

Detecting hydrolysis products of blister agents in water by surface-enhanced Raman spectroscopy

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ABSTRACT

Protecting the nation's drinking water from terrorism, requires microg/L detection of chemical agents and their hydrolysis products in less than 10 minutes. In an effort to aid military personnel and the public at large, we have been investigating the ability of surface-enhanced Raman spectroscopy (SERS) to detect microgram per liter (part-per-billion) concentrations of chemical agents in water. It is equally important to detect and distinguish the hydrolysis products of these agents to eliminate false-positive responses and evaluate the extent of an attack. Previously, we reported the SER spectra of GA, GB, VX and most of their hydrolysis products. Here we extend these studies to include the chemical agent sulfur-mustard, also known as HD, and its principle hydrolysis product thiodiglycol. We also report initial continuous measurements of thiodiglycol flowing through a SERS-active capillary.

Keywords: chemical warfare agent detection, CWA, hydrolysis, SERS, Raman spectroscopy

1. INTRODUCTION

The July 2005 terrorist bombings of the London transit system are a stark reminder that such attacks on the United Kingdom and the United States will continue. Countering such attacks requires recognizing likely deployment scenarios and having the required technology to rapidly detect the deployment event. In addition to the expected use of chemical agents released into the air, terrorists may also poison water supplies with chemical warfare agents (CWAs). The National Strategy for Homeland Security designates the Environmental Protection Agency with the task of securing the nations drinking water.¹ Presently, the EPA employs several field test kits to monitor drinking water supplies, and gas chromatography coupled with mass spectrometry in supporting laboratories to confirm positive responses.² Unfortunately, these test kits are prone to false-positive responses, and follow-up analysis typically takes a day. This is entirely inadequate for the prevention of widespread illness and potential fatalities.

In the past several years we have been investigating the use of surface-enhanced Raman spectroscopy (SERS) to be used as a field-usable analyzer that can detect chemical agents in water at the required microg/L sensitivity and 10 minute timeframe.^{3,4,5,6,7} The expected success of SERS is based on the million-fold or more Raman signal increase obtained when a molecule interacts with surface plasmon modes of metal nanoparticles.⁸ In the case of cyanide, an industrial-based CWA and methyl phosphonic acid, the final hydrolysis product for the nerve agents, we have measured at or below 10 microg/L in one minute.⁹ The expected success of SERS is also based on the unique set of Raman spectral peaks associated with the molecular vibrational modes of each molecule. The unique SER spectra should not only reduce false-positive responses, but also allow discriminating hydrolysis products of CWAs. This is important, since CWAs can hydrolyze rapidly in the presence of water,¹⁰ and detection of the hydrolysis products could allow determining 1) the state of an attack (ratio of CWA to hydrolysis product(s)), 2) the point of attack initiation, and 3) the continued extent and severity of the CWA attack throughout a water distribution system.

Previously, we used SERS to measure sarin, tabun, VX, and EA2192, and their respective hydrolysis products.^{3,4,6,7} Here we extend these studies to include the chemical warfare agent sulfur-mustard, designated HD, and its primary hydrolysis product thiodiglycol (TDG, Figure 1). The physical and chemical properties of this blister agent are well known. It's solubility in water is 0.92 g/L with a hydrolysis half-life of 8.5 min (both at 25 C).¹⁰ HD has an oral LD₅₀ of 0.7 mg/kg in humans,¹¹ and the military drinking water guideline places the 5-day 5L limit at 100 microg/L.¹² TDG is relatively non-toxic, very water soluble at 690 g/L, and stable in water with a hydrolysis half-life of approximately 6 days. Accordingly, a reasonable sensitivity goal to ensure safe water is placed at 10 microg/L for HD and an equivalent goal to map HD usage is placed at 10 microg/L for TDG.¹³

