DEMONSTRATION OF A ROBOT-BASED RAMAN SPECTROSCOPIC DETECTOR FOR THE IDENTIFICATION OF CBE THREAT AGENTS

C W. Gardner* and P. J. Treado
ChemImage Corporation
Pittsburgh, PA 15208

T. M. Jochem
Applied Perception, Inc.
Cranberry Township, PA 16066

G. R. Gilbert
University of Pittsburgh Department of Electrical & Computer Engineering
US Army Medical Research & Materiel Command (USAMRMC)
Telemedicine & Advanced Technology Research Center (TATRC)
Fort Detrick, MD 21702

ABSTRACT

This paper describes the feasibility demonstration of a chemical, biological and explosive (CBE) detection system based on Raman spectroscopic measurements integrated to a commercially available unmanned ground vehicle (UGV) platform. Raman detection of CBE agents is reagentless and offers the ability to detect a broad range of threats in a single measurement and is well suited to remote operation. The performance of this sensor system for the detection of chemical and biological warfare agents was validated through comparison of results from a system performance model and from laboratory testing of a breadboard system.

This breadboard was successfully integrated on a Joint Architecture for Unmanned Systems (JAUS)-compliant Remotec ANDROS Wolverine UGV and the ability of the unit to target and detect a bioterror threat on a complex background was demonstrated. High-level detector functions, as well as the reporting of results to the operator were performed through the UGV wireless communications link to the operator control unit. This work has application to the remote detection of chemical, biological and explosive agents in military/civilian medical and emergency response applications.

1. INTRODUCTION

Force protection is complicated by current international and coalition troop deployments for asymmetric counter terror and counterinsurgency missions, peacekeeping operations, and humanitarian assistance missions that involve highly visible, politically sensitive, low intensity combat in urban terrain. The real-time detection and identification of biological and chemical warfare agents as well as potential toxic industrial gases and improvised explosive devices (IED) is of paramount importance for protecting soldiers and first responders on the battlefield and in counter-terrorist response at home.

Several R&D efforts are underway within the Army Research, Development, and Engineering Command (RDECOM) and the Medical Research and Materiel Command (MRMC) to leverage emerging Army Future Combat System (FCS), Joint Ground Robotics Enterprise (JGRE), and PM Force Protection Family of Rapid Response Equipment (FIRRE) JAUS compliant UGV platforms for a variety of force protection missions. One example is the RDECOM Chemical, Biological, Radiological, and Nuclear (CBRN) Unmanned Ground Reconnaissance (UGR) Advanced Concept Technology Demonstration (ACTD); another is this MRMC Small Business Innovative Research (SBIR) initiative.

This paper describes the feasibility demonstration of a chemical, biological and explosive (CBE) detection system based on Raman spectroscopic measurements integrated to a commercially available unmanned ground vehicle (UGV) platform. Raman detection offers clear advantages over immunoassay and DNA–based biological detection strategies, especially when configured for use on an unmanned vehicle. Raman measurements are reagentless, greatly simplifying the logistics of deployment. In addition, Raman measurements can be used to detect a broad range of CBE threats in a single measurement cycle. No assumption of the possible threat is required as in the case of reagent-based detection schemes.

By remotely guiding this sensor system to an incident area to assess soil, water and surface contamination, exposure of personnel to a hazardous environment is prevented until the nature of the threat is fully known. Bringing the sensor to the sample also minimizes
# Demonstration of a Robot-Based Raman Spectroscopic Detector for the Identification of CBE Threat Agents

## Authors
ChemImage Corporation
Pittsburgh, PA 15208

## Distribution/Availability Statement
Approved for public release, distribution unlimited

## Supplementary Notes
See also ADM002075., The original document contains color images.

## Security Classification
- Report: unclassified
- Abstract: unclassified
- This Page: unclassified

## Limitation of Abstract
SAR

## Number of Pages
35
problems associated with sampling, such as cross-contamination and pre-analysis decontamination as well as the problems of disposal after the analysis is complete.

