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| REPORT DOCUMENTATION PAGE | Form Approved OMB NO. 0704-0188 |

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggesstions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA, 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any oenalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.
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| 1. REPORT DATE (DD-MM-YYYY)<br>07-04-2011 | 2. REPORT TYPE<br>Final Report | 3. DATES COVERED (From - To)<br>1-Oct-2008 - 31-Dec-2010 |

| | |
|---|---|
| 4. TITLE AND SUBTITLE<br>Laser Induced Breakdown Spectroscopy (LIBS) | 5a. CONTRACT NUMBER |
| | 5b. GRANT NUMBER<br>W911NF-08-C-0094 |
| | 5c. PROGRAM ELEMENT NUMBER<br>622618 |
| 6. AUTHORS<br>John Plumer, Richard Russo | 5d. PROJECT NUMBER |
| | 5e. TASK NUMBER |
| | 5f. WORK UNIT NUMBER |

| | |
|---|---|
| 7. PERFORMING ORGANIZATION NAMES AND ADDRESSES<br>A3Technologies, LLC<br>A3 Technologies, LLC<br>1201 Technology Drive<br>Aberdeen, MD 21014 - | 8. PERFORMING ORGANIZATION REPORT NUMBER |
| 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)<br>U.S. Army Research Office<br>P.O. Box 12211<br>Research Triangle Park, NC 27709-2211 | 10. SPONSOR/MONITOR'S ACRONYM(S)<br>ARO |
| | 11. SPONSOR/MONITOR'S REPORT NUMBER(S)<br>55024-EG.1 |

12. DISTRIBUTION AVAILIBILITY STATEMENT

Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

LIBS (Laser Induced Breakdown Spectroscopy) and Raman Spectroscopy address all five threats (CBRNE) for security and force protection applications. Military and civilian First Responders could utilize LIBS for CB, explosive hazards, suspicious powder, and hazardous spill analysis. Industrial applications include hazardous materials, quality control and process monitoring. Importantly, LIBS can identify innocuous materials on-site and in real-time saving time and money in response to hazardous material spills. A3 Technologies, LLC established

15. SUBJECT TERMS

LIBS, CBRN&E Detection,Lasers,Spectroscopy,First Responders

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| 16. SECURITY CLASSIFICATION OF: | | | 17. LIMITATION OF ABSTRACT | 15. NUMBER OF PAGES | 19a. NAME OF RESPONSIBLE PERSON<br>Richard Russo |
| a. REPORT<br>UU | b. ABSTRACT<br>UU | c. THIS PAGE<br>UU | UU | | 19b. TELEPHONE NUMBER<br>925-330-1431 |

Standard Form 298 (Rev 8/98)
Prescribed by ANSI Std. Z39.18

## Report Title

Laser Induced Breakdown Spectroscopy (LIBS)

## ABSTRACT

LIBS (Laser Induced Breakdown Spectroscopy) and Raman Spectroscopy address all five threats (CBRNE) for security and force protection applications. Military and civilian First Responders could utilize LIBS for CB, explosive hazards, suspicious powder, and hazardous spill analysis. Industrial applications include hazardous materials, quality control and process monitoring. Importantly, LIBS can identify innocuous materials on-site and in real-time saving time and money in response to hazardous material spills. A3 Technologies, LLC established LIBS based sensing as a commercial technology; four prototype LIBS based devices (laboratory, Pelicase. hand-held and stand-off ) were developed and evaluated againat 1st responder securities applications, forensic and commercial applications.

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## List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

### (a) Papers published in peer-reviewed journals (N/A for none)

ctrochimica Acta Part B: Atomic Spectroscopy, doi:10.1016/j.sab.2010.08.004, published online, Sept. 6, 2010. Refereed Paper -T Trejos, A Flores and JR. Almirall, Micro-spectrochemical analysis of document paper and gel inks by laser ablation inductively coupled plasma mass spectrometry and laser induced breakdown spectroscopy, Spe

T Trejos, A Flores and JR. Almirall, Micro-spectrochemical analysis of document paper and gel inks by laser ablation inductively coupled plasma mass spectrometry and laser induced breakdown spectroscopy, Spectrochimica Acta Part B: Atomic Spectroscopy, doi:10.1016/j.sab.2010.08.004, published online, Sept. 6, 2010.

**Number of Papers published in peer-reviewed journals:** 2.00

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### (b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

**Number of Papers published in non peer-reviewed journals:** 0.00

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### (c) Presentations

**Number of Presentations:** 0.00

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### Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

1. *Schenk, E.R. "Elemental analysis of unprocessed cotton by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and laser-induced breakdown spectroscopy (LIBS): a forensic application of geographic provenancing", Graduate Student Association Forum, Florida International University, March 2010 Miami, FL.

2. *Trejos, T. and Almirall J.R. "Lasers: avances tecnológicos en la comparación e identificación de documentos dudosos", III Conferencia Internacional Educativa en Ciencias Forenses CAD-IAI San Jose, Costa Rica, May 2010.
3, *Trejos, T. and Almirall J.R. Comparison of the capabilities of LIBS and LAICPMS for the forensic analysis of paper and gel ink, Pittsburgh Conference, Orlando, FL, Feb. 2010

4. Trejos, T. and *Almirall J.R. Forensic analysis of inks by Laser Induced Breakdown Spectrometry (LIBS) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) , AAFS Conference, Seattle, WA, Feb. 2010.
5. J. J. Gonzalez*1, A. A. Bolshakov2, J. Yoo2, L. J. East3, D. Wong3, D. Oropeza1, and R. Russo*1. 1Lawrence Berkeley National Laboratory, 2Applied Spectra, Inc., and 3A3 Technologies. Precision assessment of a commercial Laser Induced Breakdown Spectroscopy (LIBS) instrument based on the analysis of metal samples. Winter Plasma Conference. January. Florida. 2010
6. Jhanis J. Gonzalez1, Dayana D. Oropeza1, Jong Yoo2, Richard E. Russo,1 Femtosecond Laser Ablation Inductively Coupled Plasma Mass Spectrometry: The ultrafast road to routine solid samples chemical analysis, PITCON. Florida. March. 2010
7. Jeremiah J. Remus1, Russell Harmon2, Jhanis Gonzalez3, Diane Wong4, Jennifer Gottfried5, Dirk Baron6,, 1Clarkson University, 2ARL Army Research Office, 3Applied Spectra Inc., 4A3 Technologies LLC, 5Army Research Laboratory, 5California State University – Bakersfield, 1Clarkson University, Signal Processing Analysis of Factors Affecting LIBS-Based Obsidian Artifact Source Identification, LIBS 2010- September 13-17 Memphis, TN.
8. Katrina Shughrue1, Keith Hilferding1, Richard R. Hark1, Jeremiah J. Remus2, Russell Harmon3, Michael A. Wise4, Lucille J. East5, Jhanis Gonzalez6 and Dayana D. Oropeza7, 1Department of Chemistry, Juniata College, Huntingdon, PA 16652, USA; 2 Department of Electrical and Computer Engineering, Clarkson University, Potsdam, NY 13699, USA;3ARL Army Research Office, PO Box 12211, Research Triangle Park, NC 27709, USA; 4Division of Mineralogy, Smithsonian Institution, P.O. Box 37012, MRC 119, Washington, D.C. 20013, USA;5A3 Technologies LLC, 1200 Technology Drive, Aberdeen, MD 21001, USA; 6Applied Spectra Inc, 46661 Fremont Boulevard, Fremont, CA 94538, USA;7Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA, LIBS Analysis of Conflict Minerals: The Example of Columbite-Tantalite, LIBS 2010- September 13-17 Memphis, TN
9. Alexander A. Bolshakov,1,2 Jhanis J. Gonzalez,2 Jong H. Yoo,2 Chunyi Liu,2 John R. Plumer,1 Richard E. Russo, Material composition analysis and surface/depth profiling with a laser-induced breakdown spectrometer (LIBS), PITCON. Florida. March 2010
10. Alyssa M. Kress1, Lucille J. East2, Richard R. Hark1, Jhanis Gonzalez3,1Department of Chemistry, Juniata College, Huntingdon, PA 16652, USA2A3 Technologies, LLC, Aberdeen, MD 21001, USA; 3Applied Spectra, Inc., Fremont, CA 94538, USA, Analysis of Silver Coins by Laser-Induced Breakdown Spectroscopy (LIBS), LIBS 2010- September 13-17 Memphis, TN
11. Jennifer L. Gottfried1. Kimberly Weber2, Dana Short2, Tyler Goralski2, Stephanie McCaslin2, Rich Rossman2. Diane Wong3,1U.S. Army Research Laboratory. 2Battelle. 3A3-Technologies , Discrimination of Biological and Chemical Threat Simulants in Residue Mixtures on Multiple Substrates, LIBS 2010- September 13-17 Memphis, TN
13. Jhanis J. Gonzalez, Jong Yoo, Chunyi Liu, and Richard E. Russo. Applied Spectra, Inc. Fremont. CA, 94538, Semi-Qualitative Beryllium analysis by Laser Induced Breakdown Spectroscopy (LIBS), ASTM-Symposium on Surface and Dermal Sampling. October 14-15. San Antonio. Texas. 2010.
14. *East, L.J., Hark, R.R., Hilferding, K., Trejos, T., Almirall, J. "Analysis of paper samples by two identical-model commercial laser-induced breakdown spectroscopy (LIBS) instruments," LIBS 2010, 6th International Conference on Plasma Spectroscopy and Applications, Memphis, TN, September 13-17, 2010.
15. *Cahoon, E., Almirall, J.R. "Analysis of Metals in Solutions of Low Volumes Using LIBS", LIBS 2010, 6th International Conference on Plasma Spectroscopy and Applications, Memphis, TN, September 13-17, 2010.
16. *Schenk, E.R. and Almirall, J.R. "Elemental analysis of cotton of LIBS and LA-ICP-AES", LIBS 2010, 6th International Conference on Plasma Spectroscopy and Applications, Memphis, TN, September 13-17, 2010.
17. *Jantzi, S.C. and Almirall, J.R. "Quantitative analysis of trace metals in soil samples using LIBS for forensic applications", LIBS 2010, 6th International Conference on Plasma Spectroscopy and Applications, Memphis, TN, September 13-17, 2010.

18. LIBS 2008 (Berlin)

"Application of Laser-induced Breakdown Spectroscopy (LIBS) for the Effective Management of Hazardous Materials Incidents"
Summary: First Responders are routinely faced with the challenge of rapidly and reliably identifying unknown substances encountered in a wide range of field conditions. An extensive array of field tests and portable instrumentation have been developed and/or adapted for the purpose of detecting the presence of chemical, biological, nuclear, radiological, or explosive (CBNRE) threats, toxic industrial materials (TIM's), pharmaceuticals, and illegal drugs, along with the benign materials (e.g., harmless white powders) commonly encountered during First Responder operations. Laser-induced breakdown spectroscopy (LIBS) is a sensor technology that could allow First Responders to manage hazardous materials incidents more efficiently, effectively, and economically than previously possible using multiple pieces of

equipment. The technique provides nearly instantaneous elemental analysis of solids, liquids and gases, does not require any sample preparation, and is amenable for use as a robust, man-portable device in the field in either stand-off or stand-near modes. LIBS utilizes a broadband spectrometer to collect the light emitted by a microplasma which is formed when a pulsed laser is used to interrogate a target. The data obtained is subjected to chemometric analysis and comparison against a spectral library to facilitate rapid identification of the material and provide the First Responder with the information vital for making crucial decisions in a timely manner. There are currently no commercially available LIBS systems that are designed specifically for use by the First Responder community. This presentation will explore some of the issues related to the development of suitable instrumentation and libraries as well as incorporation of the technique into existing First Responder protocols.

19. EMSLIBS 2009 (Italy)

"Evaluation of Laser-induced Breakdown Spectroscopy (LIBS) Instruments for First Responder Applications"
Richard R. Hark1, Adam L. Miller2, Kristin M. Beiswenger1, Alyssa M. Kress1
1Department of Chemistry, Juniata College, Huntingdon, PA 16652, USA
2Huntingdon County Emergency Management Agency, Huntingdon, PA 16652, USA
The challenge to rapidly and reliably identify unknown substances encountered in a wide variety of field conditions is a task routinely faced by First Responders. For the majority of operations multiple instruments must be employed currently to assist response managers in making decisions regarding protective actions and force protection. An extensive array of wet chemical tests and portable instrumentation have been developed and/or adapted for the purpose of detecting the presence of hazardous materials of interest. These include chemical, biological, nuclear, radiological, or explosive (CBNRE) threats, toxic industrial materials (TIM's), pharmaceuticals, and illegal drugs, along with benign substances (e.g., harmless white powders) commonly encountered during First Responder operations. Laser-induced breakdown spectroscopy (LIBS) is a sensor technology that has the potential to introduce a paradigm shift in the way First Responders manage hazardous materials incidents. There are currently no LIBS systems designed specifically for use by the First Responder community that are being sold commercially. The challenge is to transition current laboratory-based LIBS systems which have already been shown to be capable of identifying hazardous materials to fieldable instruments capable of operating under austere, uncontrolled response environments. This presentation describes a preliminary evaluation of two alpha-version LIBS instruments designed forFirst Responders. A 15-30 m standoff system and a fully self-contained unit housed in a Pelican™ case (A3 Technologies, LLC, Aberdeen, MD, USA) were evaluated against a suite of relevant materials and First Responder requirements. Our examination seeks to understand if the current LIBS technologies will assist responders to more efficiently, effectively, and economically mitigate the risks and consequences of hazardous materials incidents.

20. LIBS 2010 (Memphis)

"LIBS Analysis of Conflict Minerals: The Example of Columbite-Tantalite"

Katrina Shughrue1, Keith Hilferding1, Richard R. Hark1, Jeremiah J. Remus2, Russell Harmon3,
Michael A. Wise4, Lucille J. East5, Jhanis Gonzalez6 and Dayana D. Oropeza7

1Department of Chemistry, Juniata College, Huntingdon, PA 16652, USA
2 Department of Electrical and Computer Engineering, Clarkson University, Potsdam, NY 13699, USA
3ARL Army Research Office, PO Box 12211, Research Triangle Park, NC 27709, USA
4Division of Mineralogy, Smithsonian Institution, P.O. Box 37012, MRC 119, Washington, D.C. 20013, USA
5A3 Technologies LLC, 1200 Technology Drive, Aberdeen, MD 21001, USA
6Applied Spectra Inc, 46661 Fremont Boulevard, Fremont, CA 94538, USA
7Lawrence Berkeley National Laboratory. 1 Cyclotron Road, Berkeley, CA 94720, USA
Niobium and tantalum are two rare metals of high commercial value. Niobium (Nb) is used in the manufacture of hardened steel, superalloys, and superconducting magnets for applications like medical magnetic resonance imaging, while tantalum (Ta) is used in consumer electronics, mainly for capacitors<http://en.wikipedia.org/wiki/Capacitor> and the high-power resistors<http://en.wikipedia.org/wiki/Resistor> used in portable telephones<http://en.wikipedia.org/wiki/Portable_telephone>, personal computers<http://en.wikipedia.org/wiki/Personal_computer>, and automotive electronics<http://en.wikipedia.org/wiki/Automotive_electronics>. The primary natural occurrence of Nb and Ta is in the complex oxide minerals columbite and tantalite, which form a solid-solution series having the general composition [Fe,Mn)(Nb,Ta)2O6]. Because central Africa is a major source for columbite-tantalite ore, its illicit export from the Democratic Republic of Congo is thought to be responsible for financing the ongoing civil conflicts in this region. Determining the chemical composition of a columbite-tantalite ore is one means of ascertaining its provenance. Laser induced breakdown spectroscopy (LIBS) is an analytical technique that is simultaneously sensitive to all elements with a single laser shot. Thus, LIBS offers an attractive means of rapidly distinguishing different geographic sources for a mineral because the LIBS plasma emission spectrum provides a 'chemical fingerprint' of any material in real-time. To test this idea for columbite-tantalite, an examination of three samples sets from spodumene-bearing granite-associated pegmatite fields in Yellowknife,

Canada; Jacumba, California; and Brunswick, Maine was undertaken using a RT100-HP LIBS instrument (A3 Technologies LLC/Applied Spectra, Inc. with a 90mJ, 1064 Nd:YAG laser, and CCD detector). LIBSspectra were collected at high and low resolution over the 240-600nm wavelength range. Individual spectral emission lines and line ratios for Fe, Mn, Nb, Ta, W, Ti, and Zr as well as broad and narrowband spectra were used to determine if the provenance of the columbite-tantalite samples, all with quite similar LIBS spectra, could be discriminated using advanced multivariate statistical techniques. The LIBS results were compared with Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) data obtained from the same sample suite. LIBS analysis of matrix minerals such as quartz and mica, present on some of the samples, was also performed. Principal Component Analysis (PCA) demonstrates that some of the data shows strong clustering. Partial Least Squares Discriminant Analysis (PLS-DA) of combined narrowband data (approximately 240-280 and 315-355nm) allows 100% sample-level classification using a highest confidence approach. These promising preliminary results suggest that additional work with a larger, more geographically diverse data set is warranted.

PACIFICHEM 2010 (Honolulu)
2010.

21. Winter Plasma Conference. January. Florida. 2010

"Precision assessment of a commercial Laser Induced Breakdown Spectroscopy (LIBS) instrument based on the analysis of metal samples."

J. J. Gonzalez*1, A. A. Bolshakov2, J. Yoo2, L. J. East3, D. Wong3, D. Oropeza1, and R. Russo*1.
1Lawrence Berkeley National Laboratory,
2Applied Spectra, Inc., and
3A3 Technologies.

Abstract: The need to analyze diverse solid samples, including environmental wastes, geological materials, biological tissues, metals, thin paint coatings, semiconductors, etc., without laborious dissolution methods has driven the advancement of laser ablation based analytical techniques. In particular, one branch of such techniques known as Laser Induced Breakdown Spectroscopy (LIBS) offers the unique advantages of rapid, in situ, multi-element analyses.

Laser induced breakdown spectroscopy (LIBS) is a simple technique that uses a tightly focused laser beam to generate a small spark on the surface of a target. This spark (microplasma) contains excited elemental and molecular species that were ablated from the surface of the target.

It is well known that the measurement quality and analytical figures of merit (precision, accuracy, limit of detection, etc) for LIBS are strongly dependent on the environment conditions, laser parameters, and physical-chemical properties of samples. In this study, we assessed some of these figures of merit for a diverse group of sample matrices based on a commercial LIBS system (RT100-HP from Applied Spectra/A3 Technologies).

21. PITCON. Florida. March. 2010

"Material composition analysis and surface/depth profiling with a laser-induced breakdown spectrometer (LIBS)"

Alexander A. Bolshakov,1,2 Jhanis J. Gonzalez,2 Jong H. Yoo,2 Chunyi Liu,2 John R. Plumer,1 Richard E. Russo1,2
1 A3 Technologies LLC, 1200 Technology Dr., Aberdeen, MD 21001
2 Applied Spectra Inc., 46661 Fremont Blvd., Fremont, CA 94538

Abstract: Laser induced breakdown spectroscopy (LIBS) offers rapid localized chemical analysis with high spatial resolution in lateral and depth profiling, without a need for sample preparation. Diverse solid or liquid samples including environmental, biological, geological, industrial, forensic, food, thin coatings, semiconductors, etc., can be analyzed. LIBS also can perform remotely from a distance up to ~100 meters or greater depending on the optics. These features motivated utilization of LIBS for industrial and security applications as several commercial LIBS systems became available.

We applied principal component analysis (PCA) and partial least square (PLS) procedures to discriminate and identify a large variety of organic and inorganic samples. Our data illustrate how LIBS analyzers can answer a multitude of real-world needs for rapid chemical analysis. Examples include the determination of lead in paint and children’s toys; analysis of different solder materials; quality control of fiberglass panels; discrimination of coffee beans from different vendors; discrimination of generic and brand-name drugs, etc. Localized microanalysis with lateral and depth profiling is easily realized. Either traditional one-element calibration procedures or multivariate chemometrics can be applied for quantitative determination of elements in numerous samples.

We illustrate effectiveness of LIBS for security applications with the results obtained in field testing of the 50-meter standoff LIBS rasterizing detector.

22. "Femtosecond Laser Ablation Inductively Coupled Plasma Mass Spectrometry: The ultrafast road to routine solid samples chemical analysis."

Jhanis J. Gonzalez1, Dayana D. Oropeza1, Jong Yoo2, Richard E. Russo1.
1Lawrence Berkeley National Laboratory. Berkeley. CA. 94720
2Applied Spectra, Inc. Fremont. CA. 94538

Abstract: Laser ablation sampling for inductively coupled plasma mass spectrometry (LA-ICP-MS) has become one of the most popular approaches for analysis of solid samples. When compared with conventional dissolution techniques, laser ablation offers direct characterization of solids, reduced risk of contamination and sample loss, analysis of very small samples not separable for solution analysis, rapid analysis, and spatial resolution. Chemical analysis using laser ablation is a straightforward process in which a high energy laser pulse is used to transform a portion of a solid sample into aerosol for subsequent chemical analysis. The use of fe¬¬mtosecond laser ablation is based on improved performance metrics by controlling the amount of ablated material, particle size distribution, matrix dependence, and fractionation. Femtosecond laser ablation sampling into the ICP-MS has been shown to provide good chemical analysis precision and accuracy by reducing systematic errors related to the particle size distribution and resultant spikes in the ICP-MS response. A relaxation of matrix dependence also has been shown for the analysis of wide range of sample matrices when using femtosecond laser pulses. This paper presents an overview of the current research state in femtosecond laser ablation for chemical analysis and describes recent data using femtosecond ablation sampling for ICP-MS.

