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## DETECTION OF PERCHLORATE ANION ON FUNCTIONALIZED SILVER COLLOIDS USING SURFACE-ENHANCED RAMAN SCATTERING

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### ABSTRACT

Perchlorate anion interferes with the uptake of iodide by the human thyroid gland and consequently disrupts the regulation of metabolism. Chronic exposure to high levels of perchlorate may lead to the formation of thyroid gland tumors. Although the Environmental Protection Agency (EPA) has not set a maximum contaminant level (MCL) for perchlorate, a draft drinking water range of 4-18 ppb based on 2 liter daily consumption of water has been established. The current EPA approved method for detecting perchlorate uses ion chromatography which has a detection limit of ~1ppb and involves lengthy analytical time in the laboratory. A unique combination of the surface-enhanced Raman scattering (SERS) effect and the bifunctional anion exchange resin's high selectivity may provide an alternative way to detect perchlorate at such low concentrations and with high specificity. SERS, which uses laser excitation of adsorbed perchlorate anions on silver nanoparticles, has been shown to detect perchlorate anions at concentrations as low as 50 ppb. Normal micro-Raman analysis of perchlorate sorbed onto the resin beads has detected an even lower concentration of 10 ppb. In an effort to integrate these two effects, silver nanoparticles were coated with N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride, a functional group similar to that found on the resin bead, and subsequently inserted into different perchlorate concentration environments. This method has resulted in perchlorate detection down to ~10 ppb and a more consistent detection of perchlorate anion at ~50 ppb than that of earlier methods. As suggested by the direct insertion of functionalized silver colloids into perchlorate samples, this technique may potentially allow for the development of a probe using on-site Raman spectrometry to detect significantly low concentrations of perchlorate *in situ* rather than in the laboratory.

### INTRODUCTION

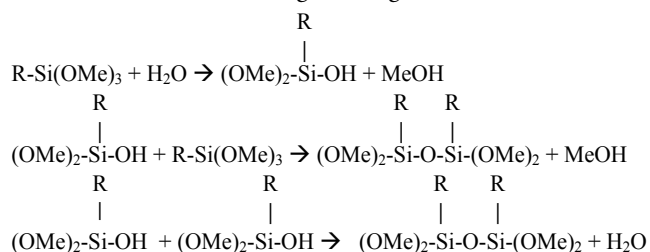
Perchlorate anion ( $\text{ClO}_4^-$ ) is a kinetically inert, nonvolatile, water soluble anion that is found in rocket propellants, munitions, fireworks, and some nitrate fertilizers [1,2]. Traces of  $\text{ClO}_4^-$  are increasingly being detected in soil, groundwater, drinking water, and irrigation water systems, and it is suspected to threaten human health by competitively inhibiting iodide uptake by the thyroid gland. The thyroid gland plays an important role in regulating metabolism, and changes in its hormone production may especially affect the proper development of children and fetuses [2].

The Environmental Protection Agency has not yet set a maximum contaminant level (MCL) for  $\text{ClO}_4^-$ , but a draft drinking water range of 4-18 ppb (based on a 2 liter daily consumption of water for a 70 kg adult) has been established [3]. The current EPA Method 314 uses ion chromatography to detect  $\text{ClO}_4^-$  at low concentrations by its chromatographic retention time. Other techniques utilize mass spectrometry and detect  $\text{ClO}_4^-$  based on its mass ratio,  $m/z$ .

A unique combination of the surface-enhanced Raman scattering (SERS) effect and the bifunctional anion exchange resin's high selectivity may provide an alternative way to detect  $\text{ClO}_4^-$  at

even lower concentrations and with higher selectivity based on the Raman active vibrational frequency of  $\text{ClO}_4^-$ . SERS, which uses laser excitation of adsorbed analyte molecules on silver nanoparticles, has been shown to detect molecules with enhancement factors reaching up to  $10^{14}$  [4]. Bao et al. reported a detection limit of  $8.5 \times 10^{-8}$  M for uranyl ions on silver-doped silica sol-gel films [5]. In addition, bifunctional anion exchange resin beads that are coated with quaternary ammonium functional groups of large ( $C_6$ ) and small ( $C_2$ ) trialkyl groups have been shown to selectively adsorb  $\text{ClO}_4^-$  in the presence of competing anions commonly found in groundwater [6].

