Detection of perchlorate using Ag/DMAH$^+$ SERS-active capture matrices

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HIGHLIGHTS

- Silver colloidal particles were immobilized on amine-derivatized magnetic microparticles.
- The silver colloid was reacted with a thiol to form a self-assembled monolayer (SAM) selective for perchlorate.
- The thiol was dimethylaminoethanethiol hydrochloride.
- The SERS response of the capture matrices were compared to that of conventional SERS substrates.
- The use of solid phase extraction (SPE) to eliminate chloride ion interference was explored.

GRAPHICAL ABSTRACT
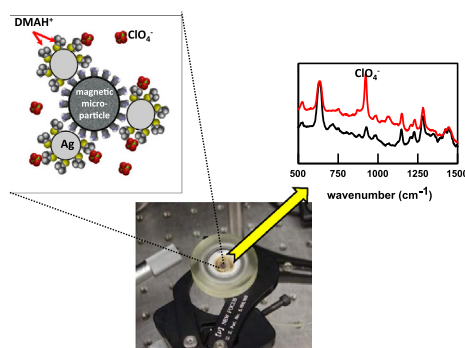
ABSTRACT

In this communication, the fabrication of SERS-active capture matrices for the detection of perchlorate is described. The amine groups of amine-modified magnetic microparticles were used to immobilize silver colloidal particles. Once immobilized, the silver was reacted with dimethylaminoethanethiol hydrochloride (DMAH$^+$Cl$^-$) to form a self-assembled monolayer (SAM). The DMAH$^+$ SAM exhibits reasonably good selectivity for perchlorate. It was shown that calibration curves could be generated by ratioing the perchlorate peak with a DMAH$^+$ peak that did not change upon interaction with the perchlorate ion. Flow experiments, using Ag/DMAH$^+$ capture matrices held in place by a magnet, showed instantaneous response to changes in perchlorate concentration. The use of solid phase extraction (SPE) to eliminate chloride ion interference was explored.

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Introduction

Perchlorate is a contaminant of environmental concern because it greatly impacts human health by interfering with iodide uptake into the thyroid gland [1]. In adults, the thyroid gland helps regulate the metabolism by releasing hormones, while in children, the thyroid helps in proper development [1]. Perchlorate has been used as the oxidizer component and primary ingredient in solid propellant for rockets and missiles [2,3]. Perchlorate is also present in several fertilizers and fertilizer components at levels up to 0.84% [4]. Consequently fertilizers could be a source for perchlorate accumulation in the food chain. Because perchlorate is highly soluble and non-reactive with soil sediments, it is exceedingly mobile in aqueous systems and can persist for many decades under typical ground and surface water conditions. Besides surface and groundwater, perchlorate has been found in food crops, such as lettuce in the southwestern states of the U.S. [5]. The uptake of perchlorate by food crops is attributed to irrigation using perchlorate contaminated water from the Colorado River. In 2003, perchlorate

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was detected in milk samples from Lubbock. TX [6]. The source of this perchlorate was attributed to perchlorate-contaminated alfalfa fed to dairy cows.

Currently monitoring of perchlorate is done by conventional soil and water sampling followed by laboratory analysis using ion chromatography (IC). Of the IC methods developed for perchlorate detection, EPA methods 6850 [7] and 6860 [8] that use IC–MS are preferred because of the specificity of mass spectrometry (MS) in identifying perchlorate in complex sample matrices. The IC methods of monitoring are time consuming, require sample preparation, and are not field deployable.

For long term monitoring purposes, it would be desirable to detect perchlorate in samples on-site and in near real time. Such a capability would minimize sample handling, processing, and overall costs. It would also be desirable to detect perchlorate in the low ppb concentration range with little or no sample preparation and with no interferences. One technology that meets many of these criteria is SERS using chemically modified silver/gold substrates. In the SERS methodology, coatings on the SERS substrate are chosen to attract the analyte of interest. The advantages of SERS using chemically derivatized substrates over other techniques are:

(i) All polyatomic species exhibit a characteristic SERS spectrum.
(ii) The SERS spectral lines are narrow allowing simultaneous detection of multiple polyatomic species.
(iii) Depending upon the dimensions of the nanostructures comprising the substrates, SERS can result in a 10^5–10^{10} enhancement of the Raman signal.
(iv) Water is a very poor Raman scatterer and does not interfere.
(v) The selective coating also exhibits SERS lines that can be used as an internal standard.