2. RAMAN SPECTROSCOPY FOR CBE DETECTION

Raman spectroscopy has been studied and used as a laboratory tool in chemistry for many years (Adar et al., 2007). It is now reaching a level of maturity that is transitioning from the laboratory to a variety of field applications. The Raman effect occurs when a photon encounters a molecule, during which time there is a chance that the energy from the scattered photon will be exchanged with vibrational bond energy of the molecule. This energy exchange manifests itself as a shift in frequency (or wavelength) in a small amount of the scattered light. Because each different chemical bond in a material causes a different frequency shift, the pattern of these shifts, known as the Raman spectrum, is unique to that material.

The Raman spectrum reveals the molecular composition of materials, including the specific functional groups present in organic and inorganic molecules. The Raman spectrum is a characteristic property of a material just like its color or melting point and can be used to determine the presence or absence of the material.

Several groups have shown the applicability of Raman spectroscopy to the detection of CBE agents. Figure 1 shows the Raman spectra from several nerve and blister chemical warfare agents. (S. Christesen 2005, personal communication)

Figure 2 shows Raman spectra of several biological organisms that have been considered in biological warfare. Also included is the Raman spectrum of a known biological toxin, Ricin. (K. Kalasinsky 2004, personal communication).

Figure 3 shows the Raman spectra of some typical explosive materials. These were taken at ChemImage on a commercially available laboratory Raman system as a part of this study.

These fundamental studies clearly demonstrate the potential for identification of CBE agents by Raman spectroscopy. However, reliable detection of CBE agents under actual environmental conditions will require more than just the ability to generate unique spectra.

The goal of this detector system is to identify CBE agents on environmental surfaces. Therefore, the detector will always be measuring an agent spectrum in the presence of the spectrum from the background or from any other material that may be present. Fortunately, in most real-world situations, the ratio of the amount of agent to the background and any other materials has significant spatial variation. This variation in composition leads to slightly different Raman spectra from different areas on the sample surface. These differences in spectra provide enough information for chemometric processing of the data, allowing identification of the agent and the background materials (Schweitzer, 2006).

Therefore, the CBE detector planned for UGV integration in this study will rely on both the inherent specificity of Raman measurements and on the improvement in identification reliability inherent in spatially resolved spectroscopic measurements.

---

**Fig. 1. Raman spectra of several chemical warfare agents.**

![Raman Spectra of Chemical Warfare Agents](image1)

**Fig. 2: Raman spectra of selected biothreat agents.**

![Raman Spectra of Biothreat Agents](image2)
3. RAMAN BIO IDENTIFICATION (RBI) DETECTOR

The overall concept of the RBI robot demonstration system was to integrate a RBI point sensor (the RBI head) onto a UGV manipulator arm, and then couple it to an instrument package mounted on the main chassis of the UGV. The coupling of the point sensor is accomplished through both electrical and fiber optic cables running along the manipulator structure.

The RBI detector is a Raman point sensor, or perhaps more appropriately, a Raman proximity detector. For operation, it needs to be close but not necessarily touching the surface to be measured. The RBI detector contains subsystems to allow targeting of the head (video camera and fine positioning system), laser illumination of the sample to induce the Raman effect, optics to collect and focus the scattered light, a fiber optic bundle to transport the scattered light to a spectral analyzer (spectrometer subsystem) and a system computer to provide control and communications.

Using a single laser illumination spot and a single spectrometer, the RBI detector can produce up to 19 spatially resolved spectra from a sample region of interest (ROI). As previously discussed, these spatially resolved spectra can be processed using a mixture analysis algorithm coupled with library searching to provide robust identification of threat and non-threat materials present in complex environmental samples.

Figure 4 shows a schematic of the RBI detection system (without the fine positioning subsystem). A performance model of this system was built using the Mathcad software environment. This model allowed the estimation of the system response as a function of the specification of each subcomponent and of the operating conditions. The model was then used to select the subsystem components described in the following sections.

3.1 Video Subsystem

The video camera chosen for the RBI is a miniature color CCD camera with a cone pinhole lens. The pinhole lens has a field of view of 92°, a F/1.2 light rating and provides a large depth of field that is particularly useful for targeting of the RBI head.