In our previous study, SERS of Ag colloids aggregated by the addition of NaCl detected  $\text{ClO}_4^-$  down to concentrations of  $\sim 50$  ppb ( $\mu\text{g/L}$ ), and Raman analysis of bifunctional anion-exchange resin beads detected even lower concentrations of 10 ppb [7]. In an effort to integrate the SERS effect of Ag nanoparticles with the selectivity of the bifunctional anion exchange resin, silver nanoparticles and silver-doped silica sol-gels were coated with N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride, an organosilane with a functional group similar to that found on the resin bead. Through hydrolysis and subsequent condensation reactions shown below, the functional groups of this layer formed silicon-oxygen-silicon bridges that allowed attachment to Ag coated glass slides.



These methods resulted in a more consistent detection of  $\text{ClO}_4^-$  at  $\sim 50$  ppb than that of earlier methods, and detection of  $\text{ClO}_4^-$  at  $\sim 10$  ppb using the silver-doped silica sol-gel. This technology may eventually lead to the development of a probe using on-site Raman spectrometry to detect significantly low concentrations of  $\text{ClO}_4^-$  *in situ* rather than in the laboratory.

## MATERIALS AND METHODS

Of the several different methods that exist for preparing Ag colloids suitable for observing the SERS effect, this study used a modified method of Creighton et al. [8]. In brief, 25 ml of freshly prepared 0.01M  $\text{NaBH}_4$  (EM Science) were added to 12.5 ml of 0.01M  $\text{AgNO}_3$  (J.T. Baker) and stirred vigorously for  $\sim 1$  hour at room temperature to create a yellow, Ag sol. Sample slides were prepared by applying one drop of the Ag sol to the surface of a glass slide and dried in a  $70^\circ\text{C}$  oven. Particle size and size distribution of the Ag colloids were measured by means of dynamic light scattering using a ZetaPlus particle size analyzer (Brookhaven Instruments Corporation, Holtsville, New York). Ag-doped silica sol-gels on frosted glass slides were obtained from Bao et al. [5].

A layer of N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride (Gelest, Inc.) diluted in chloroform (EM Science) was added to the surface of Ag colloids and Ag-doped silica sol-gel

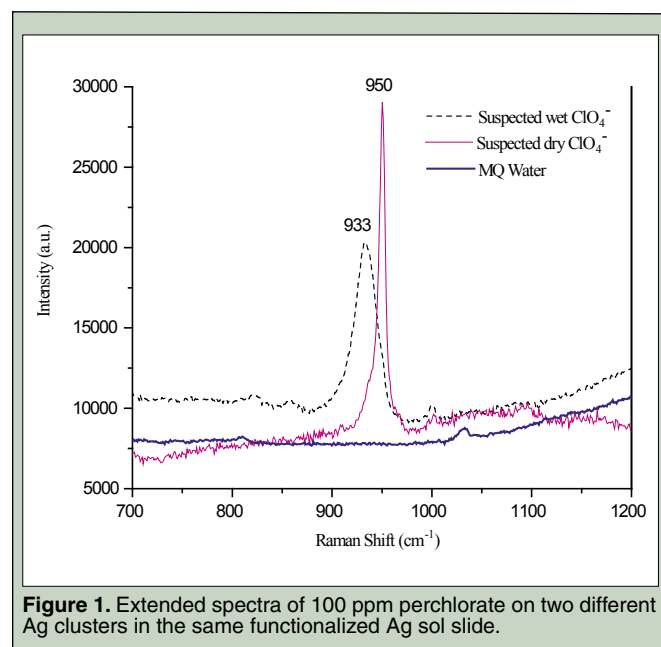
samples and was allowed to hydrolyze with water in the air. Excess organosilane was gently washed off with ethanol (Aldrich). The functionalized slides were then placed in 100 ml of Milli-Q deionized water (EASYPure, Barnstead) and background Raman spectra were obtained.

