APPLICATION NOTE #18

Raman Spectroscopy for Homeland Defense Applications*

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Introduction

Analytical technologies are currently in demand for Homeland Defense applications. Domestic preparedness requires a wide array of detection capabilities for a range of potential attack scenarios. For example, a single location could be attacked by planting an explosives package, carrying an explosive on a person, releasing a chemical/bacterial dispersion into the air supply, releasing a chemical/bacterial dispersion into the water supply, or becoming the target of an armed gunman. The task is then expanded by considering the different types of explosives, chemicals warfare (CW) agents, bacteria, spores, viruses, and toxins that need to be quickly and accurately identified. Today, no single analytical technique is able to address all of the above possibilities; the future may bring a series of sensors that can, as a whole, detect a multitude of hazardous materials in a rapid, reliable manner. As for the present time, a variety of analytical technologies are available to collectively detect and identify potential threats to the public.

Raman spectroscopy is a becoming an increasingly important technology for Homeland Defense applications. It is currently being used for the bulk identification of explosives, CW agents and other potentially hazardous chemicals. In the future, Raman may also be used for trace detection as well. Surface enhanced Raman spectroscopy (SERS) has been demonstrated for the detection of trace levels of explosives, CW agents, and bacteria both in the vapor phase and in aqueous solution. There is strong potential to use an array of SERS sensors for the rapid analysis of ambient air and drinking water supplies. Resonance Raman spectroscopy (RRS) is another technique resulting in enhanced Raman scattering. In RRS, the laser excitation wavelength is matched to the UV absorption of the analyte molecule. This results in lower detection limits compared to exciting at longer wavelengths while avoiding interfering fluorescence background. This article will discuss the role of Raman spectroscopy for forensic analysis and Homeland Defense, today and in the future.

Homeland Defense

> *“Reducing the consequences of weapons of mass destruction incidents by enhancing the preparedness, protection, and response capabilities of local, state, and federal agencies.”*[1]

Identification of Bulk Unknowns

The identification of bulk chemicals is necessary for Homeland Defense as well as for routine forensic applications both on-site and in the laboratory. As a light scattering technique, Raman is able to interrogate samples in a non-contact, non-destructive manner through clear and semi-clear packaging materials. Current instrumentation is transportable and even man-portable, enabling such analyses to be conducted in the field. For law enforcement, unknown chemicals can be identified or screened on-site. This enables preliminary evidence to be obtained immediately rather than having to wait for laboratory test results. More importantly, potentially hazardous materials, such as explosives, can be identified prior to being handled and transported.[2]

The U.S. Army has assembled mobile laboratories that are used by various agencies. These laboratories include a variety of transportable analytical techniques (e.g. GC-MS and FT-IR) to address a wide array of sample forms and

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*A version of this application note appeared in *Raman Technology for Today’s Spectrosopists: A Technology Primer, Supplement to Spectroscopy, June* (2004).

[1] U.S. Army Soldier and Biological Chemical Command's (SBCCOM's) Homeland Defense Business Unit Homepage, http://hld.sbccom.army.mil/, as of May 6, 2004.

[2] B.A. Eckenrode, E. G. Bartick, S.D. Harvey, M.E. Vucelick, B.W. Wright, and R.A. Huff, "Portable Raman Spectroscopy Systems for Field Analysis", Foren. Sci. Comm., 3(4), (2001).

