

## **SERS characterization of perchlorates in drinking water**

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*Real time monitoring of the drinking water supply network is essential to provide early warning in case of a contamination event. Pollutants like perchlorate and nitrate anions are known to produce severe health effects in the population. Raman-based sensors offer fingerprinting capabilities. Surface enhanced Raman spectroscopy (SERS) is a solution to improve the weak signals involved in Raman scattering. However, anions show low affinity for the metallic surface of SERS sensors. In this work, we show that positively charged coatings can increase this affinity. Micromolar concentrations of perchlorates in deionized water have been measured in ongoing experiments.*

### **Introduction**

Perchlorate can be found in ground fertilizer, rocket propellant, and explosives. Due to its high solubility and non-reactivity with soil-sediment, perchlorate can easily contaminate ground water, and eventually end up in the drinking water supply [1]. When intaken in sufficiently high concentration, it interferes with the functioning of the thyroid gland by inhibiting the uptake of iodide, which alters the release of hormones, having important consequences for the (brain) development of fetuses and children. While perchlorate is not yet regulated, a recommendation of the American Environmental Protection Agency proposed a threshold value for future regulation of 150 nM in drinking water [2]. Conventional perchlorate detection methods require typically sample preparation, analytical laboratories, and long analysis time [3]. Real-time monitoring of perchlorate in drinking water would help minimizing health consequences associated with this anion.

Raman spectroscopy provides a chemical fingerprint from the vibrational structure of molecules. Since water has a very small Raman signature, Raman spectroscopy is an ideal candidate for fingerprinting of water samples. However, spontaneous Raman scattering is not a very efficient process. Surface enhanced Raman spectroscopy (SERS) enhances the sensitivity of conventional Raman by a few orders of magnitude. However, perchlorate has a low affinity for SERS surfaces due to electrostatic repulsion. Furthermore SERS surfaces can be hydrophobic, preventing sensitive measurements. A cationic self-assembled monolayer (SAM) coating on the surface of the SERS sensor creates a hydrophilic environment with a positive end group resulting in a high affinity of perchlorate for the surface. Previous research into cationic coated SERS substrates has been summarized in table 1.

In this work, a SERS sensor integrated on an optical waveguide chip will be developed. The device should allow for real-time detection of perchlorate in the drinking water

network. As a first step, different coatings have been investigated on top of commercial SERS substrates in order to increase the surface affinity for perchlorate with the ultimate goal of achieving sensitivities below the targeted 150 nM.

Table 1. Limit of detection (LOD) found in literature for different cationic coated SERS substrates. In this paper, the LOD is specified as the lowest concentration measurable where the signal is without doubt from the analyte.

Coating	Abbreviation	LOD (nM)	Laser power (mW)	Source
2-mercapto-4-methyl-pyrimidine	MMP	500	80	Mosier-Boss et al, [3]
Cysteamine	Cys	50	16	Hao et al, [4]
2-dimethyl-aminoethanethiol	DMAE	10	1	Gu et al, [5]

## Materials and methods

The Au ‘SERStrate’ substrates used for SERS measurements were purchased from Silmeco (Copenhagen, Denmark), and used as delivered. Flat Au substrates were fabricated by evaporating 50 nm of Au on a silicon wafer with a 2 nm Ti adhesion layer in between. Cysteamine hydrochloride (98%), 2-mercapto-4-methyl-pyrimidine hydrochloride (99%), and sodium perchlorate (98%) were purchased from Sigma Aldrich (Schnelldorf, Germany). Ethanol absolute (99,9%) was obtained from VWR Chemicals (Fontenay-sous-Bois, France). All aqueous solutions were made with de-ionized (DI) water (18,2 MΩ cm). The SAMs were prepared by dissolving either Cys (0,5 g) or MMP (0,02 g) in ethanol (60 mL) followed by 5 minutes of sonication. The substrate was then introduced in the solution and argon gas was flown over the solution. The substrate was let to react in the solution for 24 h, after that it was rinsed with ethanol and dried with a nitrogen stream. Subsequently contact angle measurements were done to check whether a SAM was deposited on the substrate. Perchlorate solutions were made by diluting a 1 M solution in steps of 1/10<sup>th</sup>. SERS measurements were performed with an Alpha300 RAS confocal Raman microscope using a 785 nm laser source (WITec, Ulm, Germany) and an 10x MPLFLN10x objective (0,3 numerical aperture, Olympus, Zoeterwoude, Netherlands). The power and integration time utilized in each experiment will be specified in the following sections.