Perchlorate solutions of 1000 ppm and increasingly dilute concentrations were made from  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  (EM Science). Samples were then placed in 100 ml of aqueous  $\text{ClO}_4^-$  solution and allowed to equilibrate for 24 hours, whereupon Raman spectra of the samples were obtained while samples were still wet. These steps were repeated for non-functionalized Ag sol samples.

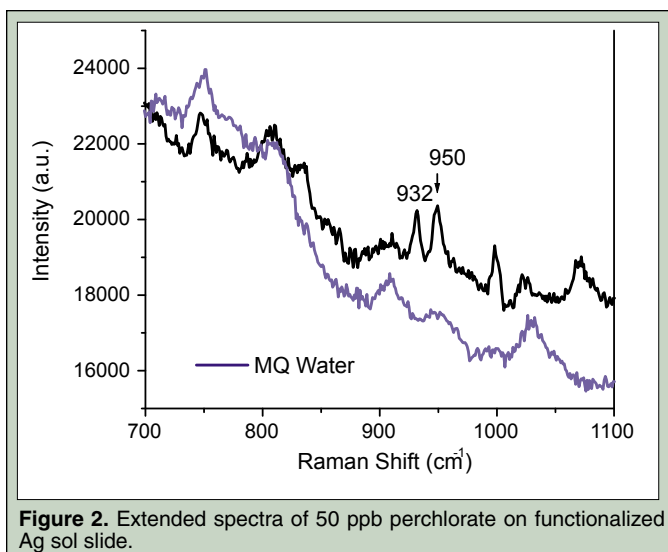
Raman spectra were obtained using a Renishaw micro-Raman system equipped with a 300 mW near-infrared diode laser at a wavelength of 785 nm operating at 10% power (Renishaw Inc., New Mills, UK). The laser beam was set in position through a Leica Raman Imaging Microscope objective (50X) set at a lateral spatial resolution of  $\sim 2 \mu\text{m}$  and a depth of field of  $\sim 1$  to  $5 \mu\text{m}$  depending on the sample. A charge-coupled device (CCD) array detector was used to achieve signal detection from a 1200 grooves/mm grating light path controlled by Renishaw WiRE software and analyzed by Galactic GRAMS software. Polarization optics was set perpendicular to the laser with an intensity of  $\sim 60$  mW at the exit of the 50X objective.

## RESULTS

Particle size and size distributions of synthesized Ag colloids were routinely analyzed by means of the dynamic light scattering technique. Particle sizes of the Ag sol remained stable and ranged from 10-30 nm over a period of  $\sim 30$  days (data not shown). Upon drying of the Ag sol on a glass slide, aggregated Ag nanoclusters formed on the micrometer scale. Although several clusters fell off the sample slides during sample preparation, a sufficient amount remained to obtain Raman spectra. Background Raman spectra verifying the absence of major peaks between  $910$ - $960 \text{ cm}^{-1}$  for



**Figure 1.** Extended spectra of 100 ppm perchlorate on two different Ag clusters in the same functionalized Ag sol slide.



**Figure 2.** Extended spectra of 50 ppb perchlorate on functionalized Ag sol slide.

all samples were taken prior to placing the samples in the  $\text{ClO}_4^-$  solution.

Frequently, wet samples would appear to dry during spectral acquisition, giving sharp peaks at  $\sim 933 \text{ cm}^{-1}$  and  $950 \text{ cm}^{-1}$ . Figure 1 shows 100 ppm  $\text{ClO}_4^-$  detection giving peaks at  $\sim 933 \text{ cm}^{-1}$  on one Ag cluster and  $\sim 950 \text{ cm}^{-1}$  on another cluster in the same Ag sol sample. Figure 2 shows 50 ppb  $\text{ClO}_4^-$  detection of another Ag sol sample where both  $\sim 932 \text{ cm}^{-1}$  and  $\sim 950 \text{ cm}^{-1}$  peaks are present in the same spectrum.