3.2 Laser Subsystem

The Raman scattered light from the sample is generated by a relatively intense, monochromatic beam of light. In almost all modern Raman instruments, a laser is used as this light source. The RBI detector uses a miniature 100 mW 532 nm (green) laser with integral thermoelectric cooler (TEC). This laser was small enough so that it could be mounted directly on the detector head assembly. The laser and TEC drive electronics were small enough so that they could either be mounted on the head or mounted remote from the laser in the instrument package. The UGV battery provided power for the laser and the TEC.

To most people familiar with Raman spectroscopy, the choice of green excitation seems counterintuitive. It is generally believed that the use of red or near infrared excitation lasers greatly minimizes or eliminates background fluorescence, a serious interference in Raman measurements. However, what is most often overlooked, is that this reduction in fluorescence comes with a significant reduction in Raman signal. Theory shows that the intensity of Raman scattering is higher when excited with shorter wavelength light. In fact, this is a fourth-power dependence so that relatively small increases in the excitation wavelength result in significant reductions in
the measured Raman signal. A second consideration is that the background fluorescence will not be evenly distributed throughout the sample. The multi-point sampling strategy of the RBI detector increases the probability of measuring Raman signal in regions of the sample with low fluorescence. Researchers at the Edgewood Chemical Biological Center have confirmed both of these reasons supporting the use of green Raman excitation (S Christesen 2005, personal communication).

As is common with many lasers in this class, the laser light was passed through a short-pass optical filter with a transition wavelength at 536 nm, which removed any extraneous emission lines.

3.3 Optical Subsystem

The RBI optics deliver the laser illumination and collects the Raman-scattered light along the same optical axis. This allows the best match of the area of the sample illuminated by the laser and the area of the sample “seen” by the collection optics. This approach known as epi-illumination has been employed successfully in other ChemImage biothreat detection instruments.

The laser light is introduced into the primary optical axis by the use of a dichroic beamsplitter. This beamsplitter, mounted at 45 degrees with respect to the primary optical axis, reflects the 532 nm laser light towards the sample yet allows the Raman scattered light (longer wavelengths) to pass through as shown in Figure 4. The reflected laser light is focused on the sample through an aspheric lens with anti-reflective coating optimized for 500 to 600 nm operation.

The selection of this lens is critical to the success of the RBI for detection of biothreat agents. Since the efficiency or cross section of Raman scattering for most biological organisms or spores is low, it is absolutely critical to collect the Raman light from as much of the illuminated sample as possible. Since the Raman effect produces scattering in essentially all directions, maximizing the solid angle over which the light is collected will maximize the sensitivity. For a lens, this translates into maximizing the numerical aperture (NA) of the lens.

However, when the NA of a lens is increased, generally the distance the lens must be placed from the sample (the working distance, WD) decreases. Therefore, the collection lens selected for the RBI (NA = 0.5) represents a compromise in the effects of NA and WD.

The Raman experiment results in scattered light of three types. The first is scattered light at the same wavelength as the laser and is known as Rayleigh scattering. The other two types of scattering are due to the Raman effect and produce light at longer wavelengths than the laser (known as Stokes lines) and at shorter wavelengths (known as anti-Stokes lines). Only the Stokes scattered Raman light is analyzed by the RBI, so for maximum sensitivity, the other two types of light must be removed before the Stokes-shifted Raman can be analyzed.

The aspheric lens collects all three types of light over its collection solid angle and produces a collimated beam passing through the RBI detector. Most of the Rayleigh and anti-Stokes light is removed when the beam passes through the dichroic beamsplitter (wavelength (λ) < 540 nm is reflected; λ > 540 nm is transmitted). In order to fully remove all of the interfering light, the beam is additionally passed through a long-pass filter having an extremely sharp transition edge.

Once the Rayleigh and anti-stokes light has been filtered, the beam is focused onto a fiber optic bundle using an achromatic lens. This fiberoptic bundle consists of 19 fibers in a “round” hexagonal-close-packed arrangement. Each fiber has 50 μm diameter core and an overall diameter of 70 μm. The fiber cable length was 5 m and was long enough to easily allow routing of the cable along the UGV manipulator, from the “hand” to the instrument package on the robot chassis. Over this fiber length, essentially no intensity loss will be observed. At the other end of the cable, the fibers are aligned in a single row linear array.