LIBS 2010- September 13-17 Memphis, TN. Deadline May 31 2010

23. "Signal Processing Analysis of Factors Affecting LIBS-Based Obsidian Artifact Source Identification"

Jeremiah J. Remus1, Russell Harmon2, Jhanis Gonzalez3, Diane Wong4, Jennifer Gottfried5, Dirk Baron6
1Clarkson University,
2ARL Army Research Office,
3Applied Spectra Inc.,
4A3 Technologies LLC,
5Army Research Laboratory,
5California State University – Bakersfield

Abstract: In a companion study (Harmon et al.), we present results of our efforts to develop methods for identifying the provenance, i.e. source of origination, of obsidian artifacts from California. A significant focus of that most recent work was the effect of LIBS laser wavelength, based on a comparison of classification performance for two data sets collected for the same set of obsidian samples with different LIBS laser systems (266 nm and 1064 nm wavelengths). This study addresses factors in that study that affected performance from a statistical signal processing and classification perspective. The outcomes of classification experiments and high-dimensional visualization techniques were used to investigate the link between effects seen in the data and subsequent classification performance as a function of three parameters of the LIBS setup and data collection: laser wavelength, the number of pre-collection 'cleansing' shots, and the number of shots recorded from each sample. The results of this study indicate that data collected using the two different laser wavelengths, as expected, displayed a wavelength-dependency in the observed emission spectra due to differences in laser light interaction with the obsidian samples. However, the results of the classification analysis also suggest that, despite the strong differences observed in the measured spectra when using lasers of different wavelengths, there is still significant information available for identification of obsidian provenance using either LIBS setup. Preliminary analysis of the potential for fusion using LIBS data collected at multiple wavelengths will also be presented. The results of the current study suggest the potential capabilities of chemometrics and signal processing techniques applied to broadband LIBS analysis when developing methods for sample classification and identification, even in suboptimal conditions of LIBS data collection.

24. "LIBS Analysis of Conflict Minerals: The Example of Columbite-Tantalite"

Katrina Shughrue1, Keith Hilferding1, Richard R. Hark1, Jeremiah J. Remus2, Russell Harmon3, Michael A. Wise4, Lucille J. East5, Jhanis Gonzalez6 and Dayana D. Oropeza7
1Department of Chemistry, Juniata College, Huntingdon, PA 16652, USA;
2 Department of Electrical and Computer Engineering, Clarkson University, Potsdam, NY 13699, USA;
3ARL Army Research Office, PO Box 12211, Research Triangle Park, NC 27709, USA;
4Division of Mineralogy, Smithsonian Institution, P.O. Box 37012, MRC 119, Washington, D.C. 20013, USA;
5A3 Technologies LLC, 1200 Technology Drive, Aberdeen, MD 21001, USA;
6Applied Spectra Inc, 46661 Fremont Boulevard, Fremont, CA 94538, USA;
7Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA

Abstract: Niobium and tantalum are two rare metals of high commercial value. Niobium (Nb) is used in the manufacture of hardened steel, superalloys, and superconducting magnets for applications like medical magnetic resonance imaging, while tantalum (Ta) is used in consumer electronics, mainly for capacitors and the high-power resistors used in portable telephones, personal computers, and automotive electronics. The primary natural occurrence of Nb and Ta is in the complex oxide minerals columbite and tantalite, which form a solid-solution series having the general composition [Fe,Mn)(Nb,Ta)2O6]. Because central Africa is a major source for columbite-tantalite ore, its illicit export from the Democratic Republic of Congo is thought to be responsible for financing the ongoing civil conflicts in this region. Determining the chemical composition of a columbite-tantalite ore is one means of ascertaining its provenance.

Laser induced breakdown spectroscopy (LIBS) is an analytical technique that is simultaneously sensitive to all elements with a single laser shot. Thus, LIBS offers an attractive means of rapidly distinguishing different geographic sources for a mineral because the LIBS plasma emission spectrum provides a ‘chemical fingerprint’ of any material in real-time. To test this idea for columbite-tantalite, an examination of three samples sets from spodumene-bearing granite-associated pegmatite fields in Yellowknife, Canada; Jacumba, California; and Brunswick, Maine was undertaken using a RT100-HP LIBS instrument (A3 Technologies LLC/Applied Spectra, Inc. with a 90mJ, 1064 Nd:YAG laser, and Avantes spectrometer) to collect LIBS spectra over the 240-700nm wavelength range. The spectral emission lines and line ratios for Fe, Mn, Fe/Mn, Nb, Ta, Nb/Ta, W, Ti, Ti/W, and Zr were used to determine if the provenance of the columbite-tantalite samples, all with quite similar LIBS spectra, could be discriminated using advanced multivariate statistical techniques.

## 25. "Analysis of Silver Coins by Laser-Induced Breakdown Spectroscopy (LIBS)."

Alyssa M. Kress1, Lucille J. East2, Richard R. Hark1, Jhanis Gonzalez3
1Department of Chemistry, Juniata College, Huntingdon, PA 16652, USA
2A3 Technologies, LLC, Aberdeen, MD 21001, USA;
3Applied Spectra, Inc., Fremont, CA 94538, USA

Abstract: Silver coins were first struck in the United States in 1794 when banks and merchants brought metals to the Philadelphia Mint for coinage. These metals mostly originated from foreign coins, as well as bullion from mines and refineries. Initially, the depositor was able to request the denomination to be minted. This led to erratic production because depositors favored large denominations causing the smaller denominations to become essentially worthless and obsolete. With the Coinage Act of February 21, 1853, the government placed regulations on silver coinage and defined values for the coins regardless of composition. This arrangement later lead to disputes over face value that persisted until the use of silver for coinage was discontinued in 1970.

Some numismatists choose to accumulate their collection on the basis of a coin’s metallurgical composition, such as only collecting gold, silver, copper, or platinum coins. For these collectors especially, accurately knowing the chemical make-up of a coin is important to verify authenticity. However, a main concern for collectors is that many analytical techniques applicable for analysis of coins are unacceptably destructive which lowers the value of the coin.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has successfully been applied to the analysis of coins without significant damage and at very low detection limits for trace elements. Unfortunately, this technique requires specialized training and involves expensive instrumentation. Laser-induced breakdown spectroscopy (LIBS) has the potential to distinguish coins based on their chemical composition and trace elements more quickly and cost effectively, without causing considerable damage. Coins from the United States and foreign mints, dating predominantly from the mid-nineteenth to mid-twentieth centuries and containing varying amounts of silver (Figure 1), were studied using an RT100-HP LIBS instrument

## 26. "Discrimination of Biological and Chemical Threat Simulants in Residue Mixtures on Multiple Substrates"

Jennifer L. Gottfried1. Kimberly Weber2, Dana Short2, Tyler Goralski2, Stephanie McCaslin2, Rich Rossman2. Diane Wong3
1U.S. Army Research Laboratory.
2Battelle.
3A3-Technologies

Laser-induced breakdown spectroscopy (LIBS) is a promising technique for detection of chemical and biological warfare agents in the field by military or first responder personnel. LIBS can be used to probe both the organic and inorganic constituents of solid/liquid/aerosol samples in realtime with no sample preparation, and therefore has the potential to serve as an early warning system to trigger analysis by confirmatory, but more time-consuming sensors. Our laboratory, as well as many others, has generated increasingly promising results with regards to chemical and biohazard detection and identification.1-3 Much of the progress is due to the improvements in the use of advanced chemometric techniques, which have converted LIBS from just an “elemental detector” to a versatile molecular and biomaterial sensor. Residue samples of biological and chemical threat simulants were prepared on polycarbonate, stainless steel, and aluminum foil by Battelle Eastern Science and Technology Center. LIBS spectra were collected by Battelle on a LIBS Pelicase (PL100-GEO) instrument developed by A3 Technologies. In this paper, the chemometric analysis of the Battelle data at the U.S. Army Research Laboratory (ARL) will be

presented. The simulant samples tested include Bacillus atrophaeus spores, Escherichia coli, MS-2 bacteriophage, _-Hemolysin from Staphylococcus aureus, 2-chloroethyl ethyl sulfide (CEES), and dimethyl methylphosphonate (DMMP). Luria broth, Phosphate Buffered Saline (PSA) with 1% Bovine Serum Albumin (BSA) and Chloroform served as inoculation controls. Models based on partial least squares discriminant analysis (PLSDA) were developed based on the full broadband spectra and on input variables derived from only the relevant emission lines. The performance of the two types of models for individual substrates and multiple substrates will be compared. In addition, mixtures of the simulants and controls with two interferents, dolomitic limestone and ovalbumin, were tested against the models.

ASTM-Symposium on Surface and Dermal Sampling. October 14-15. San Antonio. Texas. 2010.

27. "Semi-Qualitative Beryllium analysis by Laser Induced Breakdown Spectroscopy (LIBS)"

Jhanis J. Gonzalez, Jong Yoo, Chunyi Liu, and Richard E. Russo.
Applied Spectra, Inc. Fremont. CA, 94538

In recent years, there has been an increased awareness in the health risks associated with toxic metal species as Cadmium (Cd), Lead (Pb), Mercury (Hg), and Beryllium (Be). Due to increasing health risk associated with a certain class of toxic elements, the U.S. Occupational Safety and Health Administration (OSHA) has set a maximum legal limit for employees at the work place to be exposed to these chemical substances. A simple and effective analytical method for both qualitative and quantitative analysis of these toxic metals in ambient air, on surfaces, and in bulk materials is increasingly sought after by health policy regulators, health professionals as well as analytical service labs. In particular, laser ablation as a method to perform solid sampling has received tremendous interest due to its ability to analyze diverse samples without laborious acid dissolution process and generation of toxic acid waste. LIBS (Laser Induced Breakdown Spectroscopy), which is based on emission spectroscopy of the laser ablation generated plasma, has been studied and developed for trace element analysis in various types of solid materials as a rapid, in situ, multi-elemental technique.

The focus of the current work is to develop LIBS for the detection of Beryllium (Be). It has been documented that the inhalation of Beryllium-containing dusts can produce a direct corrosive effect on healthy tissues and may cause a chronic, life-threatening allergic disease called Berylliosis. A test method for determining Beryllium content in soils, rocks, sediments, and fly ashes has been developed by the American Society for Testing and Materials (ASTM) using Ammonium Bifluoride extraction and fluorescence detection1. However, one main drawback of such approach for Be analysis is the laborious and time-consuming sample preparation steps, in addition to the generation of chemical waste from processing samples. LIBS has been tested as an analytical method for determination of Be in air2 and in particle filters3. The results of these studies indicated that LIBS is an appropriate technique for both qualitative and quantitative determination of Be if an appropriate sampling protocol can be developed.

In the current study, the use of commercial LIBS system (RT100-HP, Applied Spectra, Inc., Fremont, CA) was assessed as a screening tool for quick identification of the surface Beryllium (Be) presence above the controlled limit. The surface areas of potential Be contamination were swiped with cotton swabs to collect Be particles. The swabs were then analyzed with a certain set of laser ablation sampling pattern using RT100-HP LIBS instrument. The goal was to determine whether Be signal can be detected from these samples and subsequent correlation of LIBS intensity can be made with concentration values obtained from ICP-OES analysis. A special attention was paid to developing a proper LIBS sampling protocol and data reduction scheme to differentiate samples that has Be concentration above the OSHA limit from those that are safely below it. Along with optimization of laser and detection parameters, other important sampling parameters for establishing LIBS as an effective Be screening method include the pattern of sampled locations on the swab surface, signal averaging scheme, and a number of laser pulses applied per sampled spot.

**Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):** 27

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## Peer-Reviewed Conference Proceeding publications (other than abstracts):

**Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):** 0

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## (d) Manuscripts

Application Note: - “Detection of Lead and Lead-free Solders

**Number of Manuscripts:** 1.00

## Patents Submitted

1. COMBINATION LIBS AND RAMAN ABLATION SYSTEM (Standoff Apparatus)
2. COMBINATION LIBS AND RAMAN ABLATION DATA COLLECTION SYSTEM AND METHOD

## Patents Awarded

## Awards

Awards-Erica Cahoon received second place for Best Student Poster in the LIBS 2010, 6th International Conference on Plasma Spectroscopy and Applications, Memphis, TN, September 13-17, 2010

Awards-Katie Shughrue received a First Place award for her oral presentation at the Landmark Undergraduate Research Symposium. Katie was also invited to speak at the CUR/NCUR function at the Library of Congress on October 27.

## Graduate Students

| NAME | PERCENT_SUPPORTED |
|---|---|
| :Erica Cahoon, PhD student at FIU | 0.10 |
| **FTE Equivalent:** | **0.10** |
| **Total Number:** | **1** |

## Names of Post Doctorates

| NAME | PERCENT_SUPPORTED |
|---|---|
| **FTE Equivalent:** | |
| **Total Number:** | |

## Names of Faculty Supported

| NAME | PERCENT_SUPPORTED | National Academy Member |
|---|---|---|
| Richard Hark | 0.33 | No |
| Jose Almirall | 0.10 | No |
| **FTE Equivalent:** | **0.43** | |
| **Total Number:** | **2** | |

## Names of Under Graduate students supported

| NAME | PERCENT_SUPPORTED |
|---|---|
| **FTE Equivalent:** | |
| **Total Number:** | |

## Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

| | |
|---|---|
| The number of undergraduates funded by this agreement who graduated during this period: ...... | 1.00 |
| The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... | 1.00 |
| The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... | 1.00 |
| Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... | 0.00 |
| Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... | 0.00 |
| The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense ...... | 0.00 |
| The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: ...... | 0.00 |

---

## Names of Personnel receiving masters degrees

NAME

**Total Number:**

---

## Names of personnel receiving PHDs

NAME

**Total Number:**

---

## Names of other research staff

| NAME | PERCENT_SUPPORTED |
|---|---|

**FTE Equivalent:**

**Total Number:**

---

## Sub Contractors (DD882)

1 a. Applied Spectra, Inc.

1 b. 46661 Fremont Blvd.

Fremont CA 945387368

**Sub Contractor Numbers (c):**

**Patent Clause Number (d-1):**

**Patent Date (d-2):**

**Work Description (e):** Develop and construct and modify protype LIBS equipment for testing and potential fielding to 1st

**Sub Contract Award Date (f-1):** 5/12/2008 12:00:00AM

**Sub Contract Est Completion Date(f-2):** 12/31/2010 12:00:00AM

---

1 a. Applied Spectra, Inc.

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**Sub Contract Award Date (f-1):** 5/12/2008 12:00:00AM

**Sub Contract Est Completion Date(f-2):** 12/31/2010 12:00:00AM

---

1 a. Florida International University

1 b. 11200SW 8th ST

Miami FL 33199

**Sub Contractor Numbers (c):**

**Patent Clause Number (d-1):**

**Patent Date (d-2):**

**Work Description (e):** Evaluate and qualify A3 Technologies, LIBS instrumentation for forensic applications

**Sub Contract Award Date (f-1):** 10/8/2009 12:00:00AM

**Sub Contract Est Completion Date(f-2):** 6/1/2010 12:00:00AM

---

1 a. Juniata College

1 b. Juniata College
1700 Moore Street
Huntingdon PA 166522119

**Sub Contractor Numbers (c):**

**Patent Clause Number (d-1):**

**Patent Date (d-2):**

**Work Description (e):** Develop 1st Responder operational, performance and configuration requirements for new LIBS dete

**Sub Contract Award Date (f-1):** 6/1/2007 12:00:00AM

**Sub Contract Est Completion Date(f-2):** 12/31/2010 12:00:00AM

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## Inventions (DD882)

# Scientific Progress

Evaluation of the accuracy, precision and sensitivity of the four developmental products resulting from this program were found to be acceptable for a number of commercial and 1st Responder applications including qualification by the FIU study as a Forensic Analysis instrument ; however the only commercial sales (fourteen to date) have been from the RT-100 for laboratory applications. This is understandable as A3 fully understands the operational, configuration and performance needs of the scientific and analytical marketplace well enough to mature the prototype instrument into commercial item. Round-Robin testing between ASI, FIU, Juniata and A3 demonstrated commonality and reproducibility of results between multiple instruments, this is a major element required by the forensic community.

The Pelicase instrument is currently a Beta+ prototype; the capability of this instrument to operate remotely - on battery power but with performance capabilities equal to the RT-100 is unique the scientific community. A customer is needed to mature this device to a commercial product by providing engineering and design requirements for configuration and performance - to include environmental hardening. In addition, Demonstration & Validation funding will be required to conduct the necessary field trials to mature a commercial design.

A similar development scenario is required to commercialize the Mini-ST instrument, i.e. customer engineering requirements, Demonstration & Validation funding for field trials to mature a commercial design.

The hand-held instrument demonstrated the ability to detect single or double elements of interest specifically to the OSOHA community, additional developmental work is required to benchmark the accuracy and precision capabilities against health standard concentrations. User standards and developmental funding is required to mature this prototype to commercialization.

Initial configurations of both the Pelicase and mini-standoff instruments included an on-board Ramon sensor as well as the LIBS sensor. Preliminary testing with both sensor in both devices showed no clear advantage afforded by the Ramon sensor in the detection of explosives or similar elemental analysis; as such it was dropped from the instruments in afford simpler construction and lower unit costs.

The major barrier to the commercialization of LIBS based field sensors is "purpose-built" components (lasers and spectrometers) designed and built to fit the performance and space configuration of the intended instrument. All demonstration prototypes produced during this program made use of commercial components to build the various instruments. When demand for purpose-built LIBS instruments increases, then economics will support "purpose-built" components that will reduce both size and cost of the final instrument.

# Technology Transfer

# Technical Report

# Title: Laser Induced Breakdown Spectroscopy (LIBS)

Solicitation Number – W911NF – 07 – R – 003

Contract Number – W911NF-08-C-004

U.S. Army RDECOM Acquisition Center

Research Triangle Park Contracting Division

P. O. BOX 12211

Research Triangle Park, NC  27709-2211

**by**
**John Plumer**

**& Richard Russo**

**A3 Technologies, LLC**

**Aberdeen, MD**

**31 March 2010**

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**Formatted:** Centered

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Appendix (2) - Configuration Standard

Appendix (3) - Summary of Papers, Presentations, Posters

Appendix (4) - Patents

# Introduction

## Background

LIBS (Laser Induced Breakdown Spectroscopy) and Raman Spectroscopy address all five threats (CBRNE) for security and force protection applications. Example applications include unexploded ordnance (UXO), Base Realignment and Closure (BRAC), on-site hazardous material monitoring, and soil and water contamination analysis. Military and civilian First Responders could utilize LIBS for CB, explosive hazards, suspicious powder, and hazardous spill analysis. Industrial applications include hazardous materials, quality control and process monitoring. Importantly, LIBS can identify innocuous materials saving time and money in response to chemical spills.

LIBS has become one of the most powerful analytical technologies for real time chemical analysis of diverse and complex samples, including explosives, chem/bio agents and toxic industrial compounds (TICs). LIBS is a relatively simple analytical technology to determine the chemical composition of any sample (solid, liquid or gas); merely point a laser beam at the sample, ablate and ionize to emission, and record the optical spectrum. LIBS provides immediate real-time answers on chemical composition. LIBS is sensitive to all elements in a sample, with typical limits of detection between 10-200 parts per million, and with known enhancement technologies for extending sensitivity when necessary. No sample preparation is needed and no consumables are required. LIBS can be used for contact as well as open path stand-off applications. No other technology can provide these capabilities in a single measurement.

Raman spectroscopy is a molecular based chemical analysis approach, and can provide complementary signature characterization to LIBS measurements. The integration of these two technologies with data fusion will provide improved accuracy for detection (enhanced probability of detection, lower false alarm rates). Closure (BRAC), on-site hazardous material monitoring, and soil and water contamination analysis. Military and civilian First Responders could utilize LIBS for CB, explosive hazards, suspicious powder, and hazardous spill analysis. Industrial applications include hazardous materials, quality control and process monitoring. Importantly, LIBS can identify innocuous materials saving time and money in response to chemical spills.

## A3 Technology goals

1. To interact locally and effectively with the ARL to provide hardware for advancing the Army technical program, create new jobs in MD, produce spectroscopic sensors as defined in the tasks below, and grow the company capabilities to address security and force protection

2. To establish LIBS based sensing as a commercial technology utilized in a variety of off-the-shelf products (COTS) designed to meet detection and characterization requirements for DoD, Federal, commercial and 1st responder securities applications.

## Relevance to the Army

The Army has a need /requirement for a new technology capable of real-time detection of chem/bio and explosive threats in the laboratory and at stand-off distances greater than 30 meters for counter IED detection.

## Approach

The 3 year (FY2007, FY2008, FY2009) funding for this effort was a congressional "earmark" from the state of MD; as such the goals for the program were more than research and subsequent approach for the program was similar to a "Phase III SBIR, that being to first "engineer specific instruments to match well defined User requirements. evaluate the operation, configuration and performance of prototypes then to commercialize the resultant field tested hardware.