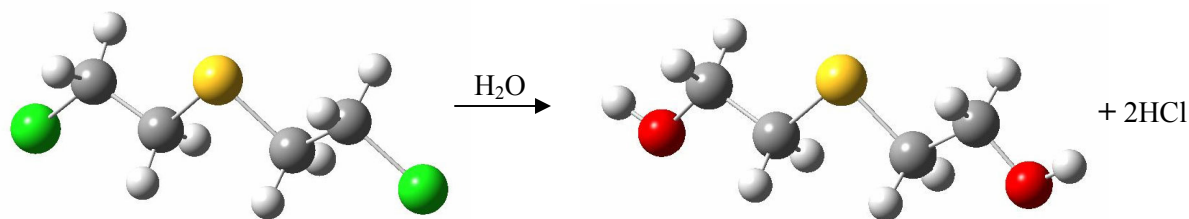


Figure 1. Hydrolysis of bis(2-chloroethyl)sulfide (HD) to bis(2-hydroxyethyl)sulfide (TDG).

2. EXPERIMENTAL

Highly distilled sulfur mustard, designated HD (bis(2-chloroethyl)sulfide), was measured at the U.S. Army's Edgewood Chemical Biological Center (Aberdeen, MD). Thiodiglycol, designated TDG here (bis(2-hydroxyethyl)sulfide), was purchased as an analytical reference material from Cerilliant (Round Rock, TX). TDG was measured at Real-Time Analyzers, Inc. (RTA, Middletown, CT). All solvents, including methanol, ethanol, and HPLC water, as well as all sol-gel precursor chemicals including AgNO_3 , tetramethyl orthosilicate, methyltrimethoxysilane, HNO_3 and NaBH_4 , were purchased from Sigma-Aldrich (St. Louis, MO). HD samples prepared for SERS analysis consisted of 0.1% v/v HD in methanol. The methanol was used to minimize hydrolysis. The final concentration is 1000 parts-per-million (ppm, EPA definition). TDG samples were prepared for SERS analysis using methanol for static measurements and HPLC grade water for flow measurements. All HD measurements were performed in SERS-active vials (*Simple SERS Sample Vials*, RTA),¹⁴ while all TDG measurements were performed in SERS-active capillaries (1-mm diameter glass capillaries filled with silver-doped sol-gels).^{15,16} In the case of flow measurements, a peristaltic pump (variable flow mini-pump, Control Co., Friendswood, TX) was used to flow the 1 and 10 ppm TDG samples through a SERS-active capillary at 1 mL per min.

The vials or capillaries were mounted horizontally on an XY positioning stage (Conix Research, Springfield, OR), such that the focal point of an $f/0.7$ aspheric lens was positioned just inside the glass wall. The probe optics and fiber optic interface have been described previously.¹⁶ In all cases a 785 nm diode laser was used to deliver ~ 100 mW of power to the SERS samples and 300 mW to the Raman samples. A Fourier transform Raman spectrometer equipped with a silicon photo-avalanche detector (RTA, model *IRA-785*), was used to collect both the RS and SERS at 8 cm^{-1} resolution.

3. RESULTS AND DISCUSSION

The surface-enhanced and normal Raman spectra of HD have been measured and are shown in Figure 2. The SER spectrum is dominated by a peak at 630 cm^{-1} with an extended high frequency shoulder composed of two or more peaks ($695, 830\text{ cm}^{-1}$), as well as a moderately intense peak at 1045 cm^{-1} . It is possible to assign these peaks based on the normal Raman spectrum of HD, and previous assignments.¹⁷ Theoretical studies assigned the $640, 655, 700\text{ cm}^{-1}$ peaks to C-Cl stretching modes and the $740, 760\text{ cm}^{-1}$ peaks to C-S stretching modes. Additional peaks are observed at $1040, 1190, 1270, 1295, 1410, 1425, 1440\text{ cm}^{-1}$. The first peak is assigned to a C-C stretch, while the remaining peaks are all CH_2 deformation modes (scissors, twists, and wags). Based on these assignments, then only the C-Cl peak maintains significant intensity in the SER spectrum occurring at 630 cm^{-1} . If the C-Cl assignments are correct, then the SER spectra suggest that the molecule to metal interaction is strongest through the chlorine end groups. Alternatively, the electron lone pairs of the tetrahedrally coordinated sulfur of HD could interact with the silver surface. Consequently, the 630 cm^{-1} SERS peak could be assigned to CS or CSC stretching modes (see below).¹⁸