3.4 Spectrometer Subsystem

The analysis of the Raman scattered light in the RBI system is done using a 150 mm focal length, grating-based spectrometer with integrated CCD detector. This unit is a true imaging design, allowing discrete spectra to be measured from different points along the height of the entrance slit. By aligning the linear fiber array coming from the RBI head along the spectrometer entrance slit, a discrete spectrum can be measured from each fiber. The real benefit of this is that each spectrum is from a different spatial location on the sample or surface being tested. Therefore, the multiple Raman spectra needed for reliable CBE agent identification can be obtained each time the spectrometer detector is “read”. The simultaneous collection of these spatially resolved Raman spectra greatly reduces the analysis time.

Power for the spectrometer comes from the robot battery and a USB1.1 interface is used for spectrometer control and data transfer. The spectrometer is directly interfaced with the system computer.
3.5 Computer Subsystem

For the proof of concept demonstration, the system computer was an EBX format single-board Pentium M system, operating at 1.6 GHz processor speed and running Windows XP Embedded. Power was provided to the computer from the robot battery pack using a 200 W 12 VDC inverter powering a standard 180 W computer power supply. The RBI system software was based on the ChemImage Xpert™ package and provided system control, data acquisition, spectral processing, spectral unmixing and spectral library search functions. In addition, the computer received commands from the UGV CPU unit to adjust the fine positioning stage and start/abort a measurement through a RS-232 serial communications protocol. The system computer also transmitted the results of a measurement as ASCII data to the UGV CPU for conversion to the JAUS messaging standard and transmission back to the operator control unit (OCU) through a wireless link.

3.6 Data Collection and Pre-processing

The RBI system computer receives a command to acquire and analyze a sample from the UGV CPU (initiated by the operator). Using software previously developed by ChemImage, up to 19 spectra are acquired from the sample. The laser power is typically 12 mW, resulting in a laser power density of 86 W/cm². The exposure time used to acquire the spectra in breadboard testing was 10 seconds and each measurement is the product of 10 averages.

A number of corrections are applied to the acquired spectra. Dark current correction divides the acquired spectra by a spectrum taken with no light. Instrument response is removed by correction with the NIST SRM 2242 Raman Intensity standard. This compares a spectrum taken of the NIST standard to the standard NIST spectra provided with the SRM. The difference is the instrument response, which is divided from the acquired spectra. Baseline fit is used to remove a sloped or curved baseline. It finds the best baseline fit based on a least-squares calculation and subtracts it from each spectrum. Each spectrum is truncated to a range of 800 through 3150 cm⁻¹, which is where the features that have the highest probability of differentiation lie. Finally, the spectra are normalized to bring them all to the same intensity scale. Figure 5 shows the corrected, average Raman spectra taken on the breadboard of several CBE simulants. All three spectra taken on the breadboard are essentially the same as those taken on a laboratory Raman system.

3.6 Data Analysis

There are a variety of algorithms that could be used to identify the components of a mixture. The algorithm used at ChemImage is a target-testing factor analysis based algorithm. To summarize, a set of mixture spectra is collected and is used to describe a mixture space using principal components analysis (PCA). Each library spectrum is then mapped into this space as a vector. If the mixture space completely describes all information about a given library spectrum, its angle of projection into the mixture space will be 0 (or a very small angle if there is noise in the set of mixture spectra). The library spectra can be ranked based on their angles and the top n matches are determined to be the pure components in the mixture, where n is the rank of the matrix associated with the mixture spectra. The angle of projection can also be used to determine if a given compound is a close enough match to be considered as a member of the mixture.

The details of the implementation are as follows. A data set of 19 spectra is acquired and processed as described above. The spectra are then submitted to the spectral searching routine. The routine will mathematically analyze the set of spectra to determine if there is sufficient variability to indicate a mixture. If there is not sufficient variability, a mean spectrum will be calculated from the 19 spectra and a simple Euclidean distance comparison will be performed between the mean spectrum and each library spectrum. If there is sufficient variability, the set of 19 spectra will be submitted to the spectral unmixing algorithm as described above. In both cases, a score (Euclidean distance or target testing angle) will be calculated for each entry in the library. A cutoff value for the score will be used to determine if a library
entry should be considered as the identified substance (either pure or as a member of a mixture). The classification of each identified substance (threat vs. non-threat) determines whether the physical substance under analysis is identified as a threat or non-threat.