The second goal was to establish a commercial capability to fabricate, evaluate and refine the “tailored” laser based systems with single or multiple sensors for military , 1st Responders and commercial Users capable of detecting unknown substances in the field with no sample preparation and with high sensitivity and specificity.

This report describes the three year contract effort, to produce the deliverables and carry-out the commercialization program involved in the creation of a Maryland based enterprise chartered "to address the Security needs of the Federal, DOD and civilian 1st Responders through Engineering, Manufacturing, Support and Training on new sensors for the detection of CBER&N."

The primary tenant for all on-site detection and analysis of unknown materials is to INCREASE to speed and accuracy of the detection of unknown materials, time saves money and lives for 1st Responders.

## Objectives by Year

**The FY07 program** contracted with 1st Responder experts located at Juniata College in Huntingdon PA to develop two representative USER requirements against which of prototype sensors could be evaluated. The first standard was to identify a panel of hazardous and toxic materials that would be candidates likely to be found at a 1s responder incident; the second standard was to be a "incident time-line procedure" that identified key events in typical 1stResponder turn-out and would allow "time-savings" or performance metrics afforded by on-site detection to be evaluated. Evaluation of hardware under an "operational setting" would permit assignment of a higher **Technical Readiness Level reflecting a successful User evaluation - TRL5 or 6.**

The second thrust of the FY2007 program was use existing commercial LIBS systems as a point of departure for engineering 3 distinct prototype instruments including integration of Raman with LIBS systems. The system designs were to be based on user performance and configuration requirements, including recommendations from civilian First Responders.

The FY2007 year was executed as a sub-contractor (subcontract # 212756) to Battelle as the prime contractor to ARL - W9CRB-04-D-0016/DO51.

A sub-contract was awarded to Applied Spectra Inc. (ASI) in Fremont CA to carry-out the bulk of the engineering development, soft-ware development  and prototype instrument fabrication for the life of the program. A second sub-contract was awarded to Juniata College to define the operational, configuration and performance requirements for instrumentation to support the 1 st Responders.

**The FY2008 program**

### Company Development

The company goal for FY2008 was to continue to grow the A3 Technologies, LLC facilities and infrastructure, increase staffing and continue product development as measured by the following:

- A3 will be a self-sufficient MD based company by the end of FY2009 to include
    - **a.** Commercial and military products
    - **b.** GSA (and 1st Responder procurement lists)
    - **c.** Expanded staff to include software and interface engineers
- Expanded company interactions within the MD technical and business community
    - **a.** Expand outside of military-only activities to environment and energy and academic applications
    - **b.** Join and interact with MD business development associations
- In FY2008, A3 will move to a new facility capable of applications engineering, stand-off testing and manufacturing.
- Develop the capability to monitor and respond to national technical needs and requirements and MD specific needs and opportunities.

## Contract Deliverables for FY2008

The goal for FY08 was to utilize the 3 specific devices produced at the end FY2007 as a point of departure and modify/mature these items to achieve the following capabilities:

- **Two each Handheld LIBS only sensors** with the following capability
    - One each - Single threat detection capability -Lead or Asbestos detection
    - One each - **Explosive threat detection only – 1st responder requirement**
    - Battery power
    - Wireless control and feedback to central computer
    - Configurable to separate components for robotic applications
- **One each LIBS/Raman sensor** at Alpha stage of development
    - Limited library < 50 materials from the Common Hazard Index(CHI)
    - Limited durability to environmental conditions
- **One each LIBS/Raman sensor** at Beta stage of development
    - Expanded library >50 materials from the Common Hazard Index
    - Demonstrated improved accuracy over Alpha device (enhanced probability of detection, lower false alarm rates) through data fusion to user performance requirements
    - Durable hardware designed to user operational requirements and Mil-STD 810F guidance
- **One each mini-ST-LIBS /Raman system** at Beta stage of development

  - Single laser/spectrometer components
  - Alpha testing with <50 threat materials from CHI
  - Beta testing with >50 threat materials form CHI
  - Demonstrated improved accuracy over Alpha device (enhanced probability of detection, lower false alarm rates) through data fusion to user performance requirements
  - Durable hardware designed to user operational requirements and Mil-STD 810F guidance

**Microwave Enhanced LIBS Sensor**

- The goal for the second year of this task was to produce and incorporate a microwave cavity into an A3 LIBS sensor and evaluate performance enhancements. Sub-tasks are as follows;
  - Combined microwave device with A3 LIBS sensor
  - Demonstration of enhanced "analytical figures of merit" for selected NESTT explosives
- **One each training module** for each user group (military and 1st Responder) and each LIBS/Raman device (mini-ST-LIBS and Pelicase X military and 1st responder)
- **One each training session** for selected device and user group.

In addition, Carry out product development efforts to include the evaluation of the above 3 products through Beta testing against a defined Operational Test and Evaluation Plan consisting of:

- Specific measures of effectiveness for Military and 1st Responder requirements (what does it do)
- Specific and defined measures for Critical Operational Effectiveness and Suitability (how well does it do it and under what conditions)

Produce a "best and final version" of three specific **Objective Systems** (handheld, mini-ST and Pelicase) utilizing **purpose built components and a common computer system** where feasible.

- Develop limited production design packages for manufacturing of products

**The FY2009 program**

## Company Development

A3 planned to accomplish the following by the end of the contract in 2009:

- A3 will have an established commercial and DoD product line based on completed product Beta testing
- A3 will have an established assemble/manufacturing operation at the 1201 Technology drive facility
- A3 will have an established training capability offering courses covering field and forensic operation of A3 devices
    - A3 will provide on-site college courses in conjunction will Juniata College and Dr Hark
    - Develop a hardware/technology/ academic training partnership with FIU
    - Develop technology and systems integration for common components with ASI
- A3 will attempt to foster the out-side development of purpose-built electronic components (lasers and spectrometers) for integration into the company products
- A3 will develop new partnerships with other DoD and Federal agencies i.e. EPA and OSHA as well local environment groups promoting the clean-up Bay and watershed recourses
- Develop analytical services capability for hazardous materials identification on site and laboratory
- Develop manufacturing product lines

## Contract Deliverables

- Continue maturing product designs based on iterative user beta tests conducted in FY08
- Develop and exploit new technologies for LIBS based products to include:
    - Double pulse lasers
    - Microwave enhanced LIBS system (LAMPS)
    - Develop understanding of parameter space requirements to achieve common spectral libraries
- Continue to develop, manufacture, and commercialize pre-production prototypes for:
    - Mini stand-off LIBS-Raman
    - Mini - Hand-held LIBS only system – Lead detector
    - Pella Case –self contained (battery powered) LIBS-Raman system.

- Develop an Operational Test and Evaluation plan for Alpha and Beta testing by 1st Responders.
- Develop specific measures of effectiveness for each Military and 1st Responder requirement (goals and thresholds for performance).
- Develop critical operational Issues for each Military and requirement (operational effectiveness and suitability).
- Develop ***objective systems*** with ***purpose built components***.
- Florida International University effort
    - Development of Forensic Analysis and Characterization of Materials by LIBS

## Results

**In FY2007** A3 Technologies accomplishments include the following:

- Established a new company in MD at the Aberdeen HEATCenter incubator facility; the facility provided a developing but limited capability to manufacture and support sensor products, and train the customer.
- Developed and demonstrated of prototype versions of specific detector devices to include:
    - LIBS only Field hazards Portable Sensor (FHPS-1) for 1st Responder evaluation
    - LIBS-Raman Pella Case system -figure 1
    - LIBS-Raman stand-off system - figure 2
    - Close-contact miniature hand-held system - figure 3
    - Bread-board Microwave Enhance LIBS system - figure 4
- Identified of 1st Responder requirements as development and evaluation standard:
    - Common Hazard Index – Materials of Interest in Mid-Atlantic states
    - Configuration Standard for Incident Response –CONOPS

"Two key standards representing a typical mid-Atlantic state 1st Responder USER requirements were developed, the first was the "Common Hazard Index" - (Appendix 1); this document identified 50 hazardous materials and concentration levels of concern.

  - The second standard to be developed by the Juniata team was called the "Configuration Standard for Man-Portable Laser Induced Breakdown Spectrometers Used in Domestic First Responder Applications"; the standard was designed to provide a configuration framework for all developments ( including the tracking of changes) of man-portable LIBS technology applied for the use by the domestic first responder community. This document is provided in Appendix 2."
  - Established subjective User Group Alpha and Beta Operation Test and Evaluation criteria
- Identified candidate 1st responder user group for Beta testing of A3 prototypes
- Chemical – Biological Agent Test
  - Defined a sub-contract with Battelle test chemical-biological stimulants in 2007; goal increase TRL
- Testing – Explosive – Chemical
  - In-house LIBS testing of CBE materials
- Training
  - A Training Module for each Alpha and Beta Testing organization.
- Partnerships
  - Established working relationships (Miller & Hark) PA, VA, MD based 1st Responders and Military Tech Escort – 20th Support command. Alliances with Applied Spectra, Juniata College, Envimetrics, JMAR, MegaWatt Laser, and other vendors.

In FY07, A3 established numerous alliances/collaborations with scientists and engineers at several companies to support our mission. We established subcontracts to Juniata College to establish 1st Responder user requirements, Envimetrics to demonstrate the use of microwave integration for enhanced LIBS performance, and Applied Spectra Inc (ASI); personnel are providing support in growing A3 Technologies to become a self-sufficient independent entity, dedicated to security and force protection. ASI contributed to the FY07 project by developing new sensor platforms for LIBS and LIBS/Raman (see photographs). ASI established the prototypes for the mini-ST-LIBS sensor, handheld Er-laser based LIBS sensor, and a transportable (Pellican case) LIBS sensor. Each of these units is at the alpha prototype stage and ready for initial testing by Adam Miller (1st Responder) and Diane Wong. These sensors have provided preliminary measurements of RDX, TNT, their residues, and numerous clutter species. ASI also demonstrated Raman measurements for the same class of explosives. 3 COTS transportable LIBS systems were ordered from Applied Photonics, Ltd in the UK. Additional collaborations were established with JMAR to evaluate the use of a battery operated double pulse Nd:YAG laser. Characteristics of this laser include the ideal small footprint and 15lb weight, while providing two 100mJ laser pulses, this laser would be integrated in the following year into a mini-ST LIBS sensor. A smaller 50mJ version of this laser exists that may be suitable for integration into the handheld LIBS sensor. The initial plan was for A3 to subcontract to Chemimage to provide Raman capabilities. Due to programmatic issues, Chemimage was not able to perform this effort. ASI demonstrated the capability to perform LIBS/Raman using the same laser and spectrometer, a critical advance in developing small, inexpensive fused sensors. The FY07 plan called for fabrication of a large 30-50 meter ST-LIBS sensor with Raman capability by Applied Photonics Ltd (APL) in the UK. Based on discussions with the ARL, a decision was made that a large LIBS sensor would not be a viable attractive product. Based on these discussions and the desire to have State-side sensor development capabilities, the ARL approved the development of a mini-ST LIBS system at ASI. ASI fabricated and tested the mini-ST-LIBS sensor on several explosives at a distance of 30 meters. The mini ST-LIBS sensor is approximately 1/3 the size, weight and footprint of the Gen 4 ST-LIBS sensor proposed by APL in the UK. ASI is in the process of integrating Raman into the mini ST-LIBS at the date of this renewal proposal.

In FY07, A3 was also awarded a contract through BAE systems at the same time as the Battelle-congressional project. The basis of the BAE work was to develop a Applied Photonics Ltd Gen4 ST-LIBS sensor for use at the National Training Facility in Ft. Irwin CA. A3 worked with APL and other companies to provide the sensor capabilities for this demonstration of LIBS in a field environment. A3 provided appropriate management and technical capabilities that resulted in a successful demonstration at NTC. This was a major field trial for a start-up company.

**In FY2008,** A3 Technologies engaged in robust activities to grow the company facilities and staff, increase our participation in MD business community and developed the process and infrastructure to qualify and sell LIBS based sensor instruments to the securities community. Highlights of the efforts include the following:

- A3 Technologies graduated from the Aberdeen MD HEAT center “incubator facility” after a year as a start-up company. The new space at 1200 Technology Drive maintained the same advantages of location to Aberdeen Proving Ground; at 4500 square feet, it provides a 2.5X increase of space that has now been specially designed to meet A3 needs for corporate offices, engineering laboratory, light manufacturing capability and 100 foot laser test range. A3 and the Office of Economic Development hosted an Open House at the new facility on April 28th 2009; it was attended by 77 invitees including technical colleagues, customers and politicians. Follow-up visits to A3 have been made by staffers for MD Congressman Kratovil and Senator Cardin; Senator Cardin is scheduled to visit A3 in August.

- A3 has been proactive in joining local business organization to include:
    - Army Alliance
    - NMTC
    - Chamber of Commerce
    - AUSA
    - NDIA
    - A3 has recruited a COOP student from the Harford Community College and interviewed Harford Technology HS students for the summer and will maintain or grow this program as a part of the technical staff.
    - A3 staff member (Dr Diane Wong) participated in theFY 2008 Capitol Hill Day resulting in her becoming a special technical advisor for the Maryland politicians and staff.
  - A3 employment, during this reporting period the Maryland based staff has grown by 6 additional full and part time employees bring the total to 9; additional hires are planned for the next 2 years.
  - A3 has formalized relationships with principles in the 1st Responder community, forensic sciences community, political and with lobbying firms as well as maintaining close ties to the federal and DoD and DOE to ensure that new opportunities (SBIRS, BAAs, etc.) are captured and evaluated by the company.

A3 has also aggressively carried out an ongoing interactive development process with representatives from the 1st Responder community (IAB).

- Interagency Board Equipment Panel co-chair (Mr. Edward Baylor) to refine the user threat and hardware requirements (Common Hazard Index-CHI and Configuration Standard-CST) developed in year 1 of the program and to establish a 3rd Party Review and acceptance criteria and test plans for each of the developmental instruments.
- Mr. Baylor, Mr. Miller and Dr. Hark (on contract) are establishing commercialization and fielding pathways for each of the 3 instruments to include:
    - In-house capability review
    - 3rd party beta testing

    - Presentation to the IAB
    - Listing on Standardized Equipment List (SEL) and GSA schedules
    - Identification of grant funds for purchase of items by 1st Responders
    - Developed 1st Responder distributor relationships for A3 products with Cottrell Associates
    - A3 participated as a product exhibitor in a 1st Responder trade shows in Chicago and New Orleans and at the Army Science Conference in Orlando.
- Beta versions of mini-stand-off LIBS and Pelicase-LIBS products undergoing 3rd party testing and evaluation as part of 1st responder qualifications.
- Standardized Production /Manufacturing of RT-100 in MD support commercial sales
- 1 Trade- Mark established; NASLIBS , EMSLIBS and UR Explosives Workshop have been attended with2 presentations, 1 paper/ 3 posters presented. Papers and presentation will be made at AAFS and PITTCON, Orlando Feb.2010.

## Hardware Development in FY2008

### Mini stand-off instrument

- The mini-standoff (LIBS/Raman) instrument was reviewed by the product development consultants and recommended for field evaluation; it is currently undergoing test and evaluation by IAB member Dr Richard Hark at Juniata College.
    - Field testing is on-going, planned test samples including CHI materials and HME; test results will be presented at EMSLIBS in September 2009. This test will strive to develop a working library of threats exceeding 50 materials from the Common Hazard Index developed last year.

Current configuration of the mini-standoff LIBS device is shown below in figure ().

**Figure (1) - Mini-standoff device**

## MINI-ST Specifications

### LIBS Laser

| | |
|---|---|
| Wavelength | 1064 nm |
| Type | Nd:YAG |
| Energy | 350mJ |
| Pulse Duration | 4-5 ns |

| | |
|---|---|
| Power Requirement | 110 VAC |

**Raman Laser**

| | |
|---|---|
| Wavelength | 532 nm |
| Type | Diode Pump |
| Energy | 400mW (Continuous) |
| Power Requirement | 110 VAC |

**Spectral detection**

**LIBS** 200-980 nm Multichannel CCD Systems

0.1 nm Resolution

**RAMAN**

200-2700 cm-1

Special design round to linear fibre

**Computer**

Standalone Notebook for remote control

Build in computer in the system

Windows XP

Remote Control

Software, Under Development

**Operation range:** 15-30 Meter

**Weight:** 300 pounds

**Viewing Camera**

1/3” CCD camera, 30fps, 720x480 pixel resolution

Motorized Zoom lens: 15-300 mm focal length

Field of View Range: 18.2°x 13.7° at 15 mm

0.9°x 0.7° at 300 mm (for reference only)

**Light collection:** 8" UV Enhanced Coating Telescope

**Stages:** Fully Automated Super Precision Stages <0.0001 Degree Resolution, Pan and Tilt

**Features:**

Compact LIBS/ Raman Standoff detection unit; fully wireless remote control. The device is capable of Broadband data acquisition.

**Pelicase instruments**

- Alpha Pelicase system demonstrated the technical feasibility of a self-contained LIBS/Raman system in a completely portable package.
  - The system functioned well when used with solid samples such as metals and plastics; however, a lack of a secure and decontamination capable sampling chamber limited the utility with hazardous materials.
  - The transportability, size and weight of the system satisfied the 1st Responder requirements .
- A completely redesigned Beta version of the Pelicase was constructed that addressed the decontamination requirement by introducing a sealed sample chamber for containment of all target

materials.

- This instrument was utilized to evaluate chemical and biological surrogate materials prepared by Battelle for an ARL task, testing in September 2009.

Current configuration of the Pelicase instrument is shown below.

**Portable**
**Battery Powered**
**(Beta Phase)**

**Figure (2) - Pelicase**

**Pelicase Specifications**

**LIBS laser**

| | |
|---|---|
| Wavelength | 1064 nm |
| Type | Nd:YAG |
| Energy | 25-35 mJ |
| Pulse Duration | 5ns |
| Power Requirement | 12/ 24 VDC or 110 AC |

**Spectral detection**

| | |
|---|---|
| Spectral Range* | 230-950 nm |
| Spectral Resolution* | 0.2 or better nm |

Special design round to linear fibre

**Computer**

Standalone Notebook (Option for Integrated touch screen PC)

Windows XP

Fully integrated software, special applications upon request

**Operation range**

Sealed Chamber

**Viewing Camera**

1280x1024 CMOS color camera

**Weight**

55 pounds

**Features:**

Utilizes automated stage for easy sample loading

Contains a broadband detection system

Completely field portable and battery powered.

No water cooling necessary.

Utilizes a viewing camera for easy targeting and auto stage for natural sample navigation.

### Hand-held Instrument

The hand-held device has undergone a radical redesign from original proof of concept device developed in the prior year effort; in this year. It  was determined that size of the device would grow excessively if broadband detection of explosives, an chem/bio agents were demanded; however, an ultra-small instrument could be produced to detect key hazardous metals e.g. lead, mercury, beryllium, etc.

- Review by the IAB consultants determined this to be a highly desirable capability for 1st responders as well as commercial, federal (BRAC) deconstruction and site clean-up activities.

- The redesigned instrument is currently under construction, final assemble, and test and evaluation are planned for September 2009.

Current configuration of the hand-held device is shown below

Figure (3) - Hand-Held LIBS Device

## Hand-held Performance Specifications

**LIBS laser**

| | |
|---|---|
| Wavelength | 1.54 microns |
| Type | Nd:YAG |
| Energy | 2-3mJ |
| Pulse Duration | 7ns |
| Power Requirement | 14 VDC |

**Spectral detection**

| | |
|---|---|
| Spectral Range* | 330-750 nm |
| Spectral Resolution* | 0.3 nm |

**Computer**

Integrated Touch Screen

Windows XP

Internal Developed Software

**Operation range**

Contact

**Weight**

Hand Unit: 1.5 lbs

Base Unit: 3.5 lbs

**Viewing Camera**

None

**Features**

Small, light weight, self contained system

Remote monitoring capable

Single element identification

## Additional Accomplishments

In-house manufacturing, complete capability has been established carry-out all manufacturing and assemble of the 3 developmental products previously discussed as well as the RT-100 product line.

The RT-100 is shown below

**Figure (4) - RT-100**

Current design-to-production manufacturing studies on the RT-100s at A3 determined that up to a 75% savings can be achieved by manufacturing the frame inside vs. on contract.

A3 studies over the next year will resulted in a standard manufacturing practices and drawings for all products.

Current manufacturing capabilities and equipment are shown below.

## A3 Manufacturing

**Equipment**
- Two Axis Mill
- 10 inch Manual Lathe
- Manual Shear
- Finger Brake
- TIG Welder
- Vertical/Horizontal Band Saw
- 10 inch Table Saw
- Misc Hand Tools
  - Grinders
  - Routers
  - Trimmers
  - Drills
  - Sanders

**Capabilities**
- Machining
- Turning
- Sheet Metal Forming
- Welding
- Wood and Metal Cutting
- Plastic Forming
- Assembly

**Figure (5) _ A3 Facility**

### Sub-contract Program

**Juniata College - Florida International University &** Envimetrics,

A3 worked on-contract with both FIU and Juniata Universities to develop LIBS based systems to support the forensic analysis markets; both schools are leading centers for forensic studies and are current contract with A3 to evaluate and develop specific products.