Figure 3 shows sample images of the functionalized Ag colloids and the functionalized Ag-doped silica sol-gel that were used to detect  $\text{ClO}_4^-$  under a 50X objective. Perchlorate detection occurred most frequently on clusters thinly covered by moisture leftover from equilibration, whereas thick wet layers yielded Raman spectra with small signal to noise ratios.

The lowest detection limit for non-functionalized Ag sol was 1000 ppm, with the characteristic  $\text{ClO}_4^-$  peak occurring at  $\sim 933 \text{ cm}^{-1}$  (data not shown). Adding the quaternary ammonium functional group layer enabled both the Ag sol and the Ag-doped silica sol-gel to detect  $\text{ClO}_4^-$  down to 50 ppb with more consistency than that of our past studies and enabled the Ag-doped silica sol-gel to detect down to 10 ppb [7]. Figure 4 shows spectra of  $\text{ClO}_4^-$  detection on functionalized Ag sol substrates at concentrations of 100 ppm, 10 ppm, 500 ppb, 100 ppb, 50 ppb and 0 ppb. Figure 5 shows spectra of  $\text{ClO}_4^-$  detection on functionalized Ag-doped silica sol-gel substrates at concentrations of 10 ppm, 1 ppm, 100 ppb, 50 ppb, 10 ppb, and 0 ppb. Figure 6 is an illustration of quaternary ammonium groups adsorbing  $\text{ClO}_4^-$  on both functionalized Ag colloids and Ag-doped silica sol-gel. For both functionalized media, Raman peak intensities decreased with decreasing perchlorate concentration until reaching the part per billion range. Here  $\text{ClO}_4^-$  signal intensities did not consistently decrease with the concentration. Moreover, at lower concentrations, samples were subjected to more spectral acquisitions, and subsequent increased exposure to the laser prompted the tendency for remaining analyte moisture to recede and concentrate in one area of the slide before drying completely.

Figures 7 shows the SERS enhancement effects of using functionalized Ag colloids as compared to functionalized Ag-doped silica sol-gel for  $\text{ClO}_4^-$  concentrations at 50 ppb and 100 ppb.

Although both Ag substrates had Raman  $\text{ClO}_4^-$  peaks of similar intensity, the  $\text{ClO}_4^-$  peaks detected using Ag colloids were sharper and less red-shifted than those detected using the Ag-doped silica sol-gel.