Once searching is complete, the results are transmitted back from the RBI system computer. This consists of reporting the name of the library entry whose spectrum matching score is greater than the established cutoff with the calculated score.

4. UGV INTEGRATION

Based on availability and the payload capacity, a JAUSS-compliant Remotec Andros Wolverine was chosen for the proof of concept demonstration. The main chassis of the Wolverine is large enough to accommodate the detector electronics and computer package. The manipulator is rated to lift and position a load up to 60 lbs. at full extension, well in excess of the weight of the Raman point detector.

Figure 6 is a picture of the RBI system installed on the Wolverine. A close-up view of the Raman point detector installed on the manipulator is shown in the inset.

The Wolverine is controlled using a radio frequency link between the robot and the operator control unit (OCU). A JAUSS payload interface was written to allow control and data transmission to and from the RBI system through this wireless interface. The interface was implemented in hardware through a RS232 serial link between the robot processor system and the RBI system computer. All command and control data between the OCU and both the UGV platform and the RBI payload adhere to the JAUSS Reference Architecture 3.2 with OPC 2.0 and 3.0 extensions message and protocol definitions.

One additional feature of the Wolverine is its integral multi-camera video system. In order to assist with the targeting, the signal from the video camera built into the RBI head is fed into this system, which relays it to the OCU through a standard JAUSS video sensor component. The operator has access to this video stream and can use it for fine control of the RBI head. The OCU screen for targeting is shown in Figure 7.

The proof of concept consisted of placing a biological toxin simulant, ovalbumin, on a flattened sheet of galvanized iron air duct material to provide a constant background for the measurement. This sheet plus sample was placed on the floor for the demonstration. The operator then moved the UGV close to the sample area and used the manipulator to position the RBI detector head directly over the sample. The fine adjustment system in the RBI head was used to set the collection lens of the detector at the proper distance from the sample through commands from the OCU.

Once the detector was positioned, the operator started the analysis. For the breadboard tests, the analysis parameters were under local control by the detector system computer and were preset. The analysis consisted of a 3 min. wait period, during which the native fluorescence of the ovalbumin is quenched by the laser excitation (through a process known as photobleaching). Next, a 1 min. acquisition of the 19 spatially resolved Raman spectra are taken as shown in Figure 8. This set of spectra are pre-processed and analyzed using the process described in the previous section.
The results of the spectral search and their ranking scores are transmitted to the OCU as shown in Figure 9. The results included the material name and the score, and included an identification of the threat class.

In order to confirm proper spectral performance, the spectra in Figure 8 were averaged, preprocessed and compared against the library spectrum for ovalbumin as shown in Figure 10. The figure shows good agreement between the RBI and library spectra and confirms the accuracy of the RBI detector.

![Fig. 8 Spatially resolved Raman spectra of the toxin simulant (ovalbumin) taken during the UGV demonstration.](image)

Once the analysis and reporting of results was complete, the operator had the option of taking another measurement or moving the detector to another sampling location. To move the detector, first the fine manipulator was used to raise the RBI head up off of the sample. Next, the UGV manipulator was used to completely raise the RBI detector head to prepare it for transport. At that point, the operator could move the UGV chassis to the next analysis site and repeat the positioning and analysis cycle.

**CONCLUSIONS**

This work has shown the feasibility of a Raman Bio Identification detector as an integral part of a UGV system. Miniature optical components and a small laser diode system allowed the detector head to be easily mounted in the “hand” of a common UGV, the Remotec Wolverine.

A mathematical model was constructed to describe the performance of the RBI detector system. This model was evaluated using a simulant for anthrax, *B. thuringiensis* (*Bt*) spores, and a biological toxin simulant, ovalbumin. This modeling confirmed the feasibility of the design for biothreat agent detection.