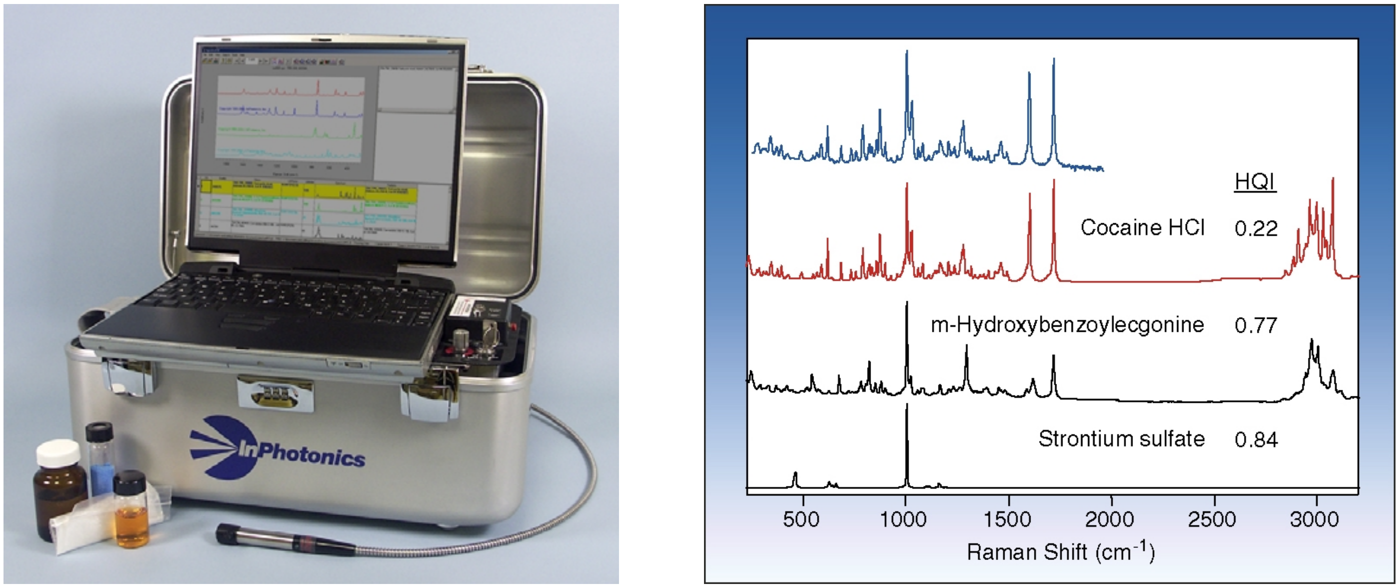

Figure 1. Typical identification result from the InPhotote™ portable Raman spectrometer. The HQI (hit quality index) is the distance from the unknown spectrum to the library result (i.e. lower HQI is a better match).

types. In the case of the Raman spectrometer, a long fiber optic probe cable enables operators to analyze samples outside of the vehicle, minimizing risk to personnel. A recent study using a full-range, 4 cm^{-1} resolution instrument (RS2000, InPhotonics, Inc.) demonstrated that Raman was a suitable technique for the rapid and reliable identification of unknowns, provided that a suitable reference database is used.[3] It was also shown that the InPhotote™ (InPhotonics, Inc.), a smaller instrument with lower spectral resolution (4 - 6 cm^{-1}) and a truncated range (250 - 1800 cm^{-1}) was just as capable of performing these types of analyses.[3,4] Figure 1 shows a typical library search result using a portable Raman system and a first-derivative correlation algorithm.

Transportable and portable Raman spectrometers have been used for the identification of chemical agent identification sets (CAIS) prior to disposal.[5] These sets were used to train military personnel in the identification, safe handling, and decontamination of CW agents. Large quantities of CAIS were produced, and many are still stored at military sites throughout the country. In order to dispose of the samples, the CW agents (mustard, nitrogen mustard, and lewisite) must be separated from those containing what are now classified as industrial compounds. A transportable spectrometer and focused fiber optic probe with a 25 m cable enabled measurements to be made under controlled conditions.

The U.S. Army is outfitted to provide immediate response capabilities for chemical and biological warfare material. Specialized units are equipped to provide worldwide response for escorting, detecting, monitoring, neutralizing, and disposing of chemical and biological hazards. A variety of analytical instruments are used in these army missions, one of these being the InPhotote™ portable Raman spectrometer that can be rapidly deployed in the field. Although routine Raman lacks the sensitivity of other techniques, the ease of use and non-contact sampling have enabled it to take its place amongst the tools of forensic and military investigators.

Trace Detection via Surface-enhanced Raman Spectroscopy

For many applications, lack of sensitivity has been a major obstacle for Raman spectroscopy. The ability to detect and identify potentially harmful materials at low concentrations has risen to the forefront of research and development efforts under the auspices of Homeland Defense. EIC Laboratories has been employing surface enhanced Raman spectroscopy (SERS) to improve detection limits by a factor of 10^{12} - 10^{14}. In SERS, an analyte is adsorbed onto a SERS-active surface, normally silver, copper, or gold. The excitation laser is selected to be in resonance with the surface absorption band, or surface plasmon, associated with the metal surface. The analyte that adsorbs in the interaction region is perturbed, leading to enhanced spectral features. Since SERS is a direct measure of the analyte's bonding structure, unique spectral sig-

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[3] S.D. Harvey, M.E. Vucelik, R.N. Lee, and B. W. Wright, "Blind Field Test Evaluation of Raman Spectroscopy as a Forensic Tool", Foren. Sci. Int., 125, 12-21 (2002).

[4] N.T. Kawai and J. A. Janni, "Chemical Identification with a Portable Raman Analyzer and Forensic Spectral Database", Spectroscopy, 15, 32-41 (2000).