- Drs Almirall (FIU) and Hark (Juniata) designed an RT-100 HP (high performance) instrument for this analysis, A3 will place these instruments their laboratories for evaluation and development in November 2009.
- Forensic studies with Dr Hark using the A3 RT-100 HP for ink analysis have been highly successful, results have been published as a poster at NASLIBS in New Orleans.

Envimetrics to evaluated the technical feasibility of microwave enhancement of the LIBS detection event.

**Results in FY2009**

**Summary**

- Standardized Production /Manufacturing of Rt-100 in MD supported commercial sales of four new sales.
- Beta version of the Pelicase instrument completed chem/bio testing protocol for Battelle in support of ARL – results published at LIBS 2010
- Beta testing by FIU successfully “qualified” RT-100 as a forensic tool – results published at LIBS 2010
- Program continued to support 2 undergraduates at Juniata and 1 PhD student at FIU.
- Round-Robin Test established with Juniata College, FIU, ASI and A3, demonstrated commonality and reproducibility of results between multiple instruments
- A3 technologies operational in the 4500 sq ft facility in Aberdeen MD designed for cooperate offices, engineering lab, manufacturing and 100 ft laser range.
- Commercialization and fielding pathways established leading to GSA, SEL and AEL availablity and sales.
- Beta versions of mini-stand-off LIBS and Pelicase-LIBS products undergoing 3rd party testing and evaluation as part of 1st responder qualifications.
- Beta version of the Pelicase instrument- PL100-GEO- completed chem/bio testing protocol for Battelle in support of ARL – results published at LIBS 2010 by ARL

- Round-Robin Test established with Juniata College, FIU, ASI and A3, demonstrated commonality and reproducibility of results between multiple instruments – full-scale results pending
- Training, A3 has developed and presented a training session to support the installation of an RT-100 device at the NDCEE in Johnstown, PA; additional training will be developed as required to support the sales of RT-100 products.
- Envimetrics generated a brief letter report documenting their effort; this report was accepted by the Army. No further work between A3 and the company was deemed necessary.
- Technology transfer resulting from this program is another metric for success of the effort, the following Table (1) summarizes the key successes.

**Table (1)**

**Summary of Technology Transfer Efforts**

1. **2** patents filed - Appendix (4), 1 Trade- Mark established; NASLIBS , EMSLIBS and UR Explosives Workshop have been attended with 2 presentations, 1 paper/ 3 posters presented. Papers and presentation will be made at AAFS and PITTCON, Orlando Feb.2010.
2. Papers (2), Presentation s (23) and Posters (4) were made at AAFS and PITTCON, Orlando Feb.2010, NASLIBS , Memphis; EMSLIBS , Rome, CAD-IAI, San Jose Costa Rica, ACS San Francisco, CA and others.
3. Awards-Erica Cahoon received second place for Best Student Poster in the LIBS 2010, 6th International Conference on Plasma Spectroscopy and Applications, Memphis, TN, September 13-17, 2010
4. Awards-Katie Shughrue received a First Place award for her oral presentation at the Landmark Undergraduate Research Symposium. Katie was also invited to speak at the CUR/NCUR function at the Library of Congress on October 27.
5. Applications Notes: - "Detection of Lead and Lead-free Solders"
6. Graduate Students:-Eric Cahoon, PhD student at FIU

## Conclusions

- Evaluation of the accuracy, precision and sensitivity of the four developmental products resulting from this program were found to be acceptable for a number of commercial and 1st Responder applications including qualification by the FIU study as a Forensic Analysis instrument ; however the only commercial sales (fourteen to date) have been from the RT-100 for laboratory applications. This is understandable as A3 fully understands the operational, configuration and performance needs of the scientific and analytical marketplace well enough to mature the prototype instrument into commercial item. Round-Robin testing between ASI, FIU, Juniata and A3 demonstrated commonality and reproducibility of results between multiple instruments, this is a major element required by the forensic community.

- The Pelicase instrument is currently a Beta+ prototype; the capability of this instrument to operate remotely - on battery power but with performance capabilities equal to the RT-100 is unique the scientific community. A customer is needed to mature this device to a commercial product by providing engineering and design requirements for configuration and performance - to include environmental hardening. In addition, Demonstration & Validation funding will be required to conduct the necessary field trials to mature a commercial design.
- A similar development scenario is required to commercialize the Mini-ST instrument, i.e. customer engineering requirements, Demonstration & Validation funding for field trials to mature a commercial design.
- The hand-held instrument demonstrated the ability to detect single or double elements of interest specifically to the OSOHA community, additional developmental work is required to benchmark the accuracy and precision capabilities against health standard concentrations. User standards and developmental funding is required to mature this prototype to commercialization.
- Initial configurations of both the Pelicase and mini-standoff instruments included an on-board Ramon sensor as well as the LIBS sensor. Preliminary testing with both sensor in both devices showed no clear advantage afforded by the Ramon sensor in the detection of explosives or similar elemental analysis; as such it was dropped from the instruments in afford simpler construction and lower unit costs.
- The major barrier to the commercialization of LIBS based field sensors is "purpose-built" components (lasers and spectrometers) designed and built to fit the performance and space configuration of the intended instrument. All demonstration prototypes produced during this program made use of commercial components to build the various instruments. When demand for purpose-built LIBS instruments increases, then economics will support "purpose-built" components that will reduce both size and cost of the final instrument.

- The current status, capabilities and potential applications for A3 Technologies commercial, Alpha & beta-prototype instrumentations are summarized in Table 2

## Table (2)

## Status of Developmental Instrumentation

• RT-100 - Application - Green Chemical Analysis – Configuration - Laboratory and mobile

laboratory capability – LIBS or LIBS & Ramon sensors– >300 pounds

– Use: Forensic studies, inks, coinage, glasses, minerals , lead-free solders,

semi-conductor materials and “conflict minerals”

– Status: Commercial Product

• Pelicase instrument– Application - Detection & Analysis – Configuration - Field Transportable

and 1stResponder “warm-zone” – Decontamination capable – LIBS only sensor- <50 pounds

– Use: Explosives, hazardous industrial mat’s, chem/bios

– Status: Beta Prototype

• Mini-standoff instrument– Application - Detection & Analysis – Configuration -Field and ROV

Transportable – 1st responder “cold-zone” – 35 meter st-off – LIBS & Ramon sensors– <250 pounds

- Use: Remote Explosive detection. CBRN&E detection

- Status: Beta Prototype

• Hand-held instrument –Application - Detection of single elements –Configuration - Field Transportable

– 1 meter max st-off - LIBS sensor- <15 pounds

- Use: Single element detection
- Status: Alpha Prototype

## List of APPENDIXES

## Appendix (1)

## Top Hazard Index for 1st Responder Detection

## (Provides an "Objective Capability" LIBS Library for Materials-of-concern for 1st Responders)

| CHEMICAL | BIOLOGICAL | RADIOLOGICAL | NUCLEAR |
|---|---|---|---|
| Ammonia | Anthrax | Cesium 137 | Plutonium 239 |
| Potassium cyanide | Botulinum toxin | Americium 241 | Uranium 235 |
| Arsenic | Ricin | Uranyl Nitrate | Uranium 238 |
| Phosgene | Smallpox | Cobalt 57, 60 | Iodine 135 |
| Sulfur mustard | E-Coli | Technetium 99m | Xenon 135 |
| 2-Chlorovinyldichloroarsine] (Lewisite 1) | Plague | Potassium 40 | Strontium 90 |
| [Bis(2-chlorovinyl)chloroarsine] (Lewisite 2) | Brucellosis | Phosphorus 32 | Zirconium 95 |
| [Tris(2-chlorovinyl)arsine] (Lewisite 3) | Cholera | Iodine 131 |  |
| Tabun (GA) | Q Fever | Radon 220, 222 |  |
| Sarin (GB) | Glanders | Carbon 14 |  |
| Soman (GD) | Ebola | Hydrogen 3 (tritium) |  |
| Cyclohexyl methylphosphonofluoridate (GF) | Marburg | Promethium 147 |  |
| *O*-Ethyl-*S*-diisopropylaminomethyl methylphosphonothiolate (VX) | Venezualen Equine Encephalitis (VEE) | Radium 226 |  |

| | | | |
|---|---|---|---|
| Nitrogen mustard (HN) | Lassa | Polonium 210 | |
| Phosgene oxime (CX) | Staphylococcal Enterotoxin B (SEB) (Food Poisoning) | Thallium 201 | |
| Hydrogen cyanide (AC) | FUNGI | Thorium 232 | |
| Cyanogen chloride (CK) | Aflatoxin | Lead 210 | |
| Arsine (SA) | Bacillus | Sodium 22 | |
| Cyclosarin (GE, GF) | Streptococcus | | |
| Methyl Isocyanate | Staphylococcus | | |
| Diborane | Erwinia | | |
| DMMP | Pseudomonas | | |
| Ethylene Oxide | Amanita echinocephala | | |
| Nitrogen Dioxide | Amatoxins | | |
| | Aminita muscaria | | |
| | Amanita pantherina | | |
| | clitocybe | | |
| | Conocybe | | |
| | Copelandia | | |
| | Entoloma rhodopolium | | |
| | Gymnopilus | | |
| | Gyromita species | | |
| | Inocybe | | |
| | Inocybe fastigiata | | |
| | Inocybe patouillardi | | |
| | Omphalutus olearus | | |
| | Panaeolus | | |
| | Pluteus | | |

|  | PLANTS |  |  |
|---|---|---|---|
|  | Abrus precatorius L. |  |  |
|  | Aconitum napellus spp. |  |  |
|  | Arum maculatum L. |  |  |
|  | Caesalpinia gilliesii |  |  |
|  | Cannabis sativa L. |  |  |
|  | Colchicum autumnale L. |  |  |
|  | Conium maculatum L. |  |  |
|  | Coriaria myrtifolia L. |  |  |
|  | Erythroxylum coca Lam |  |  |
|  | Gloriosa superba L. |  |  |
|  | Glycyrrhiza glabra L. |  |  |
|  | Hedera helix L. |  |  |
|  | Ilex aquifolium L. |  |  |
|  | Jatropha curcas L. |  |  |
|  | Jatropha gossypiifolia |  |  |
|  | Jatropha hastata |  |  |
|  | Jatropha macrorhiza |  |  |
|  | Jatropha multifida |  |  |
|  | Jatropha podagrica |  |  |
|  | Myristica fragrans Houtt. |  |  |
|  | Nerium oleander L. |  |  |
|  | Nicotiana tabacum L |  |  |
|  | Peganum harmala L. |  |  |
|  | Ricinus communis L. |  |  |
|  | Ruta graveolens L. |  |  |
|  | Scilla maritima L. Baker |  |  |
|  | Senecio Vulgaris L. |  |  |
|  | Solanum nigrum L. |  |  |
|  | Spartium junceum L. |  |  |
|  | Thevetia peruviana |  |  |
|  | Viscum album L. |  |  |

| | | | |
|---|---|---|---|
| | Wisteria sinensis (Sims) Sweet Wisteria floribunda (Willd) DC | | |

## Top Hazard Index - Continued

| EXPLOSIVE | TOXIC INDUSTRIAL CHEMICALS | WHITE POWDERS | COMMON DRUGS |
|---|---|---|---|
| HMTD POWDER | Chlorine | Talcum Powder | Marijuana |
| ANFO | Propane | Salt | Cocaine |
| TNT | Polychlorinated biphenyls (PCBs) | Sugar | Heroin/opiates |
| Flash Powder | Acetylene | Calcium hydroxide (lime) | Methamphetamine |
| HMX | Hexachlorobenzene | Corn starch | Barbiturates |
| Dynamite | Ethyl mercaptan | Acetaminophen | Ecstasy |
| PETN | Sodium hypochlorite | Baby formula **SPECIFY TYPES BY ALL BRANDS POWDERED** | GHB |
| RDX | Hydrogen peroxide | Baby powder **SPECIFY TYPES BY ALL BRANDS POWDERED** | Ketamine |
| SEMTEX | Hydrofluoric acid (conc. 50% or greater) | Flour **SPECIFY TYPES BY ALL BRANDS COMMERCIALLY AVAILABLE IN US**** | LSD |
| C-4 | Hydrogen chloride (anhydrous) | Baking soda (sodium bicarbonate) | Oxycontin |
| TATP | Hydrochloric acid (conc. 37% or greater) | Baking powder | Rohypnol |
| Black powder | Fluorine | Insecticides (wetable powders) **LIST NEEDED** | Psilocybe |
| Nitrocellulose | Chloroform | Sevin (insecticide) | PHARMACEUTICALS |
| Nitroglycerin | Sulfuric acid | Splenda | Acetazolamide (PIM 005) |

| | | | |
|---|---|---|---|
| Fulminate of Mercury | Formaldehyde | Nutra-Sweet | Acetylsalicylic acid (PIM 006) |
| | Hydrazine | Equal | Alaproclate (PIM 943) |
| Acetylides of heavy metals. | Acrolein | Brown Sugar | Alfentanyl (PIM 880) |
| Aluminum containing polymeric propellant | Monoethanolamine | Gold Bond Powder | Allopurinol (PIM 020F, French) |
| Aluminum ophorite explosive. | Methanol | Aspirin | Alphaprodine (PIM 878) |
| Amatex. | Aluminum Phosphide | Ephedrine | Alprazolam (PIM 199) |
| Amatol. | Azinphos-Methyl | Pseudo-ephedrine | Amileridine (PIM 879) |
| Ammonal. | Carbofuran | Solid/Powder Deodorant (various brands) | Amiloride Hydrochloride (PIM 026) |
| Ammonium nitrate explosive mixtures (cap sensitive). | Dimethoate | (consider) various spices and seasonings | Amodiaquine Hydrochloride (PIM 030) |
| *Ammonium nitrate explosive mixtures (non-cap sensitive). | Endosulfan | Non-dairy Creamer **SPECIFY TYPES BY ALL BRANDS COMMERCIALLY AVAILABLE IN US**** | Amphetamine (PIM 934) |
| Ammonium perchlorate having particle size less than 15 microns. | Methamidophos | | Ascorbic acid (PIM 046) |
| Ammonium perchlorate composite propellant. | Paraquat Dichloride | | Azathioprine (PIM 053) |
| Ammonium perchlorate explosive mixtures | Phosmet | | Benzalkonium chloride (PIM 897) |
| Ammonium picrate [picrate of ammonia, Explosive D]. | Creosote | | Benzethonium chloride (PIM 898) |
| Ammonium salt lattice with isomorphously substituted inorganic salts | Asbestos | | Benzphetamine (PIM 061) |
| *ANFO [ammonium nitrate-fuel oil]. | | | Bromazepam (PIM 281) |
| Aromatic nitro-compound explosive mixtures. | | | Brotizolam (PIM 919) |
| Azide explosives. | | | Bupivacaine (PIM 085F, French) |
| Baranol. | | | Buprenorphine (PIM 884) |
| Baratol. | | | Butorphanol (PIM 885) |
| BEAF [1, 2-bis (2, 2-difluoro-2-nitroacetoxyethane)]. | | | Camazepam (PIM 678) |
| Black powder. | | | Camphor (PIM 095) |
| Black powder based explosive mixtures. | | | Carbamazepine (PIM 100) |

|  |  |  |  |
|---|---|---|---|
| *Blasting agents, nitro-carbo-nitrates, including non-cap sensitive slurry and water gel explosives. |  |  | Cetalkonium chloride (PIM 899) |
| Blasting caps. |  |  | Cetrimide (PIM 111) |
| Blasting gelatin. |  |  | Cetrimonium bromide (PIM 951) |
| Blasting powder. |  |  | Cetylpyridinium chloride (PIM 952) |
| BTNEC [bis (trinitroethyl) carbonate]. |  |  | Chlordiazepoxide hydrochloride (PIM 321) |
| BTNEN [bis (trinitroethyl) nitramine]. |  |  | Chloroquine (PIM 123) |
| BTTN [1,2,4 butanetriol trinitrate]. |  |  | Chlorphentermine hydrochloride (PIM 935) |
| Bulk salutes. |  |  | Chlorpromazine (PIM 125) |
| Butyl tetryl. |  |  | Chlorthalidone (PIM 126) |
| Calcium nitrate explosive mixture. |  |  | Cinolazepam (PIM 920) |
| Cellulose hexanitrate explosive mixture. |  |  | Cisplatin (PIM 132) |
| Chlorate explosive mixtures. |  |  | Citalopram (PIM 863) |
| Composition A and variations. |  |  | Clobazam (PIM 921) |
| Composition B and variations. |  |  | Clofazimine (PIM 134) |
| Composition C and variations. |  |  | Clonazepam (PIM 326) |
| Copper acetylide. |  |  | Clorazepate dipotassium (PIM 327) |
| Cyanuric triazide. |  |  | Clorgyline (PIM 966) |
| Cyclonite [RDX]. |  |  | Clortermine hydrochloride (PIM 936) |
| Cyclotetramethylenetetranitramine [HMX]. |  |  | Clostebol acetate (PIM 900) |
| Cyclotol. |  |  | Clotiazepam (PIM 922) |
| Cyclotrimethylenetrinitramine [RDX]. |  |  | Cloxazolam (PIM 923) |
| DATB [diaminotrinitrobenzene]. |  |  | Cocaine (PIM 139) |
| DDNP [diazodinitrophenol]. |  |  | Codeine (PIM 140) |
| DEGDN [diethyleneglycol dinitrate]. |  |  | Colchicine (PIM 141) |
| Detonating cord. |  |  | Dapsone (PIM 167) |
| Detonators. |  |  | Dexamphetamine sulphate (PIM 178) |
| Dimethylol dimethyl methane dinitrate composition. |  |  | Dexfenfluramine hydrochloride (PIM 939) |
| Dinitroethyleneurea. |  |  | Dextromethorphan (PIM 179) |

|  |  |  |  |
|---|---|---|---|
| Dinitroglycerine [glycerol dinitrate]. |  |  | Dextromoramide (PIM 886) |
| Dinitrophenol. |  |  | Dextropropoxyphene (PIM 442F, French) |
| Dinitrophenolates. |  |  | Dezocine (PIM 887) |
| Dinitrophenyl hydrazine. |  |  | Diamorphine (PIM 261F, French) |
| Dinitroresorcinol. |  |  | Diazepam (PIM 181) |
| Dinitrotoluene-sodium nitrate explosive mixtures. |  |  | Diethylpropion hydrochloride (PIM 937) |
| DIPAM [dipicramide;diaminohexanitrobiphenyl]. |  |  | Dimercaprol (PIM 193) |
| Dipicryl sulfone. |  |  | Diphenoxylate (PIM 196) |
| Dipicrylamine. |  |  | Doxefazepam (PIM 924) |
| d |  |  | Drostanolone (PIM 901) |
| DNPA [2,2-dinitropropyl acrylate]. |  |  | Ephedrine (PIM 209) |
| DNPD [dinitropentano nitrile]. |  |  | Estazolam (PIM 925) |
| Dynamite. |  |  | Ethambutol (PIM 218) |
| EDDN [ethylene diamine dinitrate]. |  |  | Ethinylestradiol (PIM 221) |
| EDNA [ethylenedinitramine]. |  |  | Ethionamide (PIM 224) |
| Ednatol. |  |  | Etizolam (PIM 926) |
| EDNP [ethyl 4,4-dinitropentanoate]. |  |  | Eucalyptus oil (PIM 031) |
| EGDN [ethylene glycol dinitrate]. |  |  | Fenfluramine hydrochloride (PIM 938) |
| Erythritol tetranitrate explosives. |  |  | Fentanyl (PIM 881) |
| Esters of nitro-substituted alcohols. |  |  | Flunitrazepam (PIM 021) |
| Ethyl-tetryl. |  |  | Fluoxetine(PIM 651) |
| Explosive conitrates. |  |  | Fluoxymesterone (PIM 902) |
| Explosive gelatins. |  |  | Flupenthixol (PIM 236) |
| Explosive liquids. |  |  | Flurazepam (PIM 640) |
| Explosive mixtures containing oxygen-releasing inorganic salts and hydrocarbons. |  |  | Fluvoxamine (PIM 944) |
| Explosive mixtures containing oxygen-releasing inorganic salts and nitro bodies. |  |  | Folic Acid (PIM 238) |
| Explosive mixtures containing oxygen-releasing inorganic salts and water insoluble fuels. |  |  | Furazabol (PIM 903) |

