A NEW STANDOFF CB DETECTION TECHNOLOGY BASED ON THE FUSION OF LIBS AND RAMAN

Andrzej Miziolek, Frank DeLucia, Chase Munson and Jennifer Gottfried
U.S. Army Research Laboratory (ARL/WMRD)
Aberdeen Proving Ground
Aberdeen, Maryland 21005-5069

Richard Russo
A3 Technologies LLC
HEAT Center, 1201 Technology Drive
Aberdeen, Maryland 21001

Patrick J. Treado; Matthew P. Nelson
ChemImage Corporation
7301 Penn Avenue
Pittsburgh, PA 15208

ABSTRACT
Both standoff Laser Induced Breakdown Spectroscopy (LIBS) and Raman technologies have recently made great strides towards being deployed for operational use. Both technologies have demonstrated impressive capabilities of detection and discrimination of residue amounts of explosives at distances of 50+ meters in recent tests at the National Training Center, Ft. Irwin, CA, and Yuma Proving Ground, AZ, where the temperature extremes and other environmental conditions presented significant challenges. Beyond the strong performance of the individual sensors, the emerging paradigm of data fusion is yielding even stronger performance with regards to detection and discrimination capabilities. These two standoff sensor modalities have been recently applied to a number of chemical agent simulants and biological agent surrogates along with a number of confusants. Results of initial standoff tests on CB materials along with data fusion are presented.

INTRODUCTION
In the past few years there has been a significant acceleration of research and development towards applying laser and spectroscopy-based technologies towards the significant challenge of detecting the presence of hazardous materials, many in small residue amounts, at significant practical standoff distances approaching 100 meters. The US Army Research Laboratory at Aberdeen Proving Ground, MD, has been a pioneer in this area, particularly in the development of LIBS (I). Most of the recent progress has been driven by a significant military need to detect residue explosives at standoff distances. In a laboratory setting, ARL launched a significant program for the detection of residue explosives, both at close-contact and at standoff distances of 20-60 meters (II-III). Simultaneous to our explosives residue studies, we have also analyzed a number of biological and chemical materials (IV-VI). Significant advances have thus been accomplished both in hardware (5 different standoff LIBS systems have been built so far) as well as in spectral analysis/chemometrics. LIBS has many attributes that make it a very attractive
technology for field detection of hazardous materials. These include (1) real-time analysis (on a shot-by-shot basis) and (2) no sample preparation. However, with the advent of a new generation of LIBS technology, driven by the development of the broadband high resolution spectrometer and advances in chemometric spectral data analysis, LIBS is now a very powerful tool for general materials analysis, both close-contact, and standoff, whether the target material is hazardous or benign. Thus, the same LIBS device that can detect residue explosives can be used to detect other materials including hazardous chemical and biological agents.

Likewise, standoff Raman and Raman Chemical Imaging are very effective tools for non-destructive molecular identification. CBE materials typically have strong, unique Raman spectra that are “fingerprints” of the vibrational spectrum of the molecule. The technique can be used to differentiate between two very similar molecules, and can be used to differentiate between a target analyte and its matrix. Using the Fiber Array Spectral Translator (FAST) approach provides low pixel fidelity spatially resolved Raman dispersive spectral images (i.e., chemical images) and improved reliability of detecting target analytes from a complex background matrix.

Approximately three years ago ARL and ChemImage explored the possibility of fusing LIBS and Raman data for superior performance in Probability of Detection (Pd) and reduction of False Alarm Rates (FAR). Through initial data sharing of both explosives spectra and biological materials spectra, the first example of data fusion proved effective. In the last year, ARL, A3 Technologies LLC, and ChemImage have been engaged in a sizeable project on sensor fusion. Through three field campaigns, the notion of the advantages of sensor data fusion was clearly demonstrated. Our teams (LIBS and Raman) are also interested in using our respective standoff systems on standoff analysis of chemical agent simulants, biological agent surrogates, and typical interferent materials that one would find in practical applications. This summary describes the results of this initial study of standoff CB residue analysis using LIBS and Raman data fusion.

EXPERIMENTAL

LIBS Sensor: Details of the standoff LIBS sensor have been published previously (VI). In short, a double-pulse laser system was used in conjunction with a 14 inch Meade telescope and a custom-built (Ocean Optics, Inc.) three-channel spectrometer that provided broadband high-resolution spectral coverage. The standoff distance (distance from detector to target) was 20 meters.

Raman Sensor: The standoff Raman sensor technology developed by ChemImage and used in this work integrates two excitation wavelengths (i.e., 248nm and 532nm) and FAST Chemical Imaging technology. Widefield Chemical Imaging is applicable to the problem of detecting CB threats in the presence of background clutter. Chemical Imaging combines digital imaging and molecular/elemental spectroscopy for material analysis, and has been shown to provide improved sensitivity and specificity over non-imaging spectroscopy based sensors (VII-VIII).