## Results and discussion

The first step in this work was to characterize the LOD of perchlorate using conventional Raman spectroscopy. The main objectives of this experiment were to firstly verify the Raman signature of perchlorates and to check whether with the correct experimental conditions (i.e., pump power and integration time) the required sensitivity (150 nM) could be achieved. In this experiment, the flat Au substrates were immersed in perchlorate solutions. Aqueous perchlorate has its main Raman scattering peak at 930 cm<sup>-1</sup>, which is associated with a symmetric stretching mode. Secondary peaks are present at 625 cm<sup>-1</sup> and 460 cm<sup>-1</sup> [1]. Figure 1 shows the spontaneous Raman spectra collected on a series of samples with decreasing concentrations of perchlorate in DI water. An excitation power

of 140 mW was utilized, which is the maximum output of the laser in the system. Measurements are averaged 10 times. A LOD of  $10^{-2}$  M was obtained. In the graphs, a small peak at  $930\text{ cm}^{-1}$  can be seen for concentrations lower than  $10^{-2}$  M. This peak is also present in the DI water measurement. It is thus concluded that this peak originates from the background of the DI water. The LOD of  $10^{-2}$  M is five orders of magnitude larger than the target in this work. The use of SERS is therefore justified.

Experiments using as-received SERStrate substrates were unable to measure any perchlorate at all. This is mainly due to the hydrophobicity of the SERStrate surface, which prevents the solution from getting close enough to the surface to be in the areas with enhanced electromagnetic field. Upon coating the surface with Cys, the surface became hydrophilic (Fig. 2). The change from hydrophobic to hydrophilic is explained by the positively charged  $\text{NH}_2$  heads of the Cys molecule, which create a positive hydrophilic environment.

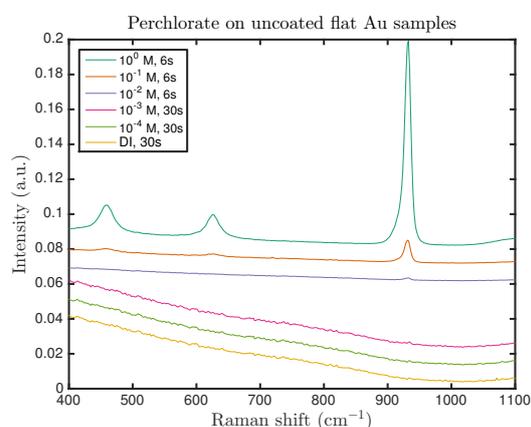


Figure 1. Unpolarized Raman spectra of perchlorate solutions in DI water with different concentrations. The LOD obtained is  $10^{-2}$  M. Experimental conditions: Integration time 6 s or 30 s, laser power 140 mW. Measurements normalized to background signal before  $400\text{ cm}^{-1}$  and offset for clarity.

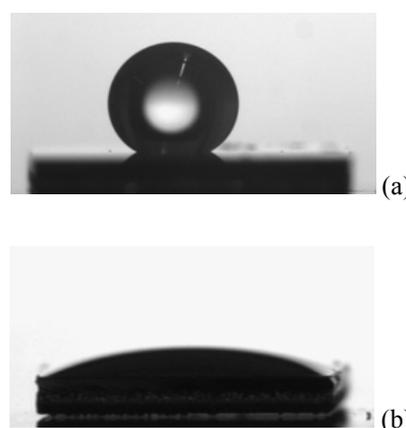


Figure 2. Contact angle measurements on SERStrate substrates: (a) as received substrate. Measured contact angle  $146,26 \pm 0,01^\circ$ ; (b) SERStrate coated with Cys. The surface is hydrophilic. The contact angle could not be determined by the software.

