

Detection of Chemical Warfare Simulants Using Raman Excitation at 1064 nm

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ABSTRACT

Raman spectroscopy is a powerful technique for material identification. The technique is sensitive to primary and higher ordered molecular structure and can be used to identify unknown materials by comparison with spectral reference libraries. Additionally, miniaturization of opto-electronic components has permitted development of portable Raman analyzers that are field deployable. Raman scattering is a relatively weak effect compared to a competing phenomenon, fluorescence. Even a moderate amount of fluorescence background interference can easily prevent identification of unknown materials. A long wavelength Raman system is less likely to induce fluorescence from a wider variety of materials than a higher energy visible laser system.

Compounds such as methyl salicylate (MS), diethyl malonate (DEM), and dimethyl methylphosphonate (DMMP) are used as chemical warfare agent (CWA) simulants for development of analytical detection strategies. Field detection of these simulants however poses unique challenges because threat identification must be made quickly without the turnaround time usually required for a laboratory based analysis. Fortunately, these CWA simulants are good Raman scatterers, and field based detection using portable Raman instruments is promising. Measurements of the CWA simulants were done using a 1064 nm based portable Raman spectrometer. The longer wavelength excitation laser was chosen relative to a visible based laser systems because the 1064 nm based spectrometer is less likely to induce fluorescence and more suitable to a wider range of materials. To more closely mimic real world measurement situations, different sample presentations were investigated.

Keywords: Raman, chemical warfare agents, simulants, dimethyl methylphosphonate, methyl salicylate, diethyl malonate

1. INTRODUCTION

The threat of chemical warfare is a persistent concern. Military and security personnel require the ability to rapidly identify CWA's in the field with high specificity and as samples are expected to be found in real world situations. Raman spectroscopy has a very high degree of chemical specificity since the peaks of a Raman spectrum are caused by molecular structure. This chemical specificity along with the advantages that Raman requires little or no sample preparation is non-contact and non-destructive make Raman ideal for chemical identification. More recent advances in opto-electronics [1] have enabled the development of small and portable Raman spectrometers which allow for rapid chemical identification in the field.

Another optical phenomenon that commonly competes with Raman is fluorescence. When present fluorescence has orders of magnitude higher intensity than Raman scattering and can easily obscure Raman signal. Fluorescence lacks the chemical specificity of Raman and its presence inhibits chemical identification. Fewer materials fluoresce at longer excitation wavelengths than at shorter ones, allowing longer excitation wavelengths, like 1064 nm, to analyze a wider array of materials. [2] When considering methods for CWA identification it is desirable to analyze the widest possible array of materials and on a wide variety of different substrates or sample presentations. Since the longer excitation wavelengths reduce fluorescence allowing for analysis of more different samples on more different substrates a portable Raman spectrometer with 1064 nm excitation was used for these studies.

This study investigates the feasibility of a portable 1064 nm based Raman system for field deployment and quick identification of chemical warfare agents. Three different CWA simulants were used in this study; methyl salicylate (MS) which is a simulant for sulfur mustard and soman, diethyl malonate (DEM) which is a simulant for soman, and dimethyl methylphosphonate (DMMP) which is a common simulant for sarin. [3-5] CWA simulants were investigated

using a number of sample presentations; as neat liquids to obtain high quality standard Raman spectra for comparison with other sample presentations, as 2 μ l drops to simulate an airburst attack scenario and in the presence of various decontaminating agents.

2. EXPERIMENTAL

2.1 Chemicals and Materials

Dimethyl methylphosphonate (DMMP), methyl salicylate (MS), and diethyl malonate (DEM), were purchased from Sigma-Aldrich Company. Aluminum foil, Clorox[®] bleach (8% sodium hypochlorite), Dawn-Ultra[®] dishwashing liquid, antifreeze, and 5W-30 engine oil were household materials obtained off the shelf from retail stores. The Dawn dishwashing liquid was not diluted before use but was added to the simulants in the concentrated form. The steel coupon with "Haze Gray" paint was a gift from Naval Surface Warfare Center (NSWC), Dahlgren, VA.

2.2 Sample Preparation

CWA simulants were applied to substrate surfaces (aluminum and painted steel coupon) using a micropipette. Droplets had an approximate volume of 2 μ l to simulate droplets that deposit as a result of an air burst. Decontaminating agents were added to the simulants and allowed to sit for approximately 10 minutes before making measurements. Substrates were held in a microscope stage while spectra of individual droplets were collected. Spectra of neat CWA simulants were also measured in glass vials for comparison.