![Fig. 9 RBI detector operator control results reporting screen.](image)

A detector breadboard system was constructed and its performance was evaluated in both laboratory tests and tests with the system mounted on a UGV. In the laboratory tests, system performance was demonstrated on *Bt* spores and on two chemical agent simulants, DMMP and MES. In the UGV tests, the RBI detector showed its ability to identify a toxin simulant, ovalbumin powder, on a sheet of galvanized air duct.

These results are important to the warfighter for the following reasons. First, this work, along with other DoD funded studies, has shown the feasibility of using Raman spectroscopy as a reagentless detection system for the detection and identification of CBE agents. This greatly minimizes the logistic support for CBE detection as well as minimizing the detection time.
The reagentless nature of Raman also means that detection and identification is not dependent on a priori knowledge of threat agents or explosives or their chemical/molecular compositions. While Raman identification of agents requires a spectra library for pattern matching recognition of molecular structure, it can still identify new, unknown agents (such as recombinant chemical agent or explosive structures or genetically altered organisms) by flagging for further investigation, those spectra that are not already present in the library, especially if they closely resemble the spectra of a known agent or class of known agents. Warning the user of the presence of an unknown substance that could possibly be a threat is of great value to the warfighter or emergency responder. Such warnings could then be incorporated into standard operating procedures (SOP) for donning mission oriented protective posture (MOPP) gear or other personal protective equipment (PPE). Ultimately, the suspect spectra would be added to the library as an unknown spectra associated with a potential hazard.

The second area of importance to the warfighter is the demonstration of the feasibility of UGV-based detection of CBE agents on environmental surfaces. Remote detection places the warfighter out of harm’s way while an area is being screened for CBE agents, minimizing the need for operations in MOPP gear or PPE and the resulting loss in soldier efficiency.

Work is continuing to refine the RBI detector hardware and software to allow integration on a wider class of UGV platforms and to optimize the system operation for field use.

ACKNOWLEDGEMENTS

The authors would like to thank Scott Anderson, Randi Assenova, Jeffrey Beckstead, Robert Stern, and Jingyun Zhang from ChemImage for their work on the design, fabrication and testing of the breadboard system. Thanks also to Matthew Shaffer from Applied Perception for his work on the detector–UGV interface.

We also thank Kathryn Kalasinsky of the Armed Forces Institute of Pathology for the biothreat agent Raman spectra and Steven Christesen of the Edgewood Chemical and Biological Center for the chemical warfare agent Raman spectra presented in this paper.

This work was supported by the US Army Medical Research and Materiel Command under Contract No. W81XWH-06-C-0010.

DISCLAIMER

The views, opinions and/or findings contained in this manuscript are those of the authors and should not be construed as an official Department of the Army position, policy or decision unless so designated by other documentation.

REFERENCES


Demonstration of a Robot-Based Raman Spectroscopic Detector for the Identification of CBE Threat Agents

C. W. Gardner and P. J. Treado
ChemImage Corporation

T. M. Jochem
Applied Perception, Inc.

G. R. Gilbert
USAMRMC - TATRC
Outline

- Project Background
- Why Use Raman Spectroscopy for CBE Agent Detection?
- Advantages of Spatially-Resolved Raman Measurements
- Detector Design
- Detector Integration on a COTS UGV
- System Demonstration Testing
- Importance to the Warfighter
- Acknowledgements

25th Army Science Conference
Project Background

- **Goal:** Show proof-of-concept of a Raman CBE detector using spatially resolved measurements, integrated to a COTS UGV system using the Joint Architecture for Unmanned Systems protocol (JAUS)

- **Sponsor:** US Army Medical Research and Materiel Command – Telemedicine and Advanced Research Center (TATRC)

- **Project Team:** ChemImage Corporation Detector Lead & Project Mgmt.
  Applied Perception, Inc.
  UGV Integration Lead

25th Army Science Conference
Why Use Raman Spectroscopy for CBE Agent Detection?

