wavelength 532 nm

A study of the effect of a pretreatment showed that the best choice is to use a dilute hydrochloric acid solution. Processing for 30 seconds and subsequent washing in a weak stream of deionized water for 10 seconds showed the following results: reduction of noise level; an increase in the intensity of characteristic TMAO peaks; reduction of the thermal decomposition. The use of an isopropanol led to a drop in the quality of the spectrum to the level of a noise.

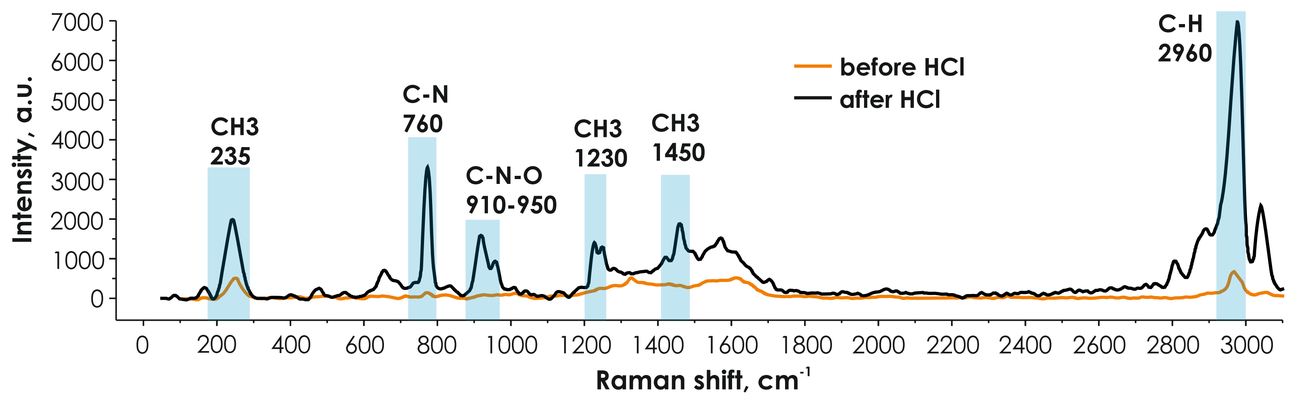

Figure 3 - Spectra of TMAO without and with preliminary treatment of the SERS substrate in 3,5% HCl solution for 30 s, wavelength 532 nm

Figure 5 demonstrates the influence of the laser wavelength on the efficiency of recording the Raman spectrum of TMAO. The TMAO spectra are of a high quality at both 532 and 785 nm. The wavelength of 532 nm provides better visibility of more peaks, due to the greater plasmonic activity of Ag NPs in the blue-green region of the spectrum. The 785 nm wavelength provides better visibility of C-N and C-N-O bond peaks and reduces the thermal degradation of the analyte.

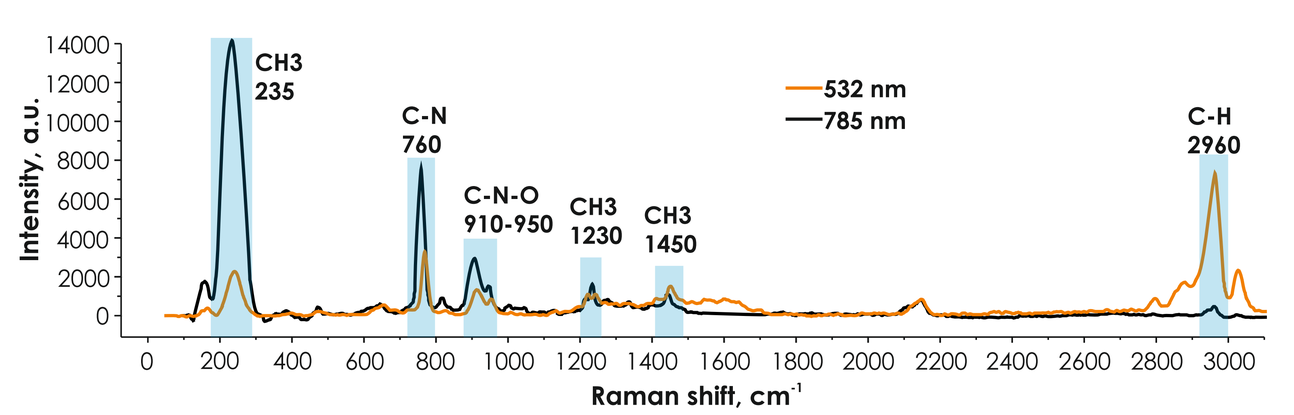

Figure 5 - TMAO spectra at different laser wavelengths, treatment time in acid solution 30 s

Conclusion

In the course of the work, it was possible to establish the importance of a pre-treatment, soaking time and the laser used on the effectiveness of the study of TMAO. It was founding that the greatest effect in the study of TMAO using SERS substrate based on Ag NPs will be provided that the following parameters are observed: treatment of the substrate in a 3,5% HCl solution for 15 to 30 seconds, followed by washing in a weak stream of deionized water; soaking time in TMAO solution for at least 30 minutes; using a 532 nm laser to search for C-H bonds of TMAO; using a 785 nm laser to search for C-N and C-N-O bonds of TMAO.

Acknowledgements

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Thanks to the organizers of the conference.

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