2.3 Instrumentation

All spectra were collected using a Rigaku Raman Technologies, Xantus-2TM spectrometer equipped with Micro 2020 software and a 1064 nm laser for Raman excitation. During data collection the Xantus-2TM was secured in a vertical position over the substrates being measured. Excitation laser power is adjustable from 30 to 490 mW and all spectra collected used exposure times of less than one minute.

3. RESULTS AND DISCUSSIONS

Identification with Raman spectroscopy is typically done by comparison of the spectrum of an unknown to that of known, or standard, spectra. These collections of standard spectra are often referred to as libraries of spectra. For this investigation of CWA simulants, initial measurements were done on the pure simulants as liquids in glass vials using a 1064 nm excitation portable Raman spectrometer. When materials are measured in order to create a library they are most often measured as the pure material. Important considerations for library spectra are good signal-to-noise and spectra which are unique from those of other materials in the library. These materials have strong enough Raman signals that spectra with good signal to noise ratios, such as are appropriate for library creation, were obtained. The measured spectra are very clearly unique from each other and the harmless control materials investigated as they will be from most, if not all other Raman spectra.

Once clear standard (or library) Raman spectra are established it is then appropriate to investigate sample presentations that are operationally relevant. In order to simulate an air burst CWA attack, 2 μ l drops of each simulant were deposited on an aluminum substrate. These drops were then measured with the portable Raman spectrometer, using laser exposure times of less than one minute. Figure 1 shows spectra of DMMP and MS, both as neat agent in vials, and as 2 μ l drops on aluminum. As can be seen in the Figure, simulated air burst spectra are nearly identical to the spectra collected from pure simulants in glass vials. The similarity between these spectra allows for the materials in the simulated air burst to be positively identified by searching a library of known materials.

For this investigation a library was built using the pure simulants measured in glass vials and the spectra measured from the 2 μ l drops on aluminum were compared to these standard (or library) spectra using a correlation algorithm. This comparison was done on the portable Raman spectrometer and an identification of the simulants could be obtained in less than a minute. The correlation algorithm reports the name of the identified material. This identification is based on a hit quality index (HQI) which is a measure of how similar the measured spectrum is to the library spectrum. HQI values range from 0, no similarity, to 100, identical spectra. The HQI values for the simulated airburst spectra of DMMP and MS on aluminum are respectively 97.8 and 96.2 when compared to library spectra collected using pure substances in glass vials. The high HQI values indicate a positive identification of the CWA simulants in the air burst presentation.

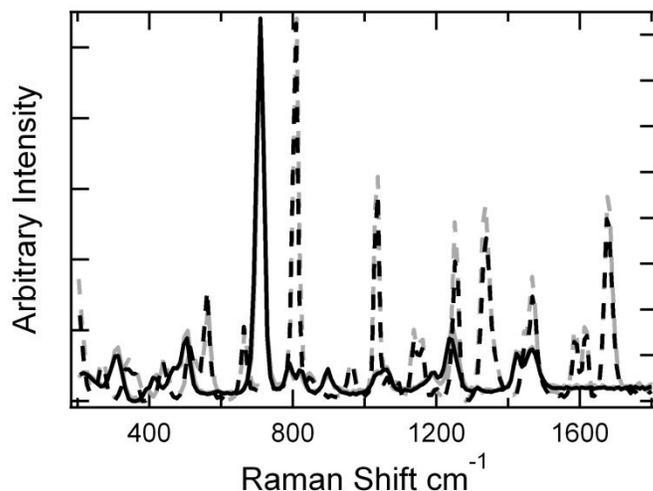


Figure 1. 1064 nm Raman spectra showing comparison of two CWA simulants measured in glass vials and as 2 μl drops on aluminum foil. Gray spectra are measured in vials and black on aluminum. DMMP is shown as the solid lines and MS as the dotted lines.

Raman spectroscopy's high degree of chemical specificity can easily distinguish between potential threats and harmless substances. To demonstrate this point in a simulated air burst situation two benign materials commonly found in the field, anti-freeze and engine oil, were also measured as 2 μl drops. Figure 2 shows the Raman spectra of four different materials measured from 2 μl drops on an aluminum substrate, the fifth spectrum was omitted from the graph for clarity. All five materials have distinct Raman spectra and the materials can easily be identified as CWA simulants or harmless materials.