[5] S. Christesen, B. MacIver, L. Process, D. Sorrick, M. Carrabba, and J. Bello, "Nonintrusive Analysis of Chemical Agent Identification Sets Using a Portable Fiber-Optic Raman Spectrometer", Appl. Spectrosc., 53(7), 850-855 (1999).

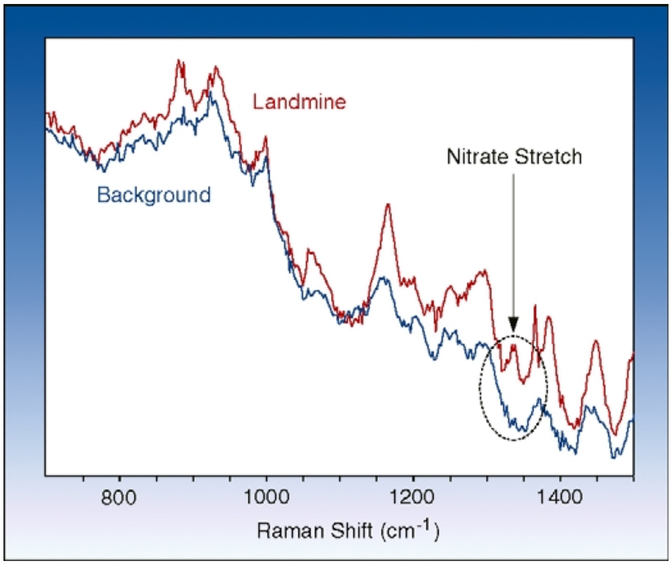

Figure 2. Detection of a buried landmine using SERS.

Figure 3. SERS vapor probe that incorporates a roughened gold substrate, fiber optic probe, and fan.

natures are collected and false positives are minimized. The technique works equally efficiently in water or in air (regardless of humidity level), and the 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 thirty seconds. The multi-environmental, multi-analyte capability of SERS makes it highly promising for Homeland Defense applications.

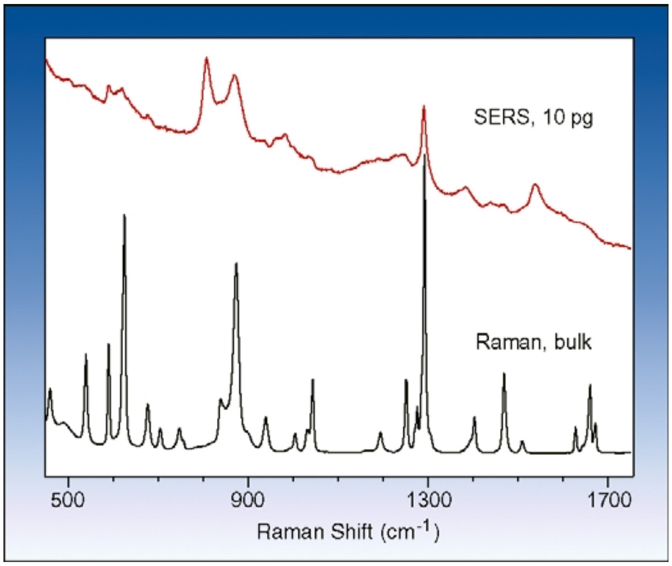

Figure 4. Raman and SERS spectra of PETN. The detection limit via SERS is 1 pg.

Vapor-Phase Detection of Explosives

Trinitrotoluene (TNT), its impurity 2,4-dinitrotoluene (2,4-DNT) and its degradation products, 1,3-dinitrobenzene and 4-amino-2,6-dinitrotoluene have been detected by SERS in the vapor phase.[6] The characteristic features are the nitrate bending modes in the 820 cm^{-1} region and the stretching modes around 1337 cm^{-1} that are strongly enhanced, indicating the explosives adsorb to the SERS substrate through the nitrate features and not the aromatic ring. Both TNT and 2,4-DNT have been detected down to 1 ppb in concentration, or 1 fg. Figure 2 shows the SERS spectrum of 2,4-DNT as detected by passing a SERS vapor probe over a buried landmine. The SERS probe, shown in Figure 3, housed a commercial fiber optic probe (RamanProbe™, InPhotonics, Inc.) oriented towards a roughened gold substrate. A small fan was incorporated to draw the ambient vapor over the substrate. Other nitro-containing explosives, HMX and RDX, could be detected down to 1-5 pg. PETN, an active component commonly used in "plastic explosives" could also be measured down to 1 pg. Raman and SERS spectra of PETN are shown in Figure 4. It should be noted that it is common to observe peak position and intensity differences when comparing Raman and SERS spectra, owing to the change in vibrational freedoms of a molecule adsorbed onto a substrate.