- **Reagentless**
  - No presumption of the threat is necessary
  - Greatly simplifies field deployment

- **Widely Applicable**
  - Demonstrated for Chemical, Biological and Explosive threat detection
  - All three types of threats can be detected simultaneously

- **Specific**
  - Raman spectrum is an inherent property of a material
  - The use of Raman spectroscopy for material identification is well documented

25th Army Science Conference
**Raman Spectroscopy**

- Inelastic scattering phenomenon
- Laser-based technique
- Very low light effect
- Probes molecular vibrations to provide molecular fingerprint

**Energy Level Diagram**

- **S₀**
- **S₁**
- **ν₁**
- **ν₂**
- **ν₀**
- **Δν**

- **Rayleigh (II)**
  - Photon emitted
  - Photon absorbed
  - Photon emitted

- **Stokes (III)**
  - Photon emitted
  - Photon absorbed
  - Photon emitted

- **Anti-Stokes (I)**
  - Photon emitted
  - Photon absorbed
  - Photon emitted

- **Rayleigh Scattering**
  - $hν_0$

- **Stokes Scattering**
  - $h(ν_0-Δν_0)$

- **Anti-Stokes Scattering**
  - $h(ν_0+Δν_0)$

- **Photon absorbed**
  - $hν_0$

- **Photon emitted**
  - $h(ν_0±Δν_0)$

- **Photon absorbed**
  - $hν_0$

- **Photon emitted**
  - $hν_0$

- **Photon emitted**
  - $hν_0$

- **Photon emitted**
  - $hν_0$

25th Army Science Conference
Chemical Agent Raman Spectra

Offset Intensity

Sulfur Mustard (HD)
Soman (GD)
Cyclosarin (GF)
Tabun (GA)
Sarin (GB)
Lewisite

Raman Shift (cm⁻¹)

25th Army Science Conference
Live Biothreat Agent Raman Spectra

Raman Shift (cm⁻¹)

Offset Intensity

Bacillus anthracis (LD Viable)
Ricin
Yersinia pestis
Burkholderia mallei
Francisella tularensis
Brucella abortus

25th Army Science Conference

© ChemImage Corporation
ChemImage Products and Services are protected by U.S. and International patents and patents pending 6,917,423 6,765,668 6,950,184 D503,642 D500,257 D500,257 6,717,668 6,965,793 6,002,476 6,734,962 6,788,860 6,985,216 6,985,233 6,954,667 7,012,695 7,046,359 7,045,757 7,060,955 7,061,606 7,084,972 7,019,296 7,068,357 7,072,770 6,992,809
Raman Spectra from Explosives

Raman Shift (cm⁻¹)

650 1150 1650 2150 2650 3150

RDX (C4)
HMX
PETN
Nitrocellulose

Ammonium Nitrate

Offset Intensity

Raman Shift (cm⁻¹)

650 1150 1650 2150 2650 3150

25th Army Science Conference
Composite Hierarchical Cluster Analysis

Dendrogram

Mahalanobis Distance

25th Army Science Conference

© ChemImage Corporation
ChemImage Products and Services are protected by U.S. and International patents and patents pending 6,917,423  6,785,668  6,950,184  D503,642  D500,257  6,717,668  6,965,793  6,002,476  6,734,962  6,788,860  6,985,216  6,985,233, 6,992,809
Principal Component Analysis (PCA)

Biologicals

J3 Criterion = 207.333102

PC 1

PC 2

25th Army Science Conference
Why Use Multiple Spatially Resolved Raman Measurements?

- Spatial sampling provides efficient means to generate “pure pixel” Raman spectra in the presence of background clutter (a means to increase Signal to Background ratio)
- Spatial sampling provides a method to increase sample throughput and manage relative insensitivity of Raman method
- Spatial sampling from multiple bioagents provides improved overall sampling statistics which enables use of probabilistic decision making algorithms and exponential improvement in false alarm performance
Why Use Multiple Spatially Resolved Raman Measurements?

- **Improved Discrimination of Threat from Background**

Mixture of Ovalbumin & Diesel Soot

![Avg. Dispersive Raman Spectrum](image)

![Dispersive Raman Spectral Set](image)
Why Use Multiple Spatially Resolved Raman Measurements?

- Improved Discrimination of Threat from Background

Mixture of Ovalbumin & Diesel Soot

Avg. Dispersive Raman Spectrum
Why Use Multiple Spatially Resolved Raman Measurements?