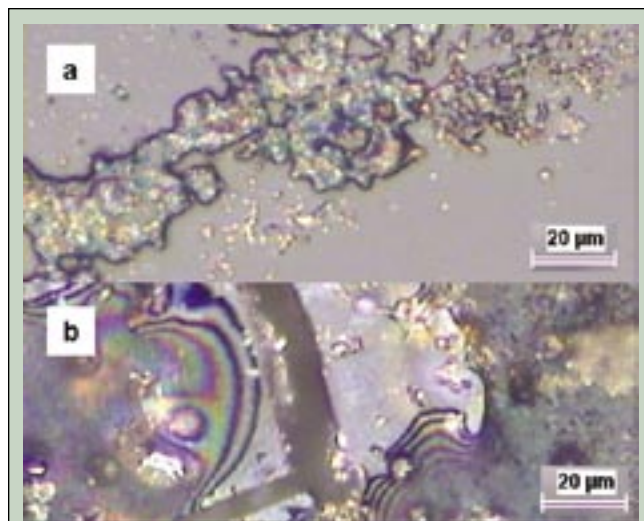
## DISCUSSION AND CONCLUSIONS

### *Characteristic Perchlorate Peaks*

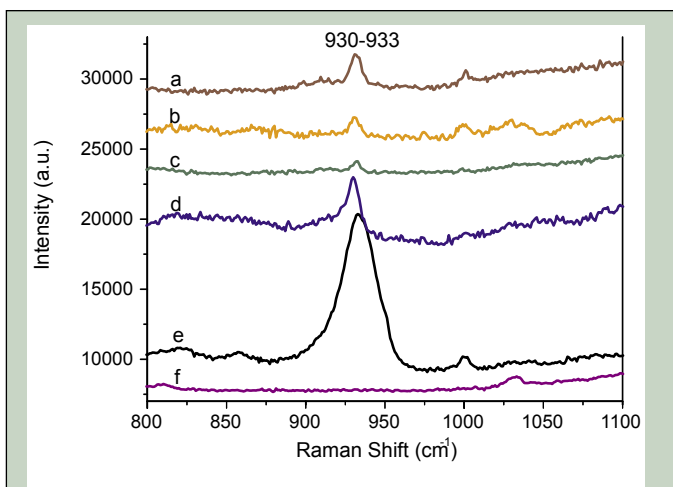
Our past studies have shown dry  $\text{ClO}_4^-$  to have a Raman peak at  $\sim 950 \text{ cm}^{-1}$  and  $\text{ClO}_4^-$  detection on bifunctional resin beads to occur at  $\sim 930 \text{ cm}^{-1}$ . The latter  $\sim 20 \text{ cm}^{-1}$  shift was expected to be the result of strong interactions between the  $\text{ClO}_4^-$  and positively charged quaternary ammonium functional groups [7]. However, in the absence of any quaternary ammonium functional groups, the characteristic  $\text{ClO}_4^-$  peak from analysis of wet non-functionalized Ag samples in this study was  $\sim 933 \text{ cm}^{-1}$ . Therefore the  $\sim 933 \text{ cm}^{-1}$  peak is most likely characteristic of  $\text{ClO}_4^-$  in its aqueous form, as other studies have reported the normal Raman peak of aqueous  $\text{ClO}_4^-$  solutions to occur at  $\sim 935 \text{ cm}^{-1}$  [9]. Figures 1 and 2 show how both peaks were observed in this study, most likely indicating the presence of wet and dry  $\text{ClO}_4^-$ , with the wet peak predominantly observed in the beginning of sample analysis and the dry peak appearing toward the end of the analysis when the samples had dried.

### *Aggregation of Nanoparticles*

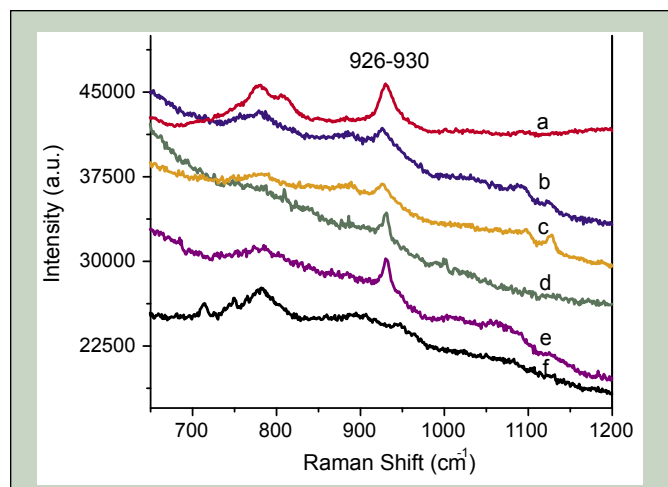
The probability of detecting  $\text{ClO}_4^-$  was higher in the presence of nanoclusters that were not too heavily clustered or isolated. Figure 3a shows strings of clusters that exhibited the SERS effect in the Ag colloid samples. Nanoclusters showing the SERS effect on the Ag-doped silica sol-gel samples were found both on the sol-gel surface and in crevices, as seen in Figure 3b. The affinity for SERS detection of molecules on Ag clusters has been observed before and may be explained by a large electromagnetic enhancement attributed to interactions between neighboring Ag particles in a fractal cluster



**Figure 3.** Functionalized Ag colloids (a) and functionalized Ag-doped silica sol-gel (b) during 50 ppb analysis under 50X objective.



**Figure 4.** Extended spectra of: (a) 50 ppb, (b) 100 ppb, (c) 500 ppb, (d) 10 ppm, (e) 100 ppm, and (f) 0 M perchlorate on functionalized Ag colloids with diameters ranging from 14-23 nm.



**Figure 5.** Extended spectra of: (a) 10 ppb, (b) 50 ppb, (c) 100 ppb, (d) 1 ppm, (e) 10 ppm, and (f) 0 M perchlorate on functionalized Ag-doped silica sol-gel films.