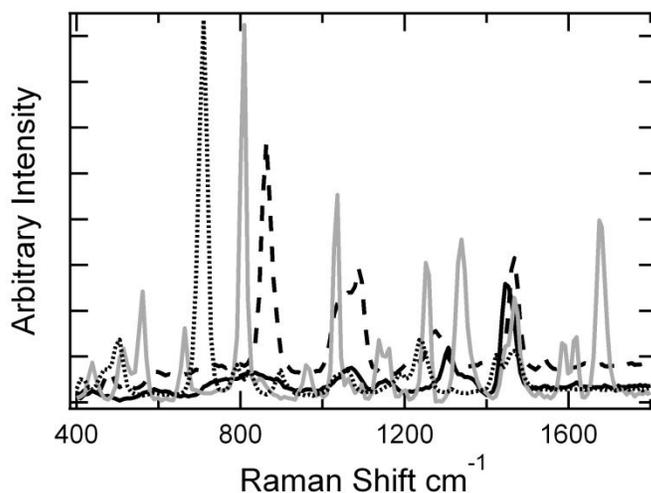


Figure 2. 1064 nm Raman spectra of two CWA simulants and two harmless control substances measured as 2 μl drops on aluminum surface. Gray spectrum is MS, dotted spectrum is DMMP, dashed spectrum is anti-freeze, and solid spectrum is engine oil.

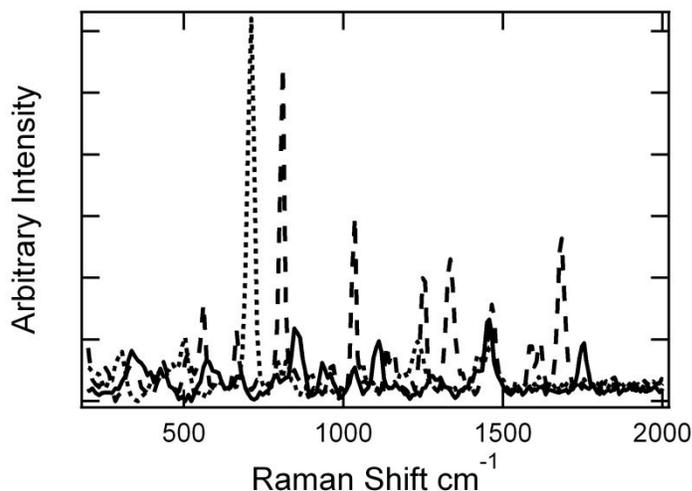


Figure 3. 1064 nm Raman spectra of three CWA simulants measured as 2 μ l drops on a stainless steel coupon painted gray. Dotted spectrum is DMMP, dashed spectrum is MS, and solid spectrum is DEM.

To further simulate a challenging real world situation Raman spectra were measured of CWA simulants on a steel coupon with “Haze Gray” paint such as what might be found on a battleship. The substrate was used to mimic real life conditions by simulating an actual chemical warfare attack. Figure 3 shows 1064 nm excitation Raman spectra of 2 μ l drops of DMMP, MS, and DEM measured on the gray painted coupon using exposure times of less than one minute. These spectra are clearly distinguishable from each other and are quite similar to the spectra of the same simulant measured in glass vials indicating that the measured Raman spectra are from the simulants not the substrate. When a correlation analysis, as described above, was performed with the spectra measured on the gray painted coupon all three materials were correctly identified and the HQI values were all above 90, indicating a high confidence for correct identification.

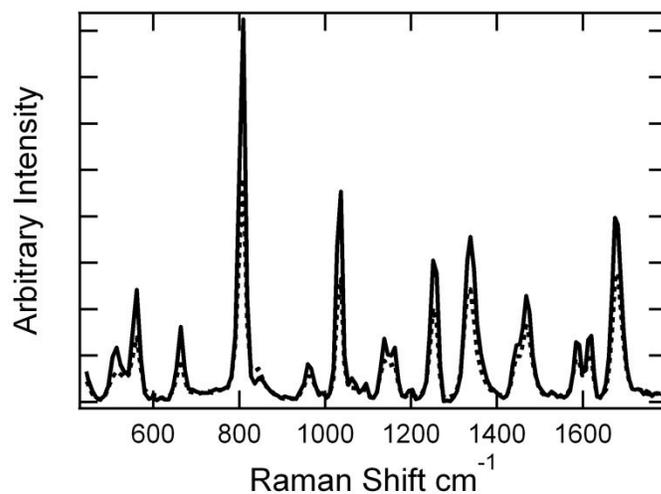


Figure 4. 1064 nm Raman spectra of 2 μ l drops of MS measured on aluminum substrate before the addition of the decontaminant bleach (solid spectrum) and after the addition of bleach (dotted spectrum).