- Improved Discrimination of Threat from Background

Mixture of Ovalbumin & Diesel Soot
Why Use Multiple Spatially Resolved Raman Measurements?

- Improved Discrimination of Threat from Background
Raman Bio Identification (RBI) Detector

- Proximity Raman Detector
- Consists of Detector Head and Instrument Package Linked by a Fiber Optic Cable
- Green Laser Excitation (532 nm, 60 mW at sample)
- Collection of Raman Scattered Light Using Spatially Separated Optical Fibers
- Integrated Spectrometer/Detector System
  - 150 mm Focal Length  1,200 groove/mm Grating
  - 122 x 1,024 Pixel CCD Operating at -20 deg C
- Integrated Video Camera for Fine Targeting
Detector Head Detail

- Fiber Optic Cable Mount
- Stage Motor
- Fine Positioning Stage
- Objective Lens
- Laser Diode
- Video Camera
- Light Shield
- Mounted on Robot Arm

25th Army Science Conference
Detector Integration on a COTS UGV

- Remotec Andros Wolverine Chosen for Demonstration
- Detector Head Mounted on the Arm Using the Gripper
- UGV Controlled Through a Wireless Control Link
- Serial RS-232 Communication Between Detector and UGV Computer
- Operator Starts the Analysis and Receives Results Through the Wireless Link to the Operator Control Unit (OCU)
- All interaction between OCU, robot and payload are JAUS compliant
System Demonstration Tests

- Test Performance of Detector System to Threat Simulants in the Lab

- Integrate RBI Detector on the UGV and Evaluate System Performance in a Simulated Operating Scenario
  - Tele-Operation of UGV and Detector
  - Toxin Simulant: Ovalbumin on Metal Sheet
RBI Detector Lab Testing

MES – Sulfur Mustard Simulant

DMMP – G-Type Nerve Agent Simulant

Bacillus thuringiensis - Anthrax Simulant

25th Army Science Conference
System Demonstration Video

25th Army Science Conference
Results of the Demonstration

Spectral Unmixing and Library Search Results
As Transmitted to UGV Operator Control Unit

Threat Detected
Class: Toxin

Collected Spectrum (Average)

1000 1500 2000 2500 3000

Ovalbumin Spectrum Taken During RBI Sensor on UGV Demonstration
Ovalbumin Spectrum from Library
Importance to the Warfighter

- Feasibility of a Reagentless UGV Raman CBE Detector for Remote Environmental Screening

- The Reagentless Nature of Raman Detection
  - Reduces Detection Time
  - No Need to Assume What Threat May Be Present
  - Eliminates the “One Reagent – One Threat” Limitation of PCR and Immunoassay Methods
  - Requires Minimal Logistics Support in the Field

- Remote CBE Screening by UGV
  - Keeps Warfighter out of Harm’s Way
  - Protective Equipment (MOPP or PPE) Not Required Until the Nature of the Threat is Known

25th Army Science Conference
Plans for Future Work

- Phase II: Smaller and More Rugged Detector
- Improvements in Detection and Identification Algorithms
- Development of a Plug-and-Play Standard for Robotic CBE Sensors Operating Through JAUS
- Feasibility of UGV Integration of...
  - Proximity LIBS
  - Standoff Raman
  - Standoff LIBS
  - Fused Raman & LIBS Detection
Acknowledgements

- Scott Anderson, Randi Assenova, Jeff Beckstead, Bob Stern and Jingyun Zhang from ChemImage Corporation

- Matt Shaffer from Applied Perception, Inc.

- Kathryn Kalasinsky (Armed Forces Institute of Pathology) for the biothreat agent Raman spectra

- Steven Christesen (Edgewood Chemical and Biological Center) for the chemical warfare agent Raman spectra

- This work is supported by the US Army Medical Research and Materiel Command under Contract No. W81XWH-06-C-0010
The views, opinions and/or findings contained in this presentation are those of the authors and should not be construed as an official Department of the Army position, policy or decision unless so designated by other documentation.

Thanks to the organizers of the 25th Army Science Conference for the opportunity to present this work!

cgardner@chemimage.com