[4,10]. Moreover, as demonstrated by Hu et al. and Kralchevsky et al. [11, 12], no chemical was needed to induce aggregation because capillary forces present during the drying of the Ag colloid solution seemed to cause particles to aggregate.

Although some studies have cited irreproducibility of results using Ag aggregates for SERS enhancement [13], our results showed that detecting  $\text{ClO}_4^-$  on aggregated Ag colloids even at 50 ppb was reproducible in different trials. This result may be explained by previous studies that have shown Ag aggregates to absorb radiation most intensely in the near-infrared region of the electromagnetic spectrum, especially in the presence of  $\text{ClO}_4^-$  [14].

The detection of  $\text{ClO}_4^-$  was relatively homogeneous per sample until concentrations entered the part per billion range, where  $\text{ClO}_4^-$  detection only occurred on certain parts of the sample. Moreover, the Ag-doped silica sol-gel, with a more consistent Ag cluster composition, did not yield a significantly more homogeneous detection of  $\text{ClO}_4^-$  per sample than the Ag sol. Also in the ppb range, as seen for both substrates in Figures 4 and 5,  $\text{ClO}_4^-$  peak intensities did not decrease with concentration. At such low concentrations and given the  $\sim 1$  cm breadth of functionalized Ag sites available for  $\text{ClO}_4^-$  adsorption, it is likely that  $\text{ClO}_4^-$  signal intensities were more dependent on the probability of finding an SERS active,  $\text{ClO}_4^-$  adsorbed Ag cluster rather than on the number of  $\text{ClO}_4^-$  molecules present in one site.

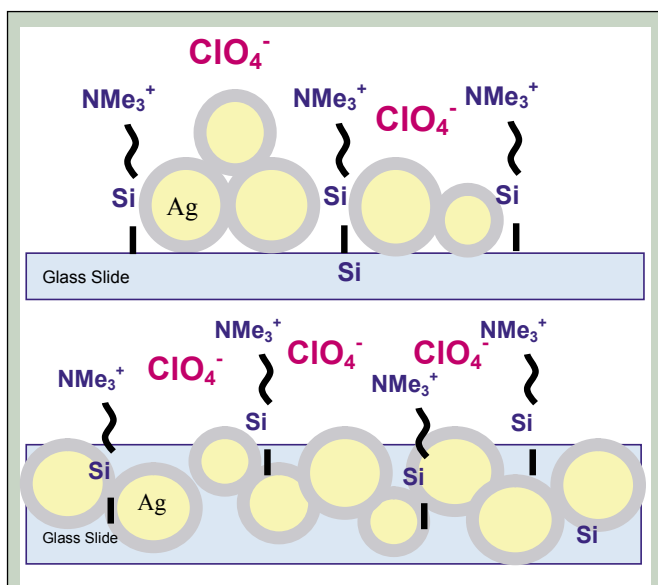
### Functional Group Enhancement

Figures 4 and 5 also show how the addition of the quaternary ammonium functional group layer allowed detection of concentrations  $10^5$  lower than on non-functionalized Ag sol particles. The application of the functional group layer, as depicted in Figure 6, was expected to have formed Si-O-Si bridges in between silver nanoparticles on the glass slide and in between silver nanoparticles embedded in the Ag-doped silica sol-gel, allowing the quaternary ammonium group to bring  $\text{ClO}_4^-$  anions into close proximity of Ag particles for SERS enhancement. Moreover, the short alkyl chains ( $\text{C}_2$ ) capped with a trimethylammonium group used in this study were sufficiently selective in adsorbing  $\text{ClO}_4^-$  molecules. Further

studies should use trihexylammonium and triethylammonium functional groups with both short ( $\text{C}_2$ ) and long ( $\text{C}_6$ ) alkyl chains to detect  $\text{ClO}_4^-$  since these groups were the primary components of the bifunctional anion-exchange resin that had previously detected  $\text{ClO}_4^-$  down to 10 ppb [7,15].