Figures 3 and 4 show Raman measurements on perchlorate solutions of different concentrations in DI water on SERStrate substrates coated with Cys (Fig. 3) and MMP (Fig. 4). A LOD of  $10^{-5}$  M was achieved. A laser power of only 0,1 mW was used in these experiments. Bigger powers are not recommended by the SERStrate manufacturer as they might degrade the substrates. There is a peak present in the  $10^{-6}$  M measurement of perchlorate on MMP coated SERStrate substrates. Since this peak is also present in the measurement with DI water, its origin is not attributed to the presence of perchlorate ions in the solution. When compensating for the used laser power in these experiments, these results are in good agreement with values previously found in literature [3, 4]. The measured increase in LOD can largely be contributed to the electromagnetic field enhancement by plasmonic resonances created on the Au surface.

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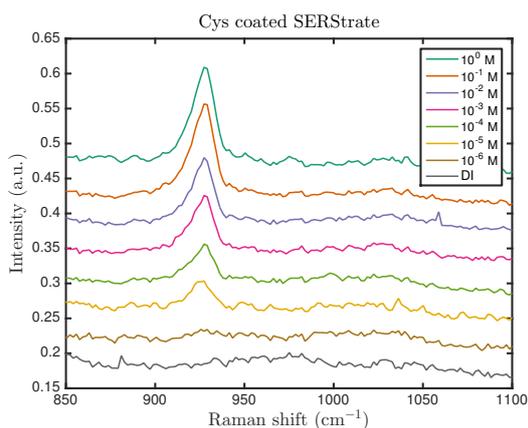


Figure 3. Perchlorate measurement on Cys coated SERStrate substrates. The LOD is  $10^{-5}$  M. Integration time 30 s, laser power 0,1 mW. Measurements normalized to background signal before  $850\text{ cm}^{-1}$  and offset for clarity.

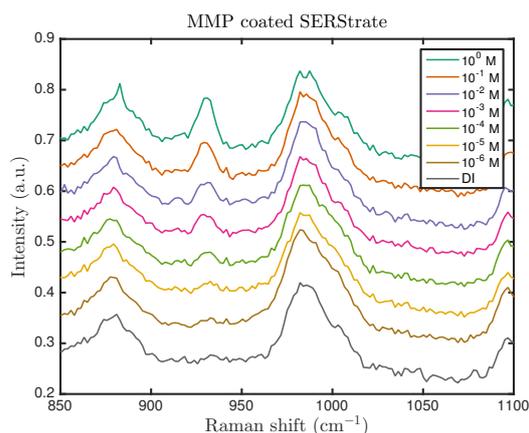


Figure 4. Perchlorate measurement on MMP coated SERStrate substrates. The LOD obtained is  $10^{-5}$  M. The peaks at  $880\text{ cm}^{-1}$  and  $983\text{ cm}^{-1}$  originate from the MMP coating. Experimental conditions identical to figure 3.

### Conclusions

Conventional Raman measurements of perchlorate solution on flat Au resulted in a LOD of  $10^{-2}$  M using 140 mW of laser power. Measurements of uncoated SERS substrates were unsuccessful in detecting perchlorate. After applying coatings to the SERS substrate surfaces, a LOD of  $10^{-5}$  M was measured using only 0,1 mW of laser power for both MMP and Cys coatings. Future work will include using DMAE coatings, measuring water with buffer ions to keep a constant ionic strength, and using a complex water matrix as found in actual drinking water.

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