| | | | |
|---|---|---|---|
| Explosive mixtures containing oxygen-releasing inorganic salts and water insoluble fuels. | | | Furosemide (PIM 240) |
| Explosive mixtures containing sensitized nitromethane. | | | Gentamicin sulfate (PIM 242) |
| Explosive mixtures containing tetranitromethane (nitroform). | | | Glutethimide (PIM 246) |
| Explosive nitro compounds of aromatic hydrocarbons. | | | Glyceryl trinitrate (PIM 247) |
| Explosive organic nitrate mixtures. | | | Halazepam (PIM 160) |
| Explosive powders | | | Haloperidol (PIM 253) |
| Flash powder. | | | Haloxazolam (PIM 927) |
| Fulminate of mercury. | | | Hydralazine (PIM 264) |
| Fulminate of silver. | | | Hydrochlorothiazide (PIM 265) |
| Fulminating gold. | | | Hydrocodone (PIM 893) |
| Fulminating mercury. | | | Hydromorphone (PIM 891) |
| Fulminating platinum. | | | Imipramine (PIM 273) |
| Fulminating silver. | | | Iodine (PIM 280) |
| Gelatinized nitrocellulose. | | | Iproniazid (PIM 967) |
| Gem-dinitro aliphatic explosive mixtures. | | | Isocarboxazid (PIM 968) |
| Guanyl nitrosamino guanyl tetrazene. | | | Isoniazid (PIM 288) |
| Guanyl nitrosamino guanylidene hydrazine. | | | Isosorbide Dinitrate (PIM 291) |
| Guncotton. | | | Ivermectin (PIM 292) |
| Heavy metal azides. | | | Ketazolam (PIM 222) |
| Hexanite. | | | Ketobemidone (PIM 888) |
| Hexanitrodiphenylamine. | | | Levodopa (PIM 305) |
| Hexanitrostilbene. | | | Lithium carbonate (PIM 309F, French) |
| Hexogen [RDX]. | | | Loperamide (PIM 896) |
| Hexogene or octogene and a nitrated N-methylaniline. | | | Loprazolam (PIM 928) |
| Hexolites. | | | Lorazepam (PIM 223) |
| HMTD [hexamethylenetriperoxidediamine]. | | | Lormetazepam (PIM 929) |
| HMX [cyclo-1,3,5,7-tetramethylene 2,4,6,8-tetranitramine; Octogen]. | | | Medazepam (PIM 460) |
| Hydrazinium nitrate/hydrazine/aluminum explosive system. | | | Meptazinol (PIM 889) |

|  |  |  |  |
|---|---|---|---|
| Hydrazoic acid. |  |  | Mesterolone (PIM 904) |
| Igniter cord. |  |  | Methadone (PIM 333) |
| Igniters. |  |  | Methamphetamine (PIM 334) |
| Initiating tube systems. |  |  | Methandienone (PIM 905) |
| KDNBF [potassium dinitrobenzo-furoxane]. |  |  | Methandriol (PIM 906) |
| Lead azide. |  |  | Methaqualone (PIM 336F, French) |
| Lead mannite. |  |  | Methenolone (PIM 907) |
| Lead mononitroresorcinate. |  |  | Methyldopa (PIM 342) |
| Lead picrate. |  |  | Methylphenidate hydrochloride (PIM 344) |
| Lead salts, explosive. |  |  | Methyltestosterone (PIM 908) |
| Lead styphnate [styphnate of lead, lead trinitroresorcinate]. |  |  | Metronidazole (PIM 347) |
| Liquid nitrated polyol and trimethylolethane. |  |  | Mexazolam (PIM 390) |
| Liquid oxygen explosives. |  |  | Miconazole (PIM 349) |
| Magnesium ophorite explosives. |  |  | Midazolam (PIM PIM 674) |
| Mannitol hexanitrate. |  |  | Moclobemide (PIM 151) |
| MDNP [methyl 4,4-dinitropentanoate]. |  |  | Morphine (PIM 353) |
| MEAN [monoethanolamine nitrate]. |  |  | Nalbuphine (PIM 883) |
| Mercuric fulminate. |  |  | Nandrolone (PIM 910) |
| Mercury oxalate. |  |  | Nandrolone phenylpropionate (PIM 909) |
| Mercury tartrate. |  |  | Nialamide (PIM 969) |
| Metriol trinitrate. |  |  | Nitrazepam (PIM 675) |
| Minol-2 [40% TNT, 40% ammonium nitrate, 20% aluminum]. |  |  | Nitrofurantoin (PIM 377) |
| MMAN [monomethylamine nitrate]; methylamine nitrate. |  |  | Nitrous oxide (PIM 381) |
| Mononitrotoluene-nitroglycerin mixture. |  |  | Nordazepam (PIM 676) |
| Monopropellants. |  |  | Norethandrolone (PIM 911) |
| NIBTN [nitroisobutametriol trinitrate]. |  |  | Oxabolone cipionate (PIM 912) |
| Nitrate explosive mixtures. |  |  | Oxandrolone (PIM 913) |
| Nitrate sensitized with gelled |  |  | Oxazepam (PIM 677) |
| nitroparaffin. |  |  | Oxazolam (PIM 931) |

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|---|---|---|---|
| Nitrated carbohydrate explosive. |  |  | Oxycodone (PIM 894) |
| Nitrated glucoside explosive. |  |  | Oxymesterone (PIM 914) |
| Nitrated polyhydric alcohol explosives. |  |  | Oxymetholone (PIM 915) |
| Nitric acid and a nitro aromatic compound explosive. |  |  | Oxymorphone (PIM 892) |
| Nitric acid and carboxylic fuel explosive. |  |  | Paracetamol (PIM 396) |
| Nitric acid explosive mixtures. |  |  | Paroxetine (PIM 175) |
| Nitro aromatic explosive mixtures. |  |  | Pemoline (PIM 940) |
| Nitro compounds of furane explosive mixtures. |  |  | Pentamorphone (PIM 890) |
| Nitrocellulose explosive. |  |  | Pentazocine (PIM 407) |
| Nitroderivative of urea explosive mixture. |  |  | Pethidine (PIM 877) |
| Nitrogelatin explosive. |  |  | Phendimetrazine tartrate (PIM 941) |
| Nitrogen trichloride. |  |  | Phenelzine (PIM 970) |
| Nitrogen tri-iodide. |  |  | Phenmetrazine hydrochloride (PIM 942) |
| Nitroglycerine [NG, RNG, nitro, glyceryl trinitrate, trinitroglycerine]. |  |  | Phentermine (PIM 415) |
| Nitroglycide. |  |  | Phenytoin (PIM 416) |
| Nitroglycol [ethylene glycol dinitrate, EGDN]. |  |  | Phytomenadione (PIM 424F, French) |
| Nitroguanidine explosives. |  |  | Pinazepam (PIM 679) |
| Nitronium perchlorate propellant mixtures. |  |  | Podophyllum (PIM 427) |
| Nitroparaffins Explosive Grade and ammonium nitrate mixtures. |  |  | Potassium chloride (PIM 430) |
| Nitrostarch. |  |  | Prazepam (PIM 680) |
| Nitro-substituted carboxylic acids. |  |  | Primaquine phosphate (PIM 434) |
| Nitrourea. |  |  | Procainamide (PIM 436) |
| Octogen [HMX]. |  |  | Promethazine (PIM 439) |
| Octol [75 percent HMX, 25 percent TNT]. |  |  | Propranolol (PIM 441) |
| Organic amine nitrates. |  |  | Quazepam (PIM 932) |
| Organic nitramines. |  |  | Quinbolone (PIM 916) |
| PBX [plastic bonded explosives]. |  |  | Quinidine (PIM 463) |
| Pellet powder. |  |  | Quinine (PIM 464) |
| Penthrinite composition. |  |  | Reserpine (PIM 467) |
| Pentolite. |  |  | Retinol (PIM 468) |
| Perchlorate explosive mixtures. |  |  | Rifampicin (PIM 472) |
| Peroxide based explosive mixtures. |  |  | Salicylic acid (PIM |

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|---|---|---|---|
| | | | 642) |
| PETN [nitropentaerythrite, pentaerythrite tetranitrate, pentaerythritol tetranitrate]. | | | Selective Serotonin Re-uptake Inhibitors (SSRI) (Group PIM G011) |
| Picramic acid and its salts. | | | Sertraline (PIM 177) |
| Picramide. | | | Stanolone (PIM 917) |
| Picrate explosives. | | | Stanozolol (PIM 918) |
| Picrate of potassium explosive mixtures. | | | Sufentanyl (PIM 882) |
| Picratol. | | | Tamoxifen citrate (PIM 517) |
| Picric acid (manufactured as an explosive). | | | Temazepam (PIM 683) |
| Picryl chloride. | | | Testosterone (PIM 519) |
| Picryl fluoride. | | | Tetanus antitoxin (PIM 520) |
| PLX [95% nitromethane, 5% ethylenediamine]. | | | Tetanus vaccine (PIM 521) |
| Polynitro aliphatic compounds. | | | Tetrazepam (PIM 933) |
| Polyolpolynitrate-nitrocellulose explosive gels. | | | Thiamine and salts (Group PIM G015) |
| Potassium chlorate and lead sulfocyanate explosive. | | | Timolol (PIM 531) |
| Potassium nitrate explosive mixtures. | | | Tofisopam (PIM 686) |
| Potassium nitroaminotetrazole. | | | Toloxatone (PIM 971) |
| Pyrotechnic compositions. | | | Tramadol (PIM 895) |
| PYX [2,6-bis(picrylamino)] 3,5-dinitropyridine. | | | Tranylcypromine (PIM 972) |
| RDX [cyclonite, hexogen, T4, cyclo-1,3,5,-trimethylene-2,4,6,-trinitramine; hexahydro-1,3,5-trinitro-S-triazine]. | | | Trenbolone (PIM 965) |
| Safety fuse. | | | Triazolam (PIM 688) |
| Salts of organic amino sulfonic acid explosive mixture. | | | Valproic acid (PIM 551) |
| Salutes (bulk). | | | Verapamil (PIM 552) |
| Silver acetylide. | | | Yohimbine (PIM 567) |
| Silver azide. | | | Zimeldine (PIM 856) |
| Silver fulminate. | | | |
| Silver oxalate explosive mixtures. | | | Amphetamine 300-62-9 |
| Silver styphnate. | | | Amphetamine phosphate 139-10-6 |
| Silver tartrate explosive mixtures. | | | Amphetamine sulfate 60-13-9 |

| | | | |
|---|---|---|---|
| Silver tetrazene. | | | Benzphetamine 156-08-1 |
| Sodium azide explosive mixture. | | | Benzphetamine hydrochloride 5411-22-3 |
| Sodium dinitro-ortho-cresolate. | | | Chlorphentermine 461-78-9 |
| Sodium nitrate explosive mixtures. | | | Chorphentermine hydrochloride 151-06-4 |
| Sodium nitrate-potassium nitrate explosive mixture. | | | Clortermine 10389-73-8 |
| Sodium picramate. | | | Clortermine hydrochloride 10389-72-7 |
| Special fireworks. | | | Dexamphetamine 51-64-9 |
| Squibs. | | | Dexamphetamine phosphate 7528-00-9 |
| Styphnic acid explosives. | | | Dexamphetamine sulphate 51-63-8 |
| Tacot [tetranitro-2,3,5,6-dibenzo-1,3a,4,6a tetrazapentalene]. | | | Dexfenfluramine 3239-44-9 |
| TATB [triaminotrinitrobenzene]. | | | Dexfenfluramine hydrochloride 3239-45-0 |
| TATP [triacetonetriperoxide]. | | | Diethylpropion 90-84-6 |
| TEGDN [triethylene glycol dinitrate]. | | | Diethylpropion hydrochloride 134-80-5 |
| Tetranitrocarbazole. | | | Fenfluramine 458-24-2 |
| Tetrazene [tetracene, tetrazine, 1(5-tetrazolyl)-4-guanyl tetrazene hydrate]. | | | |

|  |  |  |  |
|---|---|---|---|
| Tetrazole explosives. |  |  | Fenfluramine hydrochloride 404-82-0 |
| Tetryl [2,4,6 tetranitro-N-methylaniline]. |  |  | Methamphetamine (methylamphetamine) 537-46-2 |
| Tetrytol. |  |  | Methamphetamine |
| Thickened inorganic oxidizer salt slurried explosive mixture. |  |  | (methylamphetamine hydrochloride) 51-57-0 |
| TMETN [trimethylolethane trinitrate]. |  |  | Methylphenidate 113-45-1 |
| TNEF [trinitroethyl formal]. |  |  | Methylphenidate hydrochloride 298-59-9 |
| TNEOC [trinitroethylorthocarbonate]. |  |  | Pemoline 2152-34-3 |
| TNEOF [trinitroethylorthoformate]. |  |  | Pemoline hydrochloride 68942-31-4 |
| TNT [trinitrotoluene, trotyl, trilite, triton]. |  |  | Pemoline magnesium (magnesium pemoline) 18968-99-5 |
| Torpex. |  |  | Phendimetrazine 634-03-7 |
| Tridite. |  |  | Phendimetrazine hydrochloride 7635-51-0 |
| Trimethylol ethyl methane trinitrate composition. |  |  | Phendimetrazine tartrate 50-58-8 |
| Trimethylolthane trinitrate-nitrocellulose. |  |  | Phenmetrazine 134-49-6 |
| Trimonite. |  |  | Phenmetrazine hydrochloride 1707-14-8 |
| Trinitroanisole. |  |  | Phenmetrazine theoclate 13931-75-4 |

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|---|---|---|---|
| Trinitrobenzene. | | | Phentermine 122-09-8 |
| Trinitrobenzoic acid. | | | Phentermine hydrochloride 1197-21-3 |
| Trinitrocresol. | | | |
| Trinitro-meta-cresol. | | | clostebol |
| Trinitronaphthalene. | | | drostanolone |
| Trinitrophenetol. | | | fluoxymesterone |
| Trinitrophloroglucinol. | | | furazabol |
| Trinitroresorcinol. | | | mesterolone |
| Tritonal. | | | methandienone |
| Urea nitrate. | | | methandriol |
| Water-bearing explosives having salts of oxidizing acids and nitrogen bases, sulfates, or sulfamates (cap sensitive). | | | methenalone enanthate |
| Water-in-oil emulsion explosive compositions. | | | methenolone |
| Xanthamonas hydrophilic colloid explosive mixture. | | | methenolone acetate |
| | | | methyltestosterone |
| | | | nandrolone esters |
| | | | nandrolone |
| | | | norethandrolone |
| | | | oxabolone |
| | | | oxandrolone |
| | | | oxymesterone |
| | | | oxymetholone |
| | | | quinbolone |
| | | | stanolone |
| | | | stanozolol |
| | | | testosterone |

| | | | |
|---|---|---|---|
| | | | testosterone esters |
| | | | trenbolone (veterinary product) |
| | | | |
| | | | Alprazolam |
| | | | Bromazepam |
| | | | Brotizolam |
| | | | Camazepam |
| | | | Chlordiazepoxide |
| | | | Cinolazepam |
| | | | Clobazam |
| | | | Clonazepam |
| | | | Clorazepate |
| | | | Clotiazepam |
| | | | Cloxazolam |
| | | | Diazepam |
| | | | Doxefazepam |
| | | | Estazolam |
| | | | Etizolam |
| | | | Flunitrazepam |
| | | | Halazepam |
| | | | Haloxazolam |
| | | | Ketazolam |
| | | | Loprazolam |
| | | | Lorazepam |
| | | | Lormetazepam |
| | | | Medazepam |
| | | | Mexazolam |
| | | | Midazolam |
| | | | Nitrazepam |
| | | | Nordazepam |
| | | | Oxazolam |
| | | | Oxazepam |
| | | | Pinazepam |
| | | | Prazepam |
| | | | Quazepam |
| | | | Temazepam |
| | | | Tetrazepam |
| | | | Tofisopam |
| | | | Triazolam |
| | | | |
| | | | Amorph IZS |
| | | | Amorphous IZS |
| | | | Biphasic Insulin |
| | | | Cryst IZS |

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|---|---|---|---|
| | | | Crystalline IZS |
| | | | Extended Insulin Zinc Suspension |
| | | | Globin Insulin |
| | | | Globin Insulin with zinc |
| | | | Globin Zinc Injection Insulin |
| | | | Globin Zinc Insulin |
| | | | GZI |
| | | | Injectio Insulini Protaminati cum zinco |
| | | | Insulin cum zinco (crystallisati) suspension |
| | | | Insulin Hydrochloride |
| | | | Insulin Injection |
| | | | Insulin lente |
| | | | Insulin semilente |
| | | | Insulin Ultralente |
| | | | Insulin zinc suspension (mixed) |
| | | | Insulin zinci crystallisati suspension injectabilis |
| | | | Insulini cum zinco (Amorphi) suspension injectabilis |
| | | | Insulini cum zinco suspensio composita |
| | | | Insulini Isophani Protaminati Suspension injectabilis |
| | | | Insulini Solution Injectabilis |
| | | | Insulini Zinci Injectabilis Mixta |
| | | | Insulini zinci protaminati injectio |
| | | | Insulini zinci protaminati suspension injectabilis PZI |
| | | | Isophane Insulin |
| | | | Isophane Insulin (NPH) |

Isophane Insulin Suspension
Isophane Protamine Insulin Injection
IZS
Neutral Insulin
NPH Insulin
Ordinary Insulin
Prompt Insulin Zinc Suspension
Protamine zinc injection
Regular Insulin
Soluble Insulin
Unmodified Insulin

Natural Opium
Morphine
Diamorphine (Heroin)
Alphaprodine
Amileridine
Alfentanyl
Fentanyl
Sufentanyl
Nalbuphine

Buprenorphine
Butorphanol

Dextromoramide
Dezocine
Ketobemidone
Meptazinol

Pentamorphone
Pentazocine
Pethidine
Tincture Of Opium
Paregoric
Codeine

Hydromorphone
Oxymorphone
Hydrocodone
Oxycodone
Tramadol

Dextropropoxyphene
Diphenoxylate
Loperamide
Methadone

## Top Hazard Index - Continued

| SOIL CONTAMINATES | WATER CONTAMINATES | AIR CONTAMINATES |
|---|---|---|
| gasoline | Sulfuric acid | Natural gas (methane) |
| methanol | Milk | Chlorine |
| Sulfuric acid | titanium dioxide | Anhydrous Ammonia |
| ethanol | Paint Pigments | Hydrogen Cyanide |
| hydrochloric acid | **Special Benign** (Pen Ink Samples of major brands for forensic purposes) | Sulfur dioxide |
| Fuel Oil (all grades) | lead | Molds |
| Antifreeze | sodium hydroxide | |
| JP (all grades) Fuel | mercury | |
| Pesticides/herbicides | cadmium | |
| dioxin | chromium | |
| Poly-Chlorinated Biphenyls | arsenic | |
| Trichloroethylene | copper | |
| Methyl-Tert-Butyl-Ether | nickel | |

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|---|---|---|
| Benzene | gold |  |
| low lead 100 octane fuel | potassium permanganate |  |
| asphalt | hydrochloric acid |  |
| motor oil | hydroflourosilicic acid |  |
| crude oil |  |  |
| brake fluid |  |  |
| Transmission fluid |  |  |
| Dimethoate (Cygon 2E, Lagon 2E) |  |  |
| Diazinon |  |  |
| Malathion |  |  |
| Pyrethrum |  |  |
| Bacillus Thuringiensis (Thuricide, Dipel) |  |  |
| Rotenone (Rotenone, Derris Dust, Deritox) |  |  |
|  |  |  |
|  |  |  |

## Appendix (2)

## Configuration Standard

| | | |
|---|---|---|
| Authors:<br>Adam Miller<br>Richard Hark | **RESPONSE FOR A REQUEST FOR A CONFIGURATION STANDARD**<br>**Rev 1.16** | **TITLE: <u>Configuration Standard for Man-Portable Laser Induced Breakdown Spectrometers (MP-LIBS) Used in Domestic First Responder Applications</u>**<br>Effective Date: 21 December 2009 |

## 1. AUTHORITY

The United State Army Research Laboratory has commissioned the creation of this Configuration Standard under contract # W911NF-08-C-0094.

## 2. PURPOSE

This standard applies a configuration framework for all developments of man-portable LIBS technology applied for use by the domestic first responder community. The standard also provides requirements for the tracking of changes to system and software components.

## 3. SCOPE

This applies to all man-portable LIBS units designed for implementation in the domestic first response community. A man-portable LIBS unit is defined as a self-contained device consisting of at a minimum: 1) laser, 2) spectrometer, 3) focusing optics, 4) power supply and 5) supporting IT hardware and software components required to display collected information. This standard does not apply in whole to “hand-held” LIBS devices.

## 4. STANDARD

1.1. Configuration management is the management process for establishing and maintaining consistency of an MP-LIBS unit’s performance, and the functional and physical attributes with its requirements, design, and operational information throughout its life. Each manufacturer should establish a configuration management program that defines organizational responsibilities and processes that document and provide accountability for changes to devices and/or associated software components in the production IT environment. Configuration management programs should contain the following elements:

   1.1.1 Consistent, unique identification of devices and/or associated software and hardware components.

   1.1.2 Documented change control for coordination of all changes/updates to devices, operating system software, and/or associated software components, including when and how they are made, and by whom.

1.1.3 Status accounting to track the state of all configuration items, pending changes, and approved changes to configuration items.

1.1.4 Verification and auditing to ensure that the processes function as designed. In addition, ISO 10007:1995, *Quality Management – Guidelines for Configuration Management* and ANSI/EIA 649:1998, *National Consensus Standard for Configuration Management* provides broad, general guidance, applicable to both hardware and software components, on how to design, structure and implement configuration management programs.

1.2 The MP-LIBS is envisioned to operate in a cold zone. Nevertheless, aach manufacturer should design each system to be intrinsically safe as if the the MP-LIBS were to be used in hazardous environments. Each manufacturer should design their MP-LIBS to conform to the following operating environments for explosive hazards listed below. A guide to classes and zones is included in **Attachment A**.