Identifying CWAs in the field is critically important and as discussed above portable Raman is applicable to this task. Once CWAs are identified (or even if there is a potential presence of CWAs) decontamination becomes the next step and again field measurements are imperative. For this reason portable 1064 nm Raman was investigated for the measurement of the CWA simulants in the presence of two common decontaminating agents, Clorox bleach (8% sodium hypochlorite) and Dawn dishwashing liquid (concentrated form). [6-7] Again to make the measurements more similar to what might be encountered in a real world decontamination situation, 2 μ l drops of

the decontaminating agents were added to 2 μl drops of the CWA simulants on an aluminum substrate and allowed to sit for about 10 minutes before measuring. Figure 4 shows the spectra of a drop of MS on aluminum measured before and after the addition of Clorox bleach. As can be seen the spectra are very similar and the MS can still be identified in the presence of the bleach. Figure 5 shows MS measured by itself and after the addition of a 2 μl drop of Dawn dishwashing liquid. When concentrated Dawn is used as the decontaminating agent the spectral contribution from the decontaminate is much more noticeable than with the bleach. The solid spectrum in Figure 5 is MS by itself and the dotted spectrum is after the addition of Dawn. The additional peaks seen in the dotted spectrum at approximately 1060, 1305 and 1450 cm^{-1} are also seen in a spectrum of pure Dawn and are due to the addition of the decontaminate. Even though the spectra are not identical after adding the Dawn all the Raman peaks of the MS are still present and it is still possible to determine that MS is present by looking for peak positions that are representative of MS using the peak picking routine on the instrument. Identification of MS with a correlation algorithm becomes less accurate when additional peaks from another material are present and the use of different mathematical algorithms appropriate for mixture analysis would improve this accuracy. DMMP was also tested in the presence of bleach and Dawn and gave similar results to the MS, data not shown.

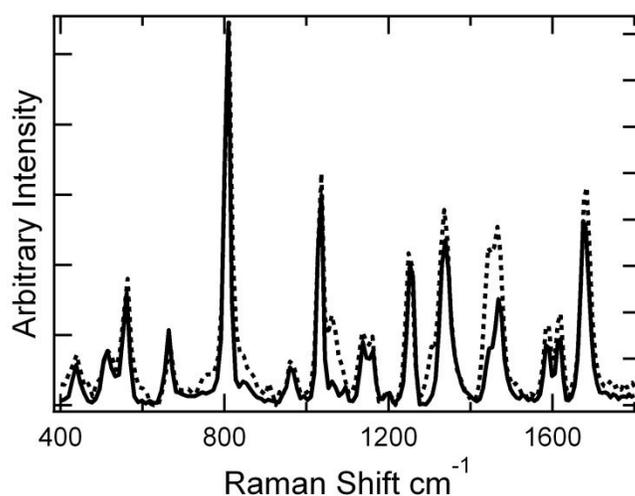


Figure 5. 1064 nm Raman spectra of 2 μl drop of MS measured on aluminum substrate before the addition of the decontaminate Dawn dishwashing liquid (solid spectrum) and after the addition of Dawn (dotted spectrum).

4. CONCLUSIONS

In conclusion portable 1064 nm Raman has demonstrated potential to identify CWAs in the field, under operationally relevant conditions. High quality Raman spectra are measurable from common CWA simulants and these spectra are easily distinguishable from one another and the non-hazardous controls investigated, as they will be from a majority of other materials. When these CWA simulants and non-hazardous controls were applied to aluminum and painted gray coupon substrates in 2 μl drops to mimic a chemical air burst attack, clear Raman spectra are still measureable. These clear Raman spectra allow for the quick identification of the CWA simulants and non-hazardous controls using the correlation algorithm available on the portable Raman spectrometer. Raman spectra from CWA simulants measured in the presence of decontaminating agents still show the peaks of the simulants although in the case of the Dawn dishwashing liquid additional peaks from the decontaminate are also seen. When additional peaks from the decontaminate are present it becomes more difficult for the correlation algorithm to positively identify the CWA simulant. Future studies will investigate mathematical approaches to mixture analysis which would improve identification in the presence of multiple materials.

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