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[6] J.M. Sylvia, J.A. Janni, J.D. Klein, and K.M. Spencer, "Surface-Enhanced Raman Detection of 2,4-Dinitrotoluene Impurity Vapor as a Marker to Locate Landmines", Anal. Chem., 72, 5834-40 (2000).

Detection of Toxins in Drinking Water

Another area of Homeland Defense research employing SERS is for the monitoring of drinking water for chemical agents and other toxic chemicals.[7] Cyanide is a prime candidate for Raman analysis as its lone, strong band appears at a unique location near 2200 cm^{-1}. Using SERS, cyanide could be detected down to 2 ppb, and the method was quantitative up to ppm concentrations. Earlier work on CW simulants showed excellent detection limits. The actual CW agents, however, did not exhibit the same SERS behavior. The agent HD (distilled mustard) could be detected down to 1 ppm, however the SERS signal became nonexistent at lower concentrations. It was proposed that the agent may be rapidly hydrolyzing at lower concentrations, and further research continues.

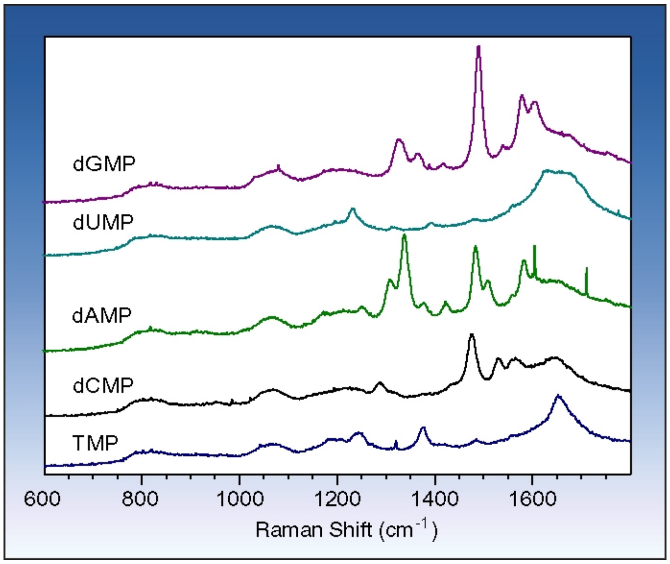

Figure 5. UV Resonance Raman spectra of nucleotides at 500 mM concentrations, measured with 95 mW of power at 244 nm excitation.

Detection of Biological Species by Resonance Raman Spectroscopy

While SERS is the preferred enhancement technique for chemical species, the detection of biological agents can be achieved with RRS. Raman spectroscopy using UV excitation is well known for the study of biological molecules such as proteins and nucleotides. Excitation in the UV results in more intense Raman scattering and avoids fluorescence backgrounds that often accompany biological compounds. UV Raman instrumentation has tended to be very large, however, and not suited to field applications; this has stalled RRS from being used in Homeland Defense applications.

EIC Laboratories has recently designed a high resolution UV-Raman spectrograph with no moving parts that is compact enough for transportation.[8] The resolution achieved by the 11" x 7" x 8" (280 x 180 x 205 mm) spectrograph is comparable to laboratory spectrographs with 1 m focal lengths. Figure 5 shows the RRS of various nucleotides at concentrations of 500 mM. This type of spectrometer may open the doors to detecting and identifying low concentrations of biological agents via Raman spectroscopy.

Conclusion

Routine Raman spectroscopy has already found its place in the hands of agencies tasked with defending our homeland. Raman provides the forensic chemist, military specialist, or first responder with the unique capability to measure interpretable vibrational data through containers and over long fiber optic cables. Current research using surface enhanced Raman spectroscopy shows promise for the detection of CW agents and other toxic chemicals in the vapor phase and in water supplies. New developments in spectrograph design may enable UV resonance Raman spectroscopy to be brought out of the laboratory and into the field for the detection of biological threats. While no single technique can satisfy all possible attack scenarios, Raman spectroscopy is, and will continue to be, an important tool for Homeland Defense.

If you would like additional copies of this note, or if you would like to speak with a member of our technical staff, please contact us at:

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[7] K.M. Spencer, J. M. Sylvia, P.J. Marren, J. F. Bertone, and S. D. Christesen, "Surface-Enhanced Raman Spectroscopy for Homeland Defense", Proc. SPIE Vol. 5469, 1-8 (2004).

[8] S.L. Clauson, S.D. Christesen and K.M. Spencer, "High Resolution UV Echelle Spectrograph for Environmental Sensing", Proc. SPIE Vol. 5469, 34-41(2004).