1.2.1 Each manufacturer should design MP-LIBS units as if they were going to operate in each zone and division listed below in the chart.

| **Zone** | **ATEX Cat.** | **CENELEC EN** | **IEC 60079** | **American Practice** | **Division** | **General Characteristics** |
|---|---|---|---|---|---|---|
| 0, 1, 2 | 1, 2, 3 | 50020 | -11 | Intrinsic Safety | 1, 2 | Suitable for process instruments. Low energy, safe with 2 faults. |

1.2.2 Each manufacturer should design MP-LIBS units as if they were going to operate in Class 1, Class 2 and Class 3 / Zone 0, Zone 1 and Zone 2 environments.

1.2.3 Each manufacturer should design MP-LIBS units as if they were going to operate in Division 1 and Division 2 / Protection Type “ia” environments.

1.2.4 Each manufacturer should design MP-LIBS units as if they were going to operate in Groups A through G / Groups I, IIA, IIB, IIC environments.

1.3 Though the MP-LIBS is not intended for use in a hot or warm zone each manufacturer should design each system to be decontaminated under field-use conditions, and to be able withstand the standard field decontamination practices of equipment in the hot-to-warm zone transition. Each device should be capable of maintaining its structural integrity, electrical system integrity and sealing mechanisms while being exposed to standard decontamination solutions, tools and techniques.

1.3.1 The sealing mechanisms and casing material used to house the MP-LIBS components should be able to withstand exposure to the common decontamination solutions indicated in **Attachment B**.

1.3.2 Each device should be able to withstand the impact, abrasion and aggressive contact of common decontamination tools. Soft and medium polymer brush bristles are the standard mediums used.

1.3.3 Each device should be able to withstand the pressure exerted by a soft spray device nozzle. The minimum operating exposure pressure to withstand is 20 pounds per square inch (psi.)

1.3.4 Each device should be able to withstand exposure to solutions introduced at a temperature up to 160 degrees Fahrenheit at the maximum pressure listed in 1.3.3.

1.4 Each manufacturer should design each system to be capable of operating without interruption, distortion or failure of any kind due to electromagnetic interference generated by the radio transmission / reception equipment in proximity of the MP-LIBS device.

1.4.1 The device (software and hardware) should be able to meet this standard during all conditions of operation of internal radio transmission and reception devices collocated within the MP-LIBS housing.

1.4.2 The device (software and hardware) should be able to meet this standard while operating within close proximity (two feet) of the antenna clusters of wireless radio devices mounted in emergency vehicles. Sample frequency output tolerances are ranged below as minimum standards:

1.4.2.1 Low Band (3-30MHz): 100 Watt output

1.4.2.2 VHF (30 MHz to 300 MHz): 110 Watt output

1.4.2.3 UHF (300-512 MHz): 110 Watt output

1.4.2.4 UHF (824-960 MHz): 35 Watt output

1.4.2.5 UHF (1850-1910 MHz): 3 Watt output

1.4.2.6 UHF (2400–2483.5 MHz): 2 Watt output

1.4.3 The radio transmission equipment contained within the MP-LIBS device should not operate in a manner that inhibits the operation, IP – based communications backbone, clarity or transmission strength of an external portable wireless device being used in proximity (> one foot) of the MP-LIBS.

1.4.3.1 The radio transmission equipment (Bluetooth, Wi-Fi, Cellular, etc.) integrated into the MP-LIBS device should comply with all federal laws and regulations respective to the type, frequency and transmission strength of the transmitting devices therein contained.

1.4.4 A manual override shutdown switch for all wireless radio transmitting equipment should be clearly and prominently displayed and accessible on the main control surface of each MP-LIBS device.

1.4.4.1 Environments with improvised explosive devices (IEDs) and commercial explosive detonation devices may be encountered during service. It is important that an operator be able to terminate radio transmission immediately should such a threat become a concern. The manual override shutdown switch should be able to cause the immediate cessation of such radio transmission (in less than one [1] second.)

1.4.4.2 Should an explosive hazard concern arise, it is desirable that a remote operator monitoring the MP-LIBS device operation be capable of disabling the transmission remotely. The radio transmission equipment's software control module should be configured to allow a remote administrator access to a manual override shutdown command. The time frame for remote termination upon activation / request should be less than three (3) seconds.

1.4.4.3 Each device should have a 'panic' button prominently visible on the operating surface of the instrument. If an emergency condition arises, the responder may activate a visible and audible alarm that alerts other responders that the operator is in distress.

1.4.4.3.1 The unit should have a 2" wide button, red in color with LED back-light, which should activate the alarm after depressed for 2 continuous seconds.

1.4.4.3.2 The audible and visual alarms should activate once the button is pressed, and remain in operation until canceled by depressing the button on the unit for 2 additional seconds.

1.4.4.3.3 The wireless radio in the unit should transmit a distress signal to the remote command post interface, providing the GPS coordinates of the unit at the time of activation.

1.5 Each manufacturer should design their MP-LIBS device to operate in climactic conditions (aside from the potential hazardous material exposure) that are defined as follows:

1.5.1 Each device should operate with full functionality at ambient air temperatures of -20 degrees Celsius (-4 degrees Fahrenheit).

1.5.2 Each device should operate with full functionality at an ambient air temperature of +54.4 degrees Celsius (+130 degrees Fahrenheit).

1.5.3 Each device should operate with full functionality at an ambient air relative humidity of 100%.

1.6 Each manufacturer should design their MP-LIBS device with sufficient ruggedness that it is capable of operating to its full capacity in field conditions likely to be encountered during hazardous incident response and in warfare theatre operations.

1.6.1 Each device should certify to the ruggedness standards of the Department of Defense (DOD) Test Method Standard for Environmental Engineering Considerations and Laboratory Tests (MIL STD-810F). A copy of this standard and the most recent change notice update are available for download from http://www.dtc.army.mil/publications/milstd.html.

1.7 Each manufacturer should ensure that their MP-LIBS device meets all applicable federal standards for laser products and is properly registered as currently required by the Federal Drug Administration's (FDA) Center for Devices and Radiological Health (CDRH). The MP-LIBS unit should be designed to provide adequate protection from exposure to laser radiation for users and auxiliary personnel.

1.7.1 Each MP-LIBS device should comply with 21 CFR 1040.10 (Performance Standards for Light-emitting Products; see http://www.accessdata.fda.gov/scripts/cdrh/cfdocs/cfcfr/CFRSearch.cfm?FR=1040.10). Comparable sections of IEC 60825-1, Am.2, and IEC 60601-2-22 (the International Electrotechnical Commission standards), may be substituted for 21 CFR 1040.10 as described in Laser Notice No. 50 (see http://www.fda.gov/cdrh/ocer/guidance/1346.html).

1.7.1.1 Each MP-LIBS device should be equipped with a key switch- or password-enabled safety interlock system. The interlock system should be separate from the trigger mechanism used to fire the laser and should operate as a dead man switch to maintain laser safety in the event that the operator is incapacitated.

1.7.2 Each MP-LIBS device should be designed to operate in such a way so as to afford an appropriate level of laser eye safety following the standards outlined in ANSI Z136.1 (American National Standard for Safe Use of Lasers) and ANSI Z136.6 (American National Standard for Safe Use of Lasers Outdoors).

1.7.2.1 The operator and non-users should be protected from exposure to laser radiation via a passive laser guard, such as a sampling chamber with high optical density shielding commensurate with the laser wavelength.

1.8 Ergonomic operations (future development)

1.9 Visual and audible interface

1.9.1 Each MP-LIBS device should have a suite of information displays that are readily visible through the 40mil PVC Level A chemical protective clothing ensemble and the (up to) 15mil PVC self-contained breathing apparatus (SCBA) face shield. The display brightness of an LCD screen for text and graphic display should have a minimum of 1700:1 contrast ratio.

1.9.1.1 The LCD screen should have a glare-reducing coating, or other accommodation that provides glare reduction.

1.9.1.2 The text characters displayed on an LCD or similar screen should be readable at a distance of 24” using the personal protective equipment described in 1.9.1. The suggested minimum font size is 36 point using the “Arial” true type font.

1.9.1.3 Chart lines should be readable at a distance of 24” using the personal protective equipment described in 1.9.1. The suggested line size is 2.5 point in width, colored in clear contrast with the background color displayed.

1.9.1.4 Warning lights, power meter or signal strength illuminated displays should be readable at a distance of 24” using the personal protective equipment described in 1.9.1.

1.9.2 Each MP-LIBS device should have audible information and alarm generators that are capable of being clearly recognized and understood by an operator wearing a Level A fully encapsulating chemical protective clothing ensemble and using a self-contained breathing apparatus (SCBA) in positive pressure mode.

1.9.2.1 Audible information messages should be able to be clearly heard at a distance of 36” (inches) from the display console of the device using the personal protective equipment described in 1.9.1.

1.9.2.2 Audible warnings and alarms should be able to be clearly heard at a distance of 20’ (feet) from the display console of the device using the personal protective equipment described in 1.9.1.

1.9.2.3 Requirements of this section are contingent on the assumption that the end-user / operator of the device has no more than a 10% hearing loss in any ear.

1.9.2.4 The audible alarm should not sound the same as a PASS alarm attached to SCBA.

1.9.2.5 A visual LED cluster at the device's lid's edge area should be installed and operate when a panic alarm is activated, or when an analysis identifies an extremely hazardous substance.

1.9.2.6 The device should have a manual override switch to disable the audible and visual alarm for law enforcement operations.

1.10 The MP-LIBS device should be able to detect a broad variety of hazardous and nonhazardous materials that may be encountered by First Responders in the course of their duties. Analysis should be performed on materials contained inside a sample chamber fitted with a suitable transparent window.

1.10.1 These materials fall into the following major classifications:

        - 1.10.1.1 Chemical Warfare Agents (CWAs)
        - 1.10.1.2 Biological Warfare Agents (BMAs)
        - 1.10.1.3 Nuclear and Radiological agents
        - 1.10.1.4 Explosives
        - 1.10.1.5 Toxic Industrial Chemicals (TICs) and Toxic Industrial Materials (TIMs)
        - 1.10.1.6 Drugs
        - 1.10.1.7 Commonly encountered nonhazardous materials, including but not limited to, benign powders such as consumer commodities that are often used to simulate hazardous materials (such as talcum powder)
    - 1.10.2 Each MP-LIBS device should be capable of analyzing materials in solid or liquid form.
    - 1.10.3 Each MP-LIBS device should allow for averaging of multiple shots to improve the analytical figures of merit.
    - 1.10.4 Each MP-LIBS device should be capable of identifying the classes of materials identified in 1.10.1 both in substantially pure form (i.e. greater than 95% purity) and also as a minor component (i.e. 5% or greater) in a mixture.
- 1.11 Each MP-LIBS device should be constructed to allow the maximum flexibility for sampling in a variety of settings and locations. It is not possible to specify every situation in which the MP-LIBS system may be used but the manufacturer should anticipate that the device may be used in areas of difficult access, restricted openings, etc. and should design the system to allow for the broadest possible use.
- 1.12 Each MP-LIBS device should be capable of performing a complete analysis cycle in less than 20 seconds. This includes triggering the laser to form a micro-plasma, collection of emitted light, analysis of the data, and display of the results.
    - 1.12.1 The MP-LIBS device should be capable of carrying out 180 analyses per hour.
    - 1.12.2 The MP-LIBS device should be capable of carrying out 900 analyses without the need to recalibrate the system.
    - 1.12.3 The MP-LIBS device should be capable of carrying out 100,000 analyses without the need for servicing or replacement of components.
    - 1.12.4 The MP-LIBS device should have a minimum working life cycle of 5 years.
- 1.13 Each MP-LIBS device should have embedded chemical analysis software that provides a probabilistic result allowing for the identification of materials.

1.13.1 Each MP-LIBS device should contain a library containing the LIBS spectra (obtained under standardized conditions) of commonly encountered materials from the classes outlined in 1.10.1.

1.13.2 The MP-LIBS software should probabilistically evaluate the consistency of the acquired data with the library standards.

1.13.3 The MP-LIBS software should have the capability to assess whether a mixture of two or more materials can account for the sample data from the library.

1.13.4 The MP-LIBS software should display a result that indicates how well one or more materials account for the sample data. The most likely candidates should be listed in decreasing order of fit.

1.13.5 Results should be classed into threat groups (Chemical, Biological, Etc.) and displayed based first on the most hazardous component identified, then to more benign components.

1.14 Each MP-LIBS device should deliver repeatable, reproducible, and reliable results as verified by testing against a battery of calibrant compounds.

1.14.1 Repeatability is defined as the ability of the MP-LIBS device to give the same result each time analysis of an identical sample is performed. The unit should meet the repeatability standard if the same top candidate is identified in 99% of the measurements.

1.14.2 Reproducibility is defined as the ability of two MP-LIBS devices to give the same results when analyzing the same material. The units should meet the reproducibility standard if both devices 99% of the time identify the same top candidate.

1.14.3 Reliability is defined as the likelihood that the MP-LIBS device will identify the correct material. It is a measure of both the sensitivity and specificity of the analysis.

1.14.3.1 The manufacturer should design each MP-LIBS device to achieve the greatest sensitivity (i.e. lowest possible limit of detection or LOD) for any given material. Since the LOD will vary depending on the material being analyzed and a variety of environmental factors the MP-LIBS device should meet the sensitivity standard if the correct material can be identified at a level commensurate with the nature of the potential hazard.

1.14.3.1.1 Each manufacturer should publish the limit of detection upon completion of the device spectra library in print format, within a user manual.

1.14.3.1.2 Each device’s software should have the capability of displaying the limit of detection to the end user, upon manual request of the user.

1.14.3.2 The manufacturer should design each MP-LIBS device to provide maximum discrimination between materials with similar LIBS spectra.

1.14.3.2.1 The MP-LIBS device should meet the specificity standard if the false negative rate is less than 0.5% and the false positive rate is less than 1% for spectral libraries containing 250 or more materials. In cases where the rate of false positives of the instrument is greater than 1% for single-shot operations, the manufacturer should develop a protocol that requires responders to perform additional sampling when a positive result is displayed for a hazardous substance.

1.14.3.2.2 The manufacturer should provide for all calibrants receiver operating characteristic (ROC) curves (i.e. a plot of the sensitivity or true positive rate versus the specificity or false positive rate). The manufacturer should design the MP-LIBS system to maximize the area under the curve (AUC) of each ROC curve.

1.15 Each MP-LIBS device and software should have a calibration subroutine.

1.15.1 The manufacturer should specify the nature and number of calibrants used to ensure the requirements outlined in Section 1.14 are satisfied.

1.15.2 The calibration routine should be able to be completed in under normal conditions typically encountered in the field in less than 5 minutes.

1.16 Each MP-LIBS device should include on board systems for automatically recording information about the sample area.

1.16.1 Each MP-LIBS device should contain a Global Positioning System (GPS) for automatically recording the specific sample location. The last exterior GPS reading should be used when taking samples within a building or under shelter.

1.16.2 Each MP-LIBS device should automatically record the date and time each analysis was performed.

1.16.2.1 This information should be obtained wirelessly from the ‘atomic clock’ standardized world time, operated by the National Institute of Standards and Technology (NIST).

1.16.3 Each MP-LIBS device should contain a video system for automatically recording an image of the sample area.

1.16.3.1 The video system should be capable of live capture and transmission wirelessly to a remote location.

1.16.3.2 The video system should record a series of still images, at a minimum resolution of 2 mega pixels, upon each laser-triggering event. These images should bear a stamp of the date, time, and GPS coordinates for the purpose of evidentiary documentation.

1.17 Each MP-LIBS device should be capable of being powered live in the field, and also capable of operating for reasonable work periods on its own self-contained power.

1.17.1 During most initial investigatory operations, the device will need to operate for a minimum of 5 hours under its own power. Each unit should be equipped with an internal rechargeable battery power supply that is able to power the entire device, including its accessories, for at least5 hours at +25 degrees Celsius (77 degrees Fahrenheit.)

1.17.1.1 Each unit operating in this mode should have a software program control that automatically powers down the graphic displays and ancillary features (excepting 2 way radio transmission) to facilitate increased battery life and prevent unnecessary power waste. It is recommended that a solid-state hard drive be incorporated into any device designed to operate in this mode.

1.17.2 During most hygienic investigations (continuous periodic sampling over a period of time) each device should operate for a minimum of 24 hours. This can be accomplished either under tethered power (i.e. plugged into an external power source.)

1.17.2.1 Each unit manufactured to operate in hygienic mode under tethered power should be equipped with a minimum 100' power cord that has a plug transformer capable of being powered by 100-240 V AC @ 50/60 Hz., as well as into a DC 12 V vehicle power system.

1.18 Each MP-LIBS device should be capable of being transported by a responder in appropriate personal protective equipment by the man-power of the responder. Each device should be designed to accommodate the personal protective equipment described in section 1.9.1, in addition to ensuring ease of manipulation while the end user is equipped in up to 3 layers of 25 mil thick chemical protective gloves.

1.18.1 This standard does not specify what the precise dimensions of the entire MP-LIBS ensemble should be, so as not to limit the manufacturer to certain applications. It is recommended that manufacturers consider how end users will transport and store each MP-LIBS device, therefore minimization of the device’s size footprint should be considered for each stated application

1.18.2 Man-Portable devices with self-contained mobility support (MP-LIBS with attached / enclosed wheels): each device designed with mobility support devices should not exceed 50 pounds in weight.

1.18.2.1 Man-Portable devices with self-contained mobility support (MP-LIBS with attached / enclosed wheels) should be of such mechanical design and tread that they can withstand rolling exposure to diverse terrains (sand, snow, soil.) Due to the variety of designs available, it is not necessary to specify precisely what the mobility support devices should be, but that they are capable of operations in the environments listed above without significant force application by the operator.

1.18.3 Man-Portable devices without self-contained mobility support (MP-LIBS with attached / enclosed wheels): each device designed without mobility support should not exceed 20 pounds in weight.

1.18.3.1 Man-Portable devices without self-contained mobility support (MP-LIBS with attached / enclosed wheels) should have a handle / handles capable of accommodating the personal protective equipment ensemble hand gear described in 1.9.1.

1.19 Each manufacturer should provide a list to the end user of materials that, if interrogated using the laser could react in a manner that could potentially harm the responder sampling the material.

1.19.1 Each manufacturer should consider the applications that they are stating their equipment can be used for. These applications should then be examined by the manufacturer for known hazards, such as interrogating flammable gases (but not limited to,) and provide a compendium of response scenario utility warnings pursuant to known or likely to be encountered hazards

1.19.1.1 The compendium should describe a response protocol for interrogating explosive materials, including a delineation of response protocols between primary and secondary high explosives.

1.19.2 Each manufacturer should indicate in this list all developmental test materials which have been shown to produce an adverse reaction which under developmental observation, would potentially cause injury to the responder, or a release of hazardous materials into the surrounding atmosphere or environment of such quantity that an environmental remediation activity would be required to bring the incident site to a safe condition.

## 5. DEFINITIONS AND ABBREVIATIONS

**CONTAMINATION:** Radioactive material deposited or dispersed into materials or places where it does not belong.

**DECONTAMINATION:** The removal of radioactive contaminants by cleaning and washing with water and/or chemicals.

**HOT ZONE:** The area immediately around an incident site in which all personnel must wear appropriate protective clothing and equipment.

**HYGIENIC SAMPLING:** The passive sampling of an environment repeatedly over time, to measure changes in environmental or sample conditions over time.

**IONIZING RADIATION:** Any type of radiation that can, directly or indirectly, change the electric charges of atoms or molecules. It is produced when radionuclides decay.

**LASER-INDUCED BREAKDOWN SPECTROSCOPY:** Laser-induced breakdown spectroscopy (LIBS) is a type of atomic emission spectroscopy that utilizes a highly energetic laser pulse as the excitation source. LIBS can analyze any matter regardless of its physical state, be it solid, liquid or gas. Slurries, aerosols, and gels can be interrogated using this technique.

**LIBS:** Laser Induced Breakdown Spectroscopy.

**MP-LIBS:** Man-portable LIBS, an integrated LIBS system capable of being carried and utilized by a single individual.

**QUALITATIVE ANALYSIS:** The determination of the identity of the components in the sample.

**QUANTITATIVE ANALYSIS:** The determination of the amount or concentration of the components in the sample.

**REPRODUCIBILITY:** To make a copy, representation, duplicate a result.

## 6. REFERENCES

6.1 Underwriters Laboratories: Hazardous Locations. http://www.ul.com/hazloc/define.htm.

6.2 Burke, Robert (2006). *Counter-terrorism for Emergency Responders.* Boca Raton, CRC Press.

6.3 Bravata DM. Sundaram V, McDonald KM, Smith WM, Szeto H, Schleinitz MD, et al. Detection and diagnostic decision support systems for bioterrorism response. Emerg Infec Dis Vol. 10, No.1, 2004 Jan. Available from http://ww.cdc.gov/ncidod/EID/vol10no1/03-0243.htm.

## 7. ATTACHMENTS

Attachment A –Hazard Classes and Zones.

Attachment B – Common Decontamination Solutions.

## *ATTACHMENT A*: Definitions of Classes and Zones

Hazardous Areas are locations where the potential for fire or explosion exists because of gases, dust, or easily ignitable fibers or flyings in the atmosphere.

In North America, hazardous areas are separated by classes, divisions, and groups to define the level of safety required for equipment installed in these locations. *Classes* define the general form of the flammable materials in the atmosphere. *Divisions* define the probability of the presence of flammable materials. *Groups* classify the exact flammable nature of the material.