### Ag Colloid versus Ag-doped Silica Sol-Gel Enhancement

As seen in Figure 7, the Raman signals detected on Ag colloids were sharper than those detected using the Ag-doped silica sol-gel although peak intensities and integral ratios were relatively the same. This may be due to the thinner layer of nanoparticles and more isolated clusters formed when Ag colloids were applied using the drop method as opposed to Ag doping in the Bao et al. method [5]. Calculations have predicted that to achieve high enhancement



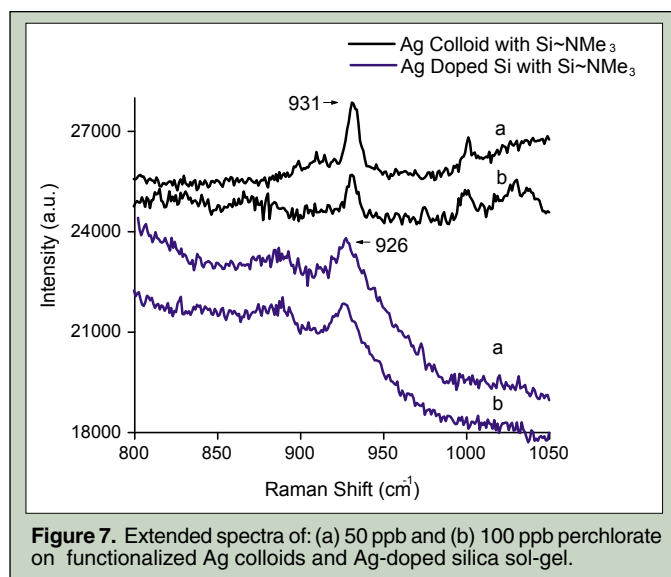
**Figure 6.** Quaternary ammonium groups adsorbing perchlorate anions on Ag colloids (top) and Ag-doped silica sol-gel films (bottom).



factors, either the average cross section per molecule must be very small or the number of SERS active molecules must be very small [16]. The Ag colloid method had a smaller density of Ag particles than the Ag-doped silica sol-gel method, which may explain why at 50 ppb, a greater enhancement is observed for the Ag colloid method.

During analysis, however, wet Ag colloid samples dried quicker than the Ag-doped silica sol-gel samples. The Ag-doped silica substrate, pictured in Figure 3b, may have concentrated  $\text{ClO}_4^-$  within its many cracks and crevices, and therefore allowed for better sensitivity in detecting  $\text{ClO}_4^-$  at 10 ppb than the Ag colloid sample. For the Ag-doped silica sol-gel, however, some  $\text{ClO}_4^-$  peaks were broader and red-shifted to  $\sim 926 \text{ cm}^{-1}$ ; this may indicate either more robust interactions with the quaternary ammonium functional group layer were occurring with the Ag-doped silica sol-gel or interactions with other molecules present in the substrate were occurring and, therefore, changing the vibrational frequency of  $\text{ClO}_4^-$ .

Future research on  $\text{ClO}_4^-$  detection using SERS of Ag colloids or Ag-doped silica sol-gels should focus on simulating real on-site analysis of surface water or groundwater samples. This work would include studying the effect of detecting  $\text{ClO}_4^-$  in the presence of competing ions such as chloride, nitrate, sulfate, carbonates, and even chlorite; improving the stability of the SERS substrate; and finding the optimal alkyl chain length and functional groups that could be used in SERS detection of  $\text{ClO}_4^-$ . Improvements in the homogeneity of detecting  $\text{ClO}_4^-$  on a given sample slide could also be made if the functionalized SERS substrate were micro-prepared at a much smaller scale, forming much fewer functionalized Ag aggregates and increasing the likelihood of  $\text{ClO}_4^-$  detection at even lower concentrations. Considering the portable Raman systems now available, the SERS approach to  $\text{ClO}_4^-$  detection may allow for the development of a probe that can be used directly at groundwater and surface water sites for *in situ* detection of significantly low concentrations of  $\text{ClO}_4^-$ .



**Figure 7.** Extended spectra of: (a) 50 ppb and (b) 100 ppb perchlorate on functionalized Ag colloids and Ag-doped silica sol-gel.

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