The surface-enhanced and normal Raman spectra of TDG have been measured and are shown in Figure 3. The SER spectrum is dominated by three peaks at $630, 715, 1010\text{ cm}^{-1}$ with minor peaks at $400, 820, 930, 1210, 1275, 1410, 1460\text{ cm}^{-1}$. Similarly, the Raman spectrum contains two intense peaks at 660 and 1010 cm^{-1} , while moderately intense peaks occur at $400, 680$ (shoulder), $735, 770, 830, 950, 1040, 1230, 1290, 1420, 1465\text{ cm}^{-1}$. In both spectra, the assignment of the peaks near 1000 cm^{-1} can be confidently assigned to C-C stretching modes, while the peaks from 1200 to 1465 cm^{-1} can be confidently assigned to various CH_2 deformation modes. Here, however, it is difficult to assign the 630 cm^{-1} SERS peak to a C-Cl mode, since the chlorines have been replaced by hydroxyl groups.

Consequently, in the case of HD and TDG, assigning the 630 cm^{-1} peak to a CS or a CSC stretch, is favored. Although the $620\text{-}680\text{ cm}^{-1}$ peaks are normally assigned to C-Cl modes, and the $700\text{-}750\text{ cm}^{-1}$ peaks to CS modes, most authors concede that the reverse assignments are possible.

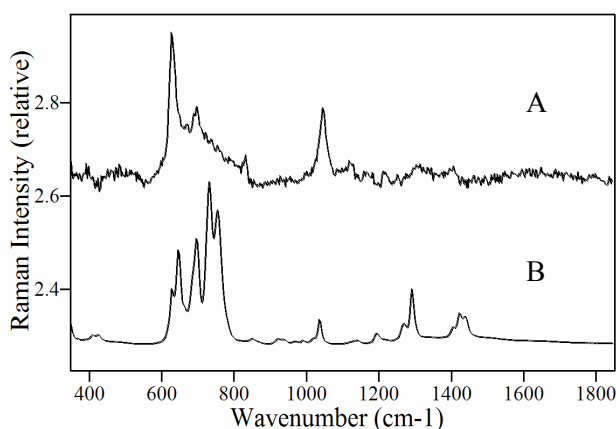


Figure 2. A) SERS and B) RS of **HD**. A) 0.1% v/v (1000 ppm) in MeOH in a SERS-active vial, 100 mW of 785 nm, 1-min, B) neat sol. in glass container, 300 mW of 785 nm, 5-min.

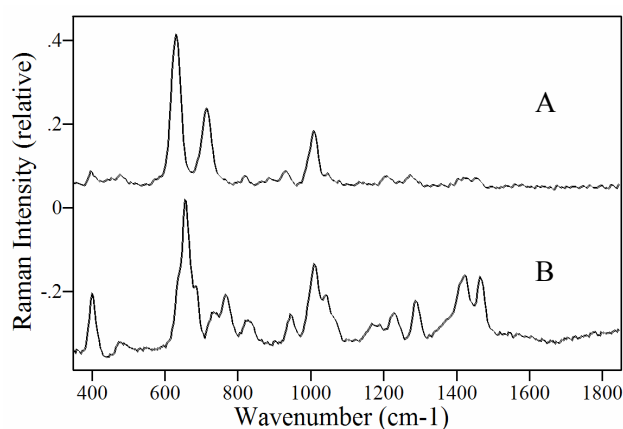


Figure 3. A) SERS and B) RS of **TDG**. A) 0.1% v/v in MeOH in SERS-active capillary, 100 mW of 785 nm, 1-min, B) neat sol. in glass capillary, 300 mW of 785 nm, 5-min.