In Europe and countries outside of North America, classification of hazardous areas is accomplished differently. *Zones* are used to define the probability of the presence of flammable materials. *Protection Types* denote the level of safety for the device. *Groups* classify the exact flammable nature of the material. These groups are separated differently than North American Groups. *Temperature Identifications* convey the maximum surface temperature of the apparatus based on 104° F (40° C) ambient. These temperature codes are selected carefully not to exceed the ignition temperature of the specific gas or vapor to be encountered in the application.

Some classifications are not shown here. For further detailed information, see specific standards published by approval organizations.

### Common Terms:

### Class I, Division 1

A Class I, Division 1 location is a location where ignitable concentrations of flammable gases, vapors or liquids:

- can exist under normal operating conditions;
- may exist frequently because of repair or maintenance operations or because of leakage; or
- may exist because of equipment breakdown that simultaneously causes the equipment to become a source of ignition

**Equipment intended for use in a Class I, Division 1 area is usually of the explosionproof, intrinsically safe, or purged/pressurized type.**

**Explosionproof apparatus:** "Apparatus enclosed in a case that is capable of withstanding an explosion of a specified gas or vapor that may occur within it and of preventing the ignition of a specified gas or vapor surrounding the enclosure by sparks, flashes, or explosion of the gas or vapor within and that operates at such an external temperature that a surrounding flammable atmosphere will not be ignited thereby." (See NFPA 70)

**Intrinsically safe apparatus:** "Apparatus in which all the circuits are intrinsically safe." (See UL 913)

**Intrinsically safe circuit:** "A circuit in which any spark or thermal effect is incapable of causing ignition of a mixture of flammable or combustible material in air under prescribed test conditions." (See UL 913)

**Purging:** "The process of supplying an enclosure with a protective gas at a sufficient flow and positive pressure to reduce the concentration of any flammable gas or vapor initially present to an acceptable level."
(See NFPA 496)

**Pressurization:**"The process of supplying an enclosure with a protective gas with or without continuous flow at sufficient pressure to prevent the entrance of a flammable gas or vapor, a combustible dust, or an ignitable fiber." (See NFPA 496)

### Class I, Division 2

**A Class I, Division 2 location is a location:**

- where volatile flammable liquids or flammable gases or vapors exist, but are normally confined within closed containers;
- where ignitable concentrations of gases, vapors or liquids are normally prevented by positive mechanical ventilation; or
- adjacent to a Class I, Division 1 location, where ignitable concentrations might be occasionally communicated.

**Equipment intended for use in a Class I, Division 2 area is usually of the nonincendive, non-sparking, purged/pressurized, hermetically sealed, or sealed device type.**

**Nonincendive circuit:** "A circuit in which any arc or thermal effect produced under intended operating conditions of the equipment is not capable, under the test conditions specified, of igniting the specified flammable gas- or vapor- air mixture."(See UL 1604)

**Nonincendive component:** "A component having contacts for making or breaking an incendive circuit and the contacting mechanism should be constructed so that the component is incapable of igniting the specified flammable gas- or vapor-air mixture. The housing of a nonincendive component is not intended to:

- exclude the flammable atmosphere, or
- contain an explosion." (See UL 1604)

**Nonincendive field circuit:** "A circuit that enters or leaves the equipment enclosure and that under intended operating conditions is not capable, under the test conditions specified, of igniting the specified flammable gas- or vapor-air mixture or combustible dust." (See UL 1604)

**Non-sparking apparatus:** "Apparatus that has no normally arcing parts or thermal effects capable of ignition. Examples of normally arcing parts are relays, circuit breakers, servo-potentiometers adjustable resistors, switches, non-latching type connectors and motor brushes. (See UL 1604)

**Purging:** See definition under Class I, Division 1

**Pressurization:** See definition under Class I, Division 1

**Hermetically sealed component:** "A component that is sealed against entrance of an external atmosphere and in which the seal is made by fusion, such as soldering, brazing, welding, or the fusion of glass to metal." (See UL 1604)

**Sealed device:** "A device that is constructed so that it cannot be opened, has no external operating mechanisms, and is sealed to restrict entry of an external atmosphere without relying on gaskets. The device may contain arcing parts or internal hot surfaces." (See UL 1604)

**Class I, Zone 0**

A Class I, Zone 0 location is a location where ignitable concentrations of flammable gases, vapors or liquids:
- are present continuously; or
- are present for long periods of time.

Equipment intended for use in a Class I, Zone 0 area is usually of the intrinsically safe, "ia," type.

Intrinsically safe: See definitions under Class I, Division 1

**Class I, Zone 1**

A Class I, Zone 1 location is a location where ignitable concentrations of flammable gases, vapors or liquids:
- are likely to exist under normal operating conditions;
- may exist frequently because of repair or maintenance operations or leakage; or
- may exist because of equipment breakdown that simultaneously causes the equipment to become a source of ignition; or
- are adjacent to a Class I, Zone 0 location from which ignitable concentrations could be communicated.

Equipment intended for use in a Class I, Zone 1 area is usually of the flameproof, purged/pressurized, oil immersed, increased safety, encapsulated or powder filled type.

**Flameproof:** "The enclosure of the equipment will withstand an internal explosion, and prevent passage of flame to the surrounding atmosphere. Care must be taken to maintain the length and clearance (gap) of flameproof joints in service." (See UL 2279)

**Purged/pressurized:** See definitions under Class I, Division I.

**Oil immersion:** "Arcing contacts are immersed in a protective liquid." (See UL 2279)

**Increased safety:** "The equipment contains no normally arcing parts, and additional measures (such as larger spacings among wiring connections) are taken to prevent the possibility of high temperatures or sparks. A minimum IP rating of IP 54 is required." (See UL 2279)

**Encapsulation:** "Arcing contacts are completely surrounded by an encapsulating material." (See UL 2279)

**Powder filling:** "Arcing contacts are surrounded by a filling material (glass or quartz powder)." (See UL 2279)

### Class I, Zone 2

A Class I, Zone 2 location is a location:

- where ignitable concentrations of flammable gases, vapors or liquids are not likely to occur in normal operation or, if they do occur, will exist only for a short period;
- where volatile flammable liquids, or flammable gases or vapors exist, but are normally confined within closed containers
- where ignitable concentrations of gases, vapors, or liquids are normally prevented by positive mechanical ventilation;
- adjacent to a Class I, Zone 1 location from which ignitable concentrations could be communicated.

Equipment that is intended for use in a Class I, Zone 2 area is usually of the nonincendive, non-sparking, restricted breathing, hermetically sealed or sealed device type.

**Nonincendive:** See definitions under Class I, Division 2

**Non-sparking:** See definition under Class I, Division 2

**Restricted breathing:** "The enclosure relies on tight seals and gaskets to prevent diffusion of the explosive atmosphere into the equipment enclosure. Provision for checking that the restricted breathing properties of the enclosure are maintained is provided." (See UL 2279)

**Hermetically sealed:** See definition under Class I, Division 2

**Sealed device:** "A device that is constructed so that it cannot be opened and is sealed to restrict entry of an external atmosphere. The device may contain arcing parts or internal hot surfaces." (See UL 2279)

### Class II, Division 1

**A Class II, Division 1 location is a location where:**

- ignitable concentrations of combustible dust can exist in the air under normal operating conditions;
- ignitable concentrations of combustible dust may exist because of equipment breakdown that simultaneously causes the equipment to become a source of ignition;

or

- electrically conductive combustible dusts may be present in hazardous quantities.

**Equipment intended for use in a Class II, Division 1 area is usually of the dust-ignition-proof, intrinsically safe, or pressurized type.**

**Dust-ignition-proof :** "Enclosed in a manner that will exclude dusts and, where installed and protected in accordance with the NEC, will not permit arcs, sparks or heat otherwise generated or liberated inside of the enclosure to cause ignition of exterior accumulations or atmospheric suspensions of a specified dust on or in the vicinity of the enclosure." (See NFPA 70)

**Intrinsically safe:** See definitions under Class I, Division 1.

**Pressurization:** See definition under Class I, Division 1.

**Class II, Division 2**

A Class II, Division 2 location is a location where:

- combustible dust is not normally in the air in ignitable concentrations;
- dust accumulations are normally insufficient to interfere with normal operation of electrical equipment;
- dust may be in suspension in the air as the result of infrequent malfunctioning of equipment; or
- dust accumulation may be sufficient to interfere with safe dissipation of heat or may be ignitable by abnormal operation.

**Equipment intended for use in a Class II, Division 2 area is usually of the dusttight, Nonincendive, non-sparking, or pressurized types.**

**Dusttight:** "Constructed so that dust will not enter the enclosing case under specified test conditions. An example of such conditions would be a UL Type 12 enclosure." (See NFPA 70)

**Nonincendive:** See definitions under Class I, Division 2

**Non-sparking:** See definition under Class I, Division 2

**Pressurization:** See definition under Class I, Division 1.

**Class III, Division 1**

A Class III, Division 1 location is a location where easily ignitable fibers or materials producing combustible flyings are handled, manufactured or used.

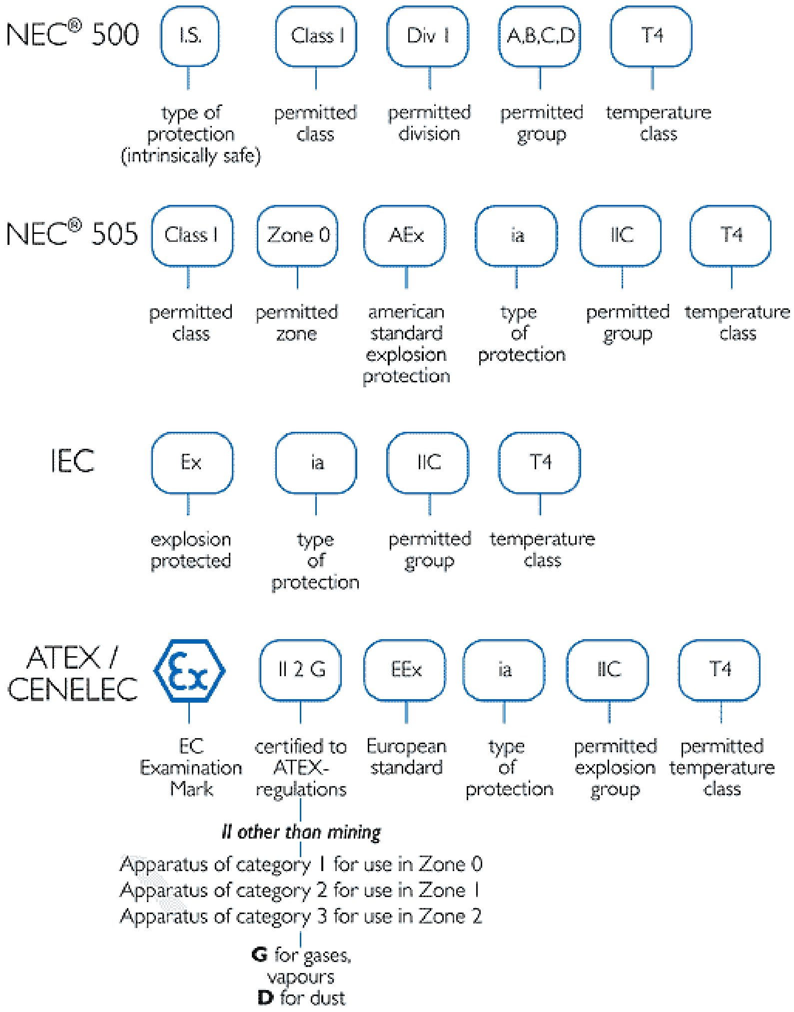
Equipment intended for use in a Class III, Division 1 area is usually of the dust-tight or intrinsically safe type (both previously defined).

### Class III, Division 2

A Class III, Division 2 location is a location where easily ignitable fibers are stored or handled.

Equipment intended for use in a Class III, Division 1 area is usually of the dust-tight or intrinsically safe type (both previously defined).

### Interpreting Rating Nomenclature:


NEC® 500
I.S.
type of protection (intrinsically safe)
Class I
permitted class
Div I
permitted division
A,B,C,D
permitted group
T4
temperature class
NEC® 505
Class I
permitted class
Zone 0
permitted zone
AEx
american standard explosion protection
ia
type of protection
IIC
permitted group
T4
temperature class
IEC
Ex
explosion protected
ia
type of protection
IIC
permitted group
T4
temperature class
ATEX / CENELEC
EC Examination Mark
II 2 G
certified to ATEX-regulations
EEx
European standard
ia
type of protection
IIC
permitted explosion group
T4
permitted temperature class
II other than mining
Apparatus of category 1 for use in Zone 0
Apparatus of category 2 for use in Zone 1
Apparatus of category 3 for use in Zone 2
G for gases, vapours
D for dust

### Classifications Inside North America

**Classes**

| | |
|---|---|
| ***Class I*** | Flammable gases or vapors are present in the air in quantities sufficient to produce explosive or ignitable mixtures. |
| ***Class II*** | Combustible or conductive dusts are present. |
| ***Class III*** | Ignitable fibers or flyings are present, but not likely to be in suspension in sufficient quantities to produce ignitable mixtures. (Group classifications are not applied to this class.) |

**Divisions**

| | |
|---|---|
| ***Division 1*** | The substance referred to by class is present during normal conditions. |
| ***Division 2*** | The substance referred to by class is present only in abnormal conditions, such as a container failure or system breakdown. |

**Groups**

| | |
|---|---|
| ***Group A*** | Acetylene |
| ***Group B*** | Hydrogen (or gases of equivalent hazard) |
| ***Group C*** | Ethylene (or gases of equivalent hazard) |
| ***Group D*** | Gasoline (or gases of equivalent hazard) |
| ***Group E*** | Metal Dust |
| ***Group F*** | Coal Dust |
| ***Group G*** | Grain Dust |

### Classifications Outside North America

### Zones

| | |
|---|---|
| ***Zone 0*** | Area in which an explosive gas-air mixture is continuously present or present for long periods. |
| ***Zone 1*** | Area in which an explosive gas-air mixture is likely to occur in normal operation. |
| ***Zone 2*** | Area in which an explosive gas-air mixture is not likely to occur, and if it occurs it will only exist for a short time. |

### Protection Types

| | | **Zone** |
|---|---|---|
| ***d*** | Flameproof (Explosion proof) Enclosure | 1,2 |
| ***e*** | Increased Safety | 1,2 |
| ***ia*** | Intrinsic Safety | 0,1,2 |
| ***ib*** | Intrinsic Safety | 1,2 |
| ***o*** | Oil Immersion | 2 |
| ***p*** | Pressurized Apparatus (Purged Apparatus) | 1,2 |
| ***q*** | Powder Filling (Sand Filling) | 2 |
| ***m*** | Encapsulation | 1,2 |
| ***n*** | Normally Nonsparking and/or Nonincendive Circuits) | 2 |

**Temperature Codes**

| | ° *F* | ° *C* |
|---|---|---|
| ***T1*** | 842 | 450 |
| ***T2*** | 572 | 300 |
| ***T3*** | 392 | 200 |
| ***T4*** | 275 | 135 |
| ***T5*** | 212 | 100 |
| ***T6*** | 185 | 85 |

**Groups**

| | |
|---|---|
| ***Group I*** | For application in below ground installations (mines) where methane (firedamp) and coal dust may be present. |
| ***Group IIA*** | For application in above ground installation where hazards due to propane may exist. This group most closely matches the North American Group D. |
| ***Group IIB*** | For application in above ground installations where hazards due to ethylene may exist. This group most closely matches the North American Group C. |
| ***Group IIC*** | For application in above ground installations where hazards due to hydrogen or acetylene may exist. This group most closely matches the North American Groups A and B. |

## *Attachment B* – Common Decontamination Solutions

| **Product Use:** | **MSDS / Product Code:** | **CAS Registry Number / Components** |
|---|---|---|
| Decontamination of Radioactive Halogens | 77101 | 7732-18-5 WATER |
| Decontamination of Radioactive Actinides | 77103 | 7732-18-5 WATER |
| Decontamination of Radioactive Transmission Metals | 77102 | 7732-18-5 WATER |
| General Cleaning | | SOAP |
| Skin decontaminant for CW and BIO agents | F5402 | RSDL (Reactive Skin Decontamination Lotion) |
| Firefighting foam that is also can be used as a general (Class A) and BIO agent decontamination (Class B) material | | FOAM Class A and B |
| Used as the first wash for unknown contaminants such as inorganic acids, metal processing wastes, solvents and organic materials, PBBs (Polybrominated Biphenyls), PCBs (Polychlorinated Biphenyls) and etiological materials. | 1018 | 497-19-8 SODIUM CARBONATE, ANHYDROUS<br>6834-92-0 SODIUM METASILICATE<br>77-09-8 PHENOLPHTHALEIN<br>7732-18-5 WATER |

| | | |
|---|---|---|
| Used as the second wash for unknown contaminates and etiological materials such as heavy metals (mercury, lead, cadmium, etc.), pesticides, chlorinated phenols, dioxins, cyanides, ammonia and non-acid inorganic wastes. | 1019 | 7681-52-9 SODIUM HYPOCHLORITE<br>7732-18-5 WATER |
| Used as the third wash for unknown contaminants such as solvents and organic compounds, PBBs, PCBs, oils and greases or unspecified wastes not suspected to be contaminated with pesticides. Can also be used as a general-purpose rinse for Decon Solutions 1 and 2. | 1020 | 6834-92-0 SODIUM METASILICATE<br>72-48-0 ALIZARIN<br>7732-18-5 WATER |
| Used for base and caustic contaminants such as organic bases, alkali and caustic wastes. | 1021 | 7647-01-0 HYDROCHLORIC ACID<br>493-52-7 METHYL RED<br>7732-18-5 WATER |
| Used for all chemical and biological warfare agents on equipment only. | 1378 | 7778-54-3 CALCIUM HYPOCHLORITE (HTH) |
| Used to dissolve and flush chemical-based contaminants on | A0446 | 67-64-1 ACETONE |

|  |  |  |
|---|---|---|
| equipment only. |  |  |
| Used to dissolve and flush chemical-based contaminants on equipment only. | 107 | 60-29-7 ETHYL ETHER |
| Used for delicate equipment in decontaminating biological agents, including spores. Equipment must withstand up to 28 hours of continuous exposure. | J.T. Baker: 2105, 2106, 2108<br>Mallinckrodt: 5014, 5016 | 50-00-0 FORMALDEHYDE 37%<br>67-56-1 METHYL ALCOHOL 10-15%<br>7732-18-5 WATER 48-53%<br>(Formalin Solution) |
| Used for all G and V agents, Lewisite, and all bacterial agents, including spores on equipment only. Note: often used with a 10% alcohol solution. | S4034 | 1310-73-2 SODIUM HYDROXIDE |
| Used for all G and V agents, Lewisite, and all bacterial agents, including spores on equipment only. Note: often used with a 10% alcohol solution. | 19431 | 1310-58-3 POTASSIUM HYDROXIDE |
| Used for G agents on equipment only. | S3242 | 497-19-8 SODIUM CARBONATE, ANHYDROUS |
| Used for G agents and non-spore producing biological agents on | A5472 | 7664-41-7 AMMONIA |

| | | |
|---|---|---|
| equipment only. | | |
| Used for both chemical and biological agents, except spores, on equipment only | 6850-00-753-4870 | 111-40-0 DIETHYLENE TRIAMINE<br>109-86-4 2-METHOXYETHANOL<br>1310-73-2 SODIUM HYDROXIDE<br>***(Military Decon Solution # DS-2)*** |
| Used for G and V agents, and biological agents on equipment only. | BPFWX | 1305-78-8 SUPERTROPICAL BLEACH (STB) |
| Used for skin decontamination. | BGLVY | 64-17-5 ETHYL ALCOHOL<br>108-95-2 PHENOL<br>1310-73-2 SODIUM HYDROXIDE<br>7664-41-7 AMMONIA<br>7732-18-5 WATER<br>***(Military Skin Decon Kit M258A1)*** |
| Used for skin decontamination. | 191072 | 7440-44-0 CARBON (32-33%)<br>9017-79-2 STRONG BASE ANION EXHANGE POLYMER,<br>HYDROSIDE ION (11-33%)<br>6540-54-61 STRONG ACID CATION EXCHANGE POLYMER,<br>HYDROGEN ION (14-24%)<br>7631-86-9 SILICA<br>7732-18-5 WATER<br>***(Military Skin Decon Kit M291)*** |

# Appendix (3)

## Papers - Presentations - Posters - Conferences

### Papers

- *ctrochimica Acta Part B: Atomic Spectroscopy,* doi:10.1016/j.sab.2010.08.004' published online, Sept. 6, 2010. Refereed Paper -T Trejos, A Flores and JR. Almirall, **Micro-spectrochemical analysis of document paper and gel inks by laser ablation inductively coupled plasma mass spectrometry and laser induced breakdown spectroscopy**, *Spe*
- T Trejos, A Flores and JR. Almirall, **Micro-spectrochemical analysis of document paper and gel inks by laser ablation inductively coupled plasma mass spectrometry and laser induced breakdown spectroscopy,** *Spectrochimica Acta Part B: Atomic Spectroscopy,* doi:10.1016/j.sab.2010.08.004' published online, Sept. 6, 2010.

