

APPLICATION SUMMARY Chemical Warfare Agent Detection using SERS

Introduction

While the first Gulf War and the Sarin attacks in the Tokyo subway, governments established a need for faster, precise field sensors for detection of chemical warfare agents, a need heightened with increased public awareness in the post 9/11 era. Chemical warfare agents occur in three classes: blood, blister and nerve agents. In addition, toxic industrial chemicals hold potential as terrorist weapons and need to be detected. These agents can be similar to commonly employed chemicals; e.g. pesticides can be mistaken for nerve agents.



Comparison of SERS and bulk Raman data.

EIC Laboratories, Inc. has been developing Surface-Enhanced Raman Spectroscopy (SERS) as a potential multi-analyte sensor for Homeland Defense. In SERS, the enhanced Raman scattering is simply a result of an analyte adsorbing to a SERSactive surface, normally silver, copper, or gold. In SERS, it is the surface absorption band, or surface plasmon associated with the metal surface, that is in resonance with the laser and generates the enhanced Raman signals. The analyte that adsorbs in the interaction region is perturbated, leading to enhanced spectral features. Since SERS is a direct measure of the analyte's bonding structure, unique spectral signatures are collected and false positives are minimized. SERS is also relatively environmentally immune; the technique works equally efficiently in water or in air (humidity independent). The multi-environmental multi-analyte capability of SERS is ideal for Homeland Defense. The SERS sensor maintains a constant background over a wide temperature range. Moreover, SERS requires no sample

pretreatment and operates by a fast-response mechanism with spectral acquisition seldom requiring more than 30 s. EIC is currently using SERS to develop the Joint Service Agent Water Monitor (JSAWM). SERS sensitivity has already allowed program goals to be met for the majority of the threats identified by the military.

Fiber Optic Probe

A custom fiber optic probe, based upon a commercial design, was developed for this application. The fiber optic Raman probe uses lenses and filters to optimize light collection only from the analyte of interest. An adaptor plate holds the SERS substrate at the probe focal length. An immersion sleeve



protects the delicate optics from water damage while the SERS adaptor plate allows flow to the sample.

Results and Discussion

Detection of Cyanide

EIC can detect cyanide to low ppb concentrations in military grade tap water, well below permissible exposure limits.



Detection of Blister Agents

Testing of SERS for blister agents has occurred using the simulant 2-chloroethyl ethylsulfide, or half mustard. A characteristic SERS spectrum at 50 ppb conection can be collected in only 30 s. This chemical can be detected at a level desired by the military.



Nerve Agent Degradation Products

Nerve agents hydrolyze in water with phosphonic acids being key degradation components. The ability to detect the degradation products is critical as some of the degradation products are toxic. In addition, an accurate description of the degradation products in the supply will allow prediction of the time the warfare agent contaminated the water supply. The ability to detect PMPA, a Soman degradation product is shown below.



Evaluation against Actual Agents

A complete EIC SERS analyzer is at Edgewood Army Depot and is currently being used for analysis of chemical warfare agents. The cyanide results have been reproduced and detection of mustard, VX and EA2192 has been shown. Some of this Edgewood data has been published; further information can be provided upon request.

Detection of Toxins

One toxin that is fairly common is the T2 toxin, associated with yellow rain. Detection of toxins is important for assurance of a safe water supply. The SERS spectrum of 1 ppm T2 toxin is shown below.



Conclusions

SERS is a powerful detection technique that can:

- detect chemical warfare agents and simulants down to JSAWM limits in <5 min;
- · differentiate agents and degradation products;
- detect TICS (comprehensive survey and detection limit analysis is ongoing);
- detect toxins (have shown ppb detection of cyanotoxins);
- · detect and differentiate bacterial species; and
- differentiate viable and non viable bacterial cells.

In addition:

- substrates can be shipped and used by nonspecialists;
- substrates have a long shelf-life;
- instrumentation is compact and modular; and
- vapors and liquids can be analyzed.

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