The standoff Raman system used in this work consists of a custom-built 16 inch clear aperture f/8.4 telescope with UV-coated mirrors (Optical Guidance Systems), a frequency doubled (532nm) Nd:YAG laser source (Quantel), a KrF excimer 248nm laser source (GAM Laser Inc.) and detection channels optimized for Raman light collection for each respective excitation wavelength consisting of laser line filters, collection optics, FAST bundles, spectrometers and gated intensified CCD detectors. The sensor is also equipped with a widefield zoom camera for large area scanning, a boresighted video camera for through-telescope viewing, a laser range finder for measuring sensor to target distances and a motorized pan/tilt unit. All
hardware control, data acquisition and data processing was performed using ChemImage Xpert software equipped with FIST – a sensor fusion software package (ChemImage, Corp.).

**Material and Methods:** Spectra of various biological warfare agent surrogates, potential confusants and chemical warfare agent stimulants were acquired at 20m and 30m standoff distances for the respective LIBS and Raman sensors. Preprocessing of the spectral data included baseline correction and normalization. The FIST software allows a user to build classification models for each spectroscopic technique, apply those models to input test data, and review the results of that analysis. In the work performed here, models were built for Raman and LIBS using Partial Least-Squares Discriminant Analysis (PLSDA) for the standoff data. After a model is applied to a given test image, the resultant scores are converted to probabilities to allow the fusion of the results from multiple models (multiple spectroscopic techniques). There are a variety of methods for fusion, where the most straightforward method is Bayesian fusion. This method is a simple multiplication of the probabilities for corresponding pixels in the probability images that result from classification. There are a number of techniques that are used for diagnostics and for verification of the correctness of the results obtained from FIST.

**RESULTS**

Figures 1-4 show classification results for LIBS alone, Raman alone and LIBS and Raman fused. Figure 1 shows representative standoff Raman and LIBS spectral signatures collected from representative biological, explosive and chemical materials.

![Figure 1](image1.png)

**Figure 1.** Representative standoff LIBS (A.) and Raman (B.) CBE spectra.

A robust indicator of classification performance among the spectra is indicated by the confusion matrix shown in Figure 2. Under the conditions employed here (spectral range: 200-850 nm; 8 PCs for LIBS data and spectral range: 400-1600 cm⁻¹; 8 PCs for Raman data), we observed 97.3% predictive performance for LIBS data and 100% predictive performance for Raman.
To obtain a detailed understanding of each spectrum's relation to all the others in the library, a dendrogram is used (Figure 3). First, PCA is performed on the library, reducing each spectrum to only 8 PC scores. Each spectrum can then be represented by a 8-point reduced spectrum. Using a simple Euclidean distance metric, each reduced spectrum is compared against every other, and all the pair-wise distance values are stored as a dissimilarity matrix. These distance values are used to create a hierarchical cluster tree by successively determining pairs of nearest neighbors, using the average distance metric to determine proximity between neighboring clusters.
Figure 3. Dendrograms for LIBS (A.) and Raman (B.) data.

Figure 4 shows the combined, automated Raman and LIBS fusion results. Each individual square in the figure is representative of either a LIBS or a Raman spectrum. For each class, there were 10 spectra used. The classification “image” is perfect when all of the squares are white. Misclassifications are indicated by gray squares. These classification results are based on a threshold that is automatically determined in the fusion software. Adjusting the threshold manually may result in fewer misclassifications, but requires human intervention. The confusion matrices shown in Figure 3 are not based on a threshold, but rather a measure of likeness to a particular class. These fusion results are significant in that the combined result provides an improved classification performance compared to either method alone.

Figure 4. Individual Raman, individual LIBS and fused LIBS/Raman classification result.
CONCLUSIONS

LIBS and Raman have both demonstrated individually the ability to detect, discriminate and identify CBE threat and common confusant candidates at standoff distances. Raman is inherently specific to molecular makeup while LIBS is more sensitive and excels in tracking the elemental inventory of the target materials. Data fusion of the orthogonal technologies provides improved discrimination over either method alone when using an autonomous data fusion approach. Combining the two orthogonal technologies into a common platform and using a data fusion engine to process the data holds real promise as a fieldable sensor for CBE defense.

ACKNOWLEDGEMENTS

Funding for standoff LIBS residue explosives detection has been provided by the Office of the Secretary of Defense, Rapid Reaction Technology Office (OSD/RRTO). The application of standoff LIBS to chemical and biological materials analysis has been supported by the Environmental Protection Agency (EPA) and with internal ARL funds. Standoff Raman detection has been funded by DOD, US ARO contract No. W911NF-06-C-0098.

REFERENCES