Of possibly greater importance, is that the TDG SER spectrum is of high quality, with three distinct peaks. With the goal of detecting this hydrolysis product of HD in water, a number of samples of decreasing concentration were prepared and measured. As Figure 4 shows, these peaks are evident even at 10 ppm (0.001% v/v in methanol). However, repeated measurements of 1 ppm did not yield any discernable peaks (lowest trace in Figure 4). Notwithstanding, measurements were also performed in a flowing stream. Initial measurements of a 10 ppm sample yielded quality spectra and prompted measurements of a 1 ppm sample. As Figure 5 shows, reasonable spectra are obtained, even at 1 minute resolution. It is worth stating that the 630 cm^{-1} peak was evident in all spectra collected over a 12 minute period. There is an important difference between the TDG spectra recorded for static and flowing samples, namely that the 715 cm^{-1} peak is noticeably more intense in the static sample. This suggests that it may represent a photo-degradation product. Further studies are required to clarify this point.

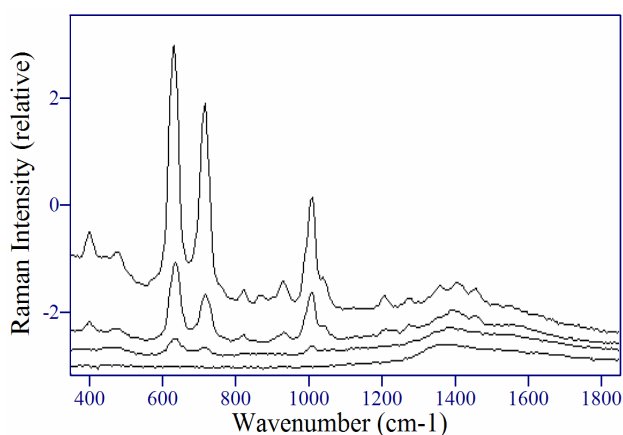


Figure 4. SERS of 1000, 100, 10 and 1 ppm TDG in water (top to bottom). All in SERS-active capillaries, 100 mW of 785 nm, 1-min.

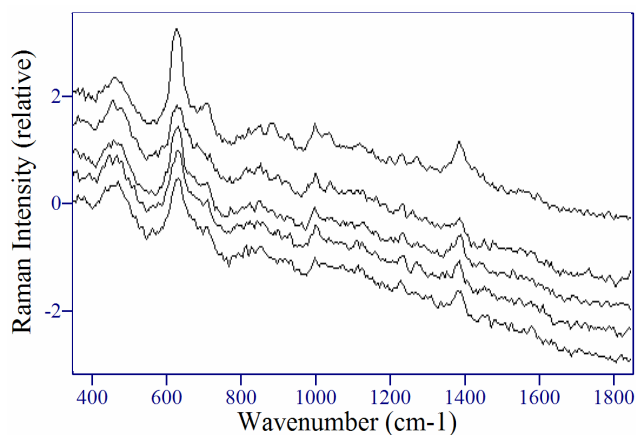


Figure 5. SERS of 1 ppm TDG in water flowing through a SERS-active capillary at 1, 2, 3, 4, and 5 min. (top to bottom), 100 mW of 785 nm, 1-min each.

4. CONCLUSIONS

The ability to measure and distinguish HD and TDG using SERS-active capillaries has been demonstrated. Specifically, the peak at 715 cm^{-1} is unique to TDG, as both chemicals produce an intense SERS peak at 630 cm^{-1} . The latter peak is likely due to CS or CSC stretching modes favorably enhanced by the interaction of the sulfur lone electron pairs to silver surface. Measurements of similar chemicals, such as diethylsulfide, are ongoing to clarify this assignment. Detection of TDG at 1 mg/L in 1 minute in a flowing system suggests that the goal of 10 microg/L in 10 minutes is possible. Improvements in the enhancement achieved by the SERS-active capillaries, as well as their durability, are the focus of current research and product development.

5. ACKNOWLEDGMENTS

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