The main limitation of the SERS technology has to do with the coating itself. The sensitivity of SERS to detect the desired analyte is dependent upon the selectivity of the coating for that analyte. However, there is a trade-off between selectivity and reversibility. The stronger the interaction between an analyte and a coating, the greater the selectivity of the coating for that analyte and the greater the sensitivity. However, reversibility is often sacrificed. The only practical way around this trade-off is to provide a fresh SERS-active surface between sampling. To address these issues and provide a fresh SERS surface between analyses, we developed SERS-active capture matrices prepared by immobilizing gold/silver colloidal particles on amine-derivatized magnetic microspheres [9]. Afterwards, the immobilized colloidal particles are reacted with a thiol to form a self-assembled monolayer (SAM). To date, the detection of naphthalene [9] using pentachlorothiophenol-derivatized, SERS-active capture matrices and hexavalent chromium [10] using 4-(2-mercaptothyl)pyridinium derivatized, SERS-active capture matrices have been demonstrated. Besides providing a fresh SERS surface between sampling, additional advantages of capture matrices in chemical detection are extraction/concentration of the target analyte from a complex sample matrix, ease of separation, and suitability for automation. In fact the use of derivatized magnetic microparticles for trace chemical analysis is growing [11]. Magnetic particles possess a high surface area which can exhibit higher adsorption capacity for analytes. They also exhibit strong superparamagnetic properties which meets the need of rapid extraction of large volume samples by employing a strong external magnetic field. These derivatized magnetic microparticles can be used in both solutions and suspensions. Since the majority of accompanying impurities in a suspension are diamagnetic, they do not interfere with magnetic particles during the magnetic separation step.

In order to detect perchlorate using SERS-active capture matrices, a coating selective for perchlorate needs to be identified.

Earlier Gu et al. [12] demonstrated the use of 2-dimethylaminoethanethiol hydrochloride (DMAH$^+$Cl$^-$) modified gold nanoparticles to detect perchlorate by SERS in both simulated and contaminated groundwater samples. Using these DMAH$^+$ derivatized-Au nanoparticles, they were able to detect concentrations of perchlorate as low as 0.1 μg/L (or 0.1 ppb). They reported that the presence of higher concentrations of background ionic species (nitrate, sulfate, phosphate, and chloride) did not impact the quantitative analysis of perchlorate. The perchlorate analysis cartridges developed by OndaVia use dimethylaminoethanethiol hydrochloride as the perchlorate selective coating. These cartridges were found it to work pretty well, at least to ~100 ppb, in pH-adjusted (2.5) northern California ground water samples that have (at least) nitrate and sulfate [13]. The interaction of anions with conventional Ag/DMAH$^+$ SERS substrates was reported [14]. It was shown that, when the anion concentration is in M, the measured response of the anion with the DMAH$^+$ coating was described by a Frumkin isotherm. The shape of the Frumkin isotherm was determined by two parameters – K, the ion-pair constant between the anion and the coating, and g, the Frumkin parameter that takes into account interactions between adsorbed species. The values for K and g obtained for the DMAH$^+$ coating and anions are tabulated in Table 1. The results in Table 1 indicate that the coating does interact with nitrate, sulfate, and chloride in addition to perchlorate. Mixtures of anions were not examined in this investigation.

Given the results of Gu et al. [12] and OndaVia [13], DMAH$^+$ was chosen to be the perchlorate selective coating. In this communication, we describe the fabrication of SERS-active Ag/DMAH$^+$ capture matrices and discuss their use to detect perchlorate.

Experimental section

Reagents

Silver nitrate (Aldrich), sodium citrate dihydrate (Aldrich), sodium perchlorate (Aldrich), sodium nitrate (Johnson Mathey), sodium sulfate (Aldrich), sodium chloride (Aldrich), potassium chloride (Aldrich), dimethylaminoethanethiol hydrochloride (DMAH$^+$, Aldrich), water (HPLC grade, Aldrich), and ethanol (HPLC grade, Aldrich) were used as received. Aqueous solutions of perchlorate were prepared using deionized water.

A 0.5 mL aliquot of 5 μm diameter, amine-terminated, silica-coated iron oxide microparticles (Bioclone, part no. FA-104) was washed ten times with 1 mL aliquots of HPLC water to remove surfactant. Between washes, a NdFeB magnet is used to separate the magnetic microparticles from the water. After the washes, the volume of the amine-terminated, magnetic microparticles was adjusted to 1.0 mL.

Preparation of conventional Ag/MEP SERS substrates

An insulated copper wire was soldered to a 0.75-cm length of 2 mm diameter silver wire (Aldrich, 99.9%). The silver wire was potted inside a 5-mm outer diameter, borosilicate glass tube using

Table 1
Ion pair constants and Frumkin parameters measured for Ag/DMAH$^+$ interactions with anions [14].

Anion	Ion pair constant (M)	Frumkin parameter
Perchlorate	404 ± 59	−0.64 ± 0.21
Nitrate	301 ± 78	−2.3 ± 1.1
Sulfate	972 ± 85	−1.14 ± 0.13
Chloride	310 ± 180	−2.3 ± 1.1
Hydrogen phosphate	No interaction	No interaction
Dihydrogen phosphate	No interaction	No interaction