### Presentations

- *Schenk, E.R. "**Elemental analysis of unprocessed cotton by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and laser-induced breakdown spectroscopy (LIBS): a forensic application of geographic provenancing",** Graduate Student Association Forum, Florida International University, March 2010 Miami, FL.

- *Trejos, T. and Almirall J.R. **"Lasers: avances tecnológicos en la comparación e identificación de documentos dudosos",** III Conferencia Internacional Educativa en Ciencias Forenses CAD-IAI San Jose, Costa Rica, May 2010.
- *Trejos, T. and Almirall J.R**. Comparison of the capabilities of LIBS and LAICPMS for the forensic analysis of paper and gel ink**, Pittsburgh Conference, Orlando, FL, Feb. 2010

- Trejos, T. and *Almirall J.R. **Forensic analysis of inks by Laser Induced Breakdown Spectrometry (LIBS) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)** , AAFS Conference, Seattle, WA, Feb. 2010.

- J. J. Gonzalez*[1], A. A. Bol'shakov[2], J. Yoo[2], L. J. East[3], D. Wong[3], D. Oropeza[1], and R. Russo*[1]. [1]Lawrence Berkeley National Laboratory, [2]Applied Spectra, Inc., and [3]A3 Technologies. **Precision assessment of a commercial Laser Induced Breakdown Spectroscopy (LIBS) instrument based on the analysis of metal samples.** Winter Plasma Conference. January. Florida. 2010

- Jhanis J. Gonzalez[1], Dayana D. Oropeza[1], Jong Yoo[2], Richard E. Russo,[1] **Femtosecond Laser Ablation Inductively Coupled Plasma Mass Spectrometry: The ultrafast road to routine solid samples chemical analysis,** PITCON. Florida. March. 2010

- Jeremiah J. Remus[1], Russell Harmon[2], Jhanis Gonzalez[3], Diane Wong[4], Jennifer Gottfried[5], Dirk Baron[6,] [1]Clarkson University, [2]ARL Army Research Office, [3]Applied Spectra Inc., [4]A3 Technologies LLC, [5]Army Research Laboratory, [5]California State University – Bakersfield, [1]Clarkson University, **Signal Processing Analysis of Factors Affecting LIBS-Based Obsidian Artifact Source Identification,** LIBS 2010- September 13-17 Memphis, TN.

- Katrina Shughrue[1], Keith Hilferding[1], Richard R. Hark[1], Jeremiah J. Remus[2], Russell Harmon[3], Michael A. Wise[4], Lucille J. East[5], Jhanis Gonzalez[6] and Dayana D. Oropeza[7,] [1]Department of Chemistry, Juniata College, Huntingdon, PA 16652, USA; [2] Department of Electrical and Computer Engineering, Clarkson University, Potsdam, NY 13699, USA;[3]ARL Army Research Office, PO Box 12211, Research Triangle Park, NC 27709, USA; [4]Division of Mineralogy, Smithsonian Institution, P.O. Box 37012, MRC 119, Washington, D.C. 20013, USA;[5]A3 Technologies LLC, 1200 Technology Drive, Aberdeen, MD 21001, USA; [6]Applied Spectra Inc, 46661 Fremont Boulevard, Fremont, CA 94538, USA;[7]Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA, **LIBS Analysis of Conflict Minerals: The Example of Columbite-Tantalite,** LIBS 2010- September 13-17 Memphis, TN

- Alexander A. Bol'shakov,[1,2] Jhanis J. Gonzalez,[2] Jong H. Yoo,[2] Chunyi Liu,[2] John R. Plumer,[1] Richard E. Russo, **Material composition analysis and surface/depth profiling with a laser-induced breakdown spectrometer (LIBS),** PITCON. Florida. March 2010

- Alyssa M. Kress[1], Lucille J. East[2], Richard R. Hark[1], Jhanis Gonzalez[3],[1]Department of Chemistry, Juniata College, Huntingdon, PA 16652, USA[2]A3 Technologies, LLC, Aberdeen, MD 21001, USA; [3]Applied Spectra, Inc., Fremont, CA 94538, USA, **Analysis of Silver Coins by Laser-Induced Breakdown Spectroscopy (LIBS),** LIBS 2010- September 13-17 Memphis, TN

- Jennifer L. Gottfried1. Kimberly Weber[2], Dana Short[2], Tyler Goralski[2], Stephanie

McCaslin[2], Rich Rossman[2]. Diane Wong[3],[1]U.S. Army Research Laboratory. [2]Battelle. [3]A3-Technologies , Discrimination of Biological and Chemical Threat Simulants in **Residue Mixtures on Multiple Substrates,** LIBS 2010- September 13-17 Memphis, TN

- Jhanis J. Gonzalez, Jong Yoo, Chunyi Liu, and Richard E. Russo. Applied Spectra, Inc. Fremont. CA, 94538, **Semi-Qualitative Beryllium analysis by Laser Induced Breakdown Spectroscopy (LIBS),** ASTM-Symposium on Surface and Dermal Sampling. October 14-15. San Antonio. Texas. 2010.

## 2010 Poster Presentations

- *East, L.J., Hark, R.R., Hilferding, K., Trejos, T., Almirall, J. "**Analysis of paper samples by two identical-model commercial laser-induced breakdown spectroscopy (LIBS) instruments,"** LIBS 2010, 6th International Conference on Plasma Spectroscopy and Applications, Memphis, TN, September 13-17, 2010.
- *Cahoon, E., Almirall, J.R. "**Analysis of Metals in Solutions of Low Volumes Using LIBS"**, LIBS 2010, 6th International Conference on Plasma Spectroscopy and Applications, Memphis, TN, September 13-17, 2010.
- *Schenk, E.R. and Almirall, J.R. "**Elemental analysis of cotton of LIBS and LA-ICP-AES",** LIBS 2010, 6th International Conference on Plasma Spectroscopy and Applications, Memphis, TN, September 13-17, 2010.
- *Jantzi, S.C. and Almirall, J.R. **"Quantitative analysis of trace metals in soil samples using LIBS for forensic applications"**, LIBS 2010, 6th International Conference on Plasma Spectroscopy and Applications, Memphis, TN, September 13-17, 2010.

## Conferences

- LIBS 2008 (Berlin)

  **"Application of Laser-induced Breakdown Spectroscopy (LIBS) for the Effective Management of Hazardous Materials Incidents"**
  Summary: First Responders are routinely faced with the challenge of rapidly and reliably identifying unknown substances encountered in a wide range of field conditions. An extensive array of field tests and portable instrumentation have been developed and/or adapted for the purpose of

detecting the presence of chemical, biological, nuclear, radiological, or explosive (CBNRE) threats, toxic industrial materials (TIM's), pharmaceuticals, and illegal drugs, along with the benign materials (e.g., harmless white powders) commonly encountered during First Responder operations. Laser-induced breakdown spectroscopy (LIBS) is a sensor technology that could allow First Responders to manage hazardous materials incidents more efficiently, effectively, and economically than previously possible using multiple pieces of equipment. The technique provides nearly instantaneous elemental analysis of solids, liquids and gases, does not require any sample preparation, and is amenable for use as a robust, man-portable device in the field in either stand-off or stand-near modes. LIBS utilizes a broadband spectrometer to collect the light emitted by a microplasma which is formed when a pulsed laser is used to interrogate a target. The data obtained is subjected to chemometric analysis and comparison against a spectral library to facilitate rapid identification of the material and provide the First Responder with the information vital for making crucial decisions in a timely manner. There are currently no commercially available LIBS systems that are designed specifically for use by the First Responder community. This presentation will explore some of the issues related to the development of suitable instrumentation and libraries as well as incorporation of the technique into existing First Responder protocols.

- EMSLIBS 2009 (Italy)

  "Evaluation of Laser-induced Breakdown Spectroscopy (LIBS) Instruments for First Responder Applications"
  Richard R. Hark1, Adam L. Miller2, Kristin M. Beiswenger1, Alyssa M. Kress1
  1Department of Chemistry, Juniata College, Huntingdon, PA 16652, USA
  2Huntingdon County Emergency Management Agency, Huntingdon, PA 16652, USA
  The challenge to rapidly and reliably identify unknown substances encountered in a wide variety of field conditions is a task routinely faced by First Responders. For the majority of operations multiple instruments must be employed currently to assist response managers in making decisions regarding protective actions and force protection. An extensive array of wet chemical tests and portable instrumentation have been developed and/or adapted for the purpose of detecting the presence of hazardous materials of interest. These include chemical, biological,

nuclear, radiological, or explosive (CBNRE) threats, toxic industrial materials (TIM's), pharmaceuticals, and illegal drugs, along with benign substances (e.g., harmless white powders) commonly encountered during First Responder operations. Laser-induced breakdown spectroscopy (LIBS) is a sensor technology that has the potential to introduce a paradigm shift in the way First Responders manage hazardous materials incidents. There are currently no LIBS systems designed specifically for use by the First Responder community that are being sold commercially. The challenge is to transition current laboratory-based LIBS systems which have already been shown to be capable of identifying hazardous materials to fieldable instruments capable of operating under austere, uncontrolled response environments. This presentation describes a preliminary evaluation of two alpha-version LIBS instruments designed forFirst Responders. A 15-30 m standoff system and a fully self-contained unit housed in a Pelican™ case (A3 Technologies, LLC, Aberdeen, MD, USA) were evaluated against a suite of relevant materials and First Responder requirements. Our examination seeks to understand if the current LIBS technologies will assist responders to more efficiently, effectively, and economically mitigate the risks and consequences of hazardous materials incidents.

- LIBS 2010 (Memphis)

  "LIBS Analysis of Conflict Minerals: The Example of Columbite-Tantalite"

  Katrina Shughrue1, Keith Hilferding1, Richard R. Hark1, Jeremiah J. Remus2, Russell Harmon3,
  Michael A. Wise4, Lucille J. East5, Jhanis Gonzalez6 and Dayana D. Oropeza7

  1Department of Chemistry, Juniata College, Huntingdon, PA 16652, USA
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  3ARL Army Research Office, PO Box 12211, Research Triangle Park, NC 27709, USA
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  5A3 Technologies LLC, 1200 Technology Drive, Aberdeen, MD 21001, USA
  6Applied Spectra Inc, 46661 Fremont Boulevard, Fremont, CA 94538,

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Niobium and tantalum are two rare metals of high commercial value. Niobium (Nb) is used in the manufacture of hardened steel, superalloys, and superconducting magnets for applications like medical magnetic resonance imaging, while tantalum (Ta) is used in consumer electronics, mainly for capacitors<http://en.wikipedia.org/wiki/Capacitor> and the high-power resistors<http://en.wikipedia.org/wiki/Resistor> used in portable telephones<http://en.wikipedia.org/wiki/Portable_telephone>, personal computers<http://en.wikipedia.org/wiki/Personal_computer>, and automotive electronics<http://en.wikipedia.org/wiki/Automotive_electronics>. The primary natural occurrence of Nb and Ta is in the complex oxide minerals columbite and tantalite, which form a solid-solution series having the general composition [Fe,Mn)(Nb,Ta)2O6]. Because central Africa is a major source for columbite-tantalite ore, its illicit export from the Democratic Republic of Congo is thought to be responsible for financing the ongoing civil conflicts in this region. Determining the chemical composition of a columbite-tantalite ore is one means of ascertaining its provenance. Laser induced breakdown spectroscopy (LIBS) is an analytical technique that is simultaneously sensitive to all elements with a single laser shot. Thus, LIBS offers an attractive means of rapidly distinguishing different geographic sources for a mineral because the LIBS plasma emission spectrum provides a ‘chemical fingerprint’ of any material in real-time. To test this idea for columbite-tantalite, an examination of three samples sets from spodumene-bearing granite-associated pegmatite fields in Yellowknife, Canada; Jacumba, California; and Brunswick, Maine was undertaken using a RT100-HP LIBS instrument (A3 Technologies LLC/Applied Spectra, Inc. with a 90mJ, 1064 Nd:YAG laser, and CCD detector). LIBSspectra were collected at high and low resolution over the 240-600nm wavelength range. Individual spectral emission lines and line ratios for Fe, Mn, Nb, Ta, W, Ti, and Zr as well as broad and narrowband spectra were used to determine if the provenance of the columbite-tantalite samples, all with quite similar LIBS spectra, could be discriminated using advanced multivariate statistical techniques. The LIBS results were compared with Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) data obtained from the same sample suite. LIBS analysis of matrix minerals such as quartz and mica, present on some of the samples, was also performed. Principal Component

Analysis (PCA) demonstrates that some of the data shows strong clustering. Partial Least Squares Discriminant Analysis (PLS-DA) of combined narrowband data (approximately 240-280 and 315-355nm) allows 100% sample-level classification using a highest confidence approach. These promising preliminary results suggest that additional work with a larger, more geographically diverse data set is warranted.

- PACIFICHEM 2010 (Honolulu)
  *2010.*

Winter Plasma Conference. January. Florida. 2010

### Precision assessment of a commercial Laser Induced Breakdown Spectroscopy (LIBS) instrument based on the analysis of metal samples.

J. J. Gonzalez*[1], A. A. Bol'shakov[2], J. Yoo[2], L. J. East[3], D. Wong[3], D. Oropeza[1], and R. Russo*[1].

[1]Lawrence Berkeley National Laboratory,

[2]Applied Spectra, Inc., and

[3]A3 Technologies.

**Abstract:** The need to analyze diverse solid samples, including environmental wastes, geological materials, biological tissues, metals, thin paint coatings, semiconductors, etc., without laborious dissolution methods has driven the advancement of laser ablation based analytical techniques. In particular, one branch of such techniques known as Laser Induced Breakdown Spectroscopy (LIBS) offers the unique advantages of rapid, *in situ*, multi-element analyses.

Laser induced breakdown spectroscopy (LIBS) is a simple technique that uses a tightly focused laser beam to generate a small spark on the surface of a target. This spark (microplasma) contains excited elemental and molecular species that were ablated from the surface of the target.

It is well known that the measurement quality and analytical figures of merit (precision, accuracy, limit of detection, etc) for LIBS are strongly dependent on the environment conditions, laser parameters, and physical-chemical properties of samples. In this study, we assessed some of these figures of merit for a diverse group of sample matrices based on a commercial LIBS system (RT100-HP from Applied Spectra/A3 Technologies).

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PITCON. Florida. March. 2010

## Material composition analysis and surface/depth profiling with a laser-induced breakdown spectrometer (LIBS)

Alexander A. Bolʹshakov,[1,2] Jhanis J. Gonzalez,[2] Jong H. Yoo,[2] Chunyi Liu,[2] John R. Plumer,[1] Richard E. Russo[1,2]

[1] A3 Technologies LLC, 1200 Technology Dr., Aberdeen, MD 21001

[2] Applied Spectra Inc., 46661 Fremont Blvd., Fremont, CA 94538

**Abstract:** Laser induced breakdown spectroscopy (LIBS) offers rapid localized chemical analysis with high spatial resolution in lateral and depth profiling, without a need for sample preparation. Diverse solid or liquid samples including environmental, biological, geological, industrial, forensic, food, thin coatings, semiconductors, etc., can be analyzed. LIBS also can perform remotely from a distance up to ~100 meters or greater depending on the optics. These features motivated utilization of LIBS for industrial and security applications as several commercial LIBS systems became available.

We applied principal component analysis (PCA) and partial least square (PLS) procedures to discriminate and identify a large variety of organic and inorganic samples. Our data illustrate how LIBS analyzers can answer a multitude of real-world needs for rapid chemical analysis. Examples include the determination of lead in paint and children’s toys; analysis of different solder materials; quality control of fiberglass panels; discrimination of coffee beans from different vendors; discrimination of generic and brand-name drugs, etc. Localized microanalysis with lateral and depth profiling is easily realized. Either traditional one-element calibration procedures or multivariate chemometrics can be applied for quantitative determination of elements in numerous samples.

We illustrate effectiveness of LIBS for security applications with the results obtained in field testing of the 50-meter standoff LIBS rasterizing detector.

## Femtosecond Laser Ablation Inductively Coupled Plasma Mass Spectrometry: The ultrafast road to routine solid samples chemical analysis.

Jhanis J. Gonzalez[1], Dayana D. Oropeza[1], Jong Yoo[2], Richard E. Russo[1].

[1]Lawrence Berkeley National Laboratory. Berkeley. CA. 94720

[2]Applied Spectra, Inc. Fremont. CA. 94538

**Abstract:** Laser ablation sampling for inductively coupled plasma mass spectrometry (LA-ICP-MS) has become one of the most popular approaches for analysis of solid samples. When compared with conventional dissolution techniques, laser ablation offers direct characterization of solids, reduced risk of contamination and sample loss, analysis of very small samples not separable for solution analysis, rapid analysis, and spatial resolution. Chemical analysis using laser ablation is a straightforward process in which a high energy laser pulse is used to transform a portion of a solid sample into aerosol for subsequent chemical analysis. The use of femtosecond laser ablation is based on improved performance metrics by controlling the amount of ablated material, particle size distribution, matrix dependence, and fractionation. Femtosecond laser ablation sampling into the ICP-MS has been shown to provide good chemical analysis precision and accuracy by reducing systematic errors related to the particle size distribution and resultant spikes in the ICP-MS response. A relaxation of matrix dependence also has been shown for the analysis of wide range of sample matrices when using femtosecond laser pulses. This paper presents an overview of the current research state in femtosecond laser ablation for chemical analysis and describes recent data using femtosecond ablation sampling for ICP-MS.

LIBS 2010- September 13-17 Memphis, TN. Deadline May 31 2010

## Signal Processing Analysis of Factors Affecting LIBS-Based Obsidian Artifact Source Identification

Jeremiah J. Remus[1], Russell Harmon[2], Jhanis Gonzalez[3], Diane Wong[4], Jennifer Gottfried[5], Dirk Baron[6]

[1]Clarkson University,

[2]ARL Army Research Office,

[3]Applied Spectra Inc.,

[4]A3 Technologies LLC,

[5]Army Research Laboratory,

[5]California State University – Bakersfield

**Abstract:** In a companion study (Harmon et al.), we present results of our efforts to develop methods for identifying the provenance, i.e. source of origination, of obsidian artifacts from California. A significant focus of that most recent work was the effect of LIBS laser wavelength, based on a comparison of classification performance for two data sets collected for the same set of obsidian samples with different LIBS laser systems (266 nm and 1064 nm wavelengths). This study addresses factors in that study that affected performance from a statistical signal processing and classification perspective. The outcomes of classification experiments and high-dimensional visualization techniques were used to investigate the link between effects seen in the data and subsequent classification performance as a function of three parameters of the LIBS setup and data collection: laser wavelength, the number of pre-collection 'cleansing' shots, and the number of shots recorded from each sample. The results of this study indicate that data collected using the two different laser wavelengths, as expected, displayed a wavelength-dependency in the observed emission spectra due to differences in laser light interaction with the obsidian samples. However, the results of the classification analysis also suggest that, despite the strong differences observed in the measured spectra when using lasers of different wavelengths, there is still significant information available for identification of obsidian provenance using either LIBS setup. Preliminary analysis of the potential for fusion using LIBS data collected at multiple wavelengths will also be presented. The results of the current study suggest the potential capabilities of chemometrics and signal processing techniques applied to broadband LIBS analysis when developing methods for sample classification and identification, even in suboptimal conditions of LIBS data collection.

## LIBS Analysis of Conflict Minerals: The Example of Columbite-Tantalite

Katrina Shughrue[1], Keith Hilferding[1], Richard R. Hark[1], Jeremiah J. Remus[2], Russell Harmon[3], Michael A. Wise[4], Lucille J. East[5], Jhanis Gonzalez[6] and Dayana D. Oropeza[7]

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[6]Applied Spectra Inc, 46661 Fremont Boulevard, Fremont, CA 94538, USA;

[7]Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA

**Abstract:** Niobium and tantalum are two rare metals of high commercial value. Niobium (Nb) is used in the manufacture of hardened steel, superalloys, and superconducting magnets for applications like medical magnetic resonance imaging, while tantalum (Ta) is used in consumer electronics, mainly for capacitors and the high-power resistors used in portable telephones, personal computers, and automotive electronics. The primary natural occurrence of Nb and Ta is in the complex oxide minerals columbite and tantalite, which form a solid-solution series having the general composition [Fe,Mn)(Nb,Ta)$_2$O$_6$]. Because central Africa is a major source for columbite-tantalite ore, its illicit export from the Democratic Republic of Congo is thought to be responsible for financing the ongoing civil conflicts in this region. Determining the chemical composition of a columbite-tantalite ore is one means of ascertaining its provenance.

Laser induced breakdown spectroscopy (LIBS) is an analytical technique that is simultaneously sensitive to all elements with a single laser shot. Thus, LIBS offers an attractive means of rapidly distinguishing different geographic sources for a mineral because the LIBS plasma emission spectrum provides a ‘chemical fingerprint’ of any material in real-time. To test this idea for columbite-tantalite, an examination of three samples sets from spodumene-bearing granite-associated pegmatite fields in Yellowknife, Canada; Jacumba, California; and Brunswick, Maine was undertaken using a RT100-HP LIBS instrument (A3 Technologies LLC/Applied Spectra, Inc. with a 90mJ, 1064 Nd:YAG laser, and Avantes spectrometer) to collect LIBS spectra over the 240-700nm wavelength range. The spectral emission lines and line ratios for Fe, Mn, Fe/Mn, Nb, Ta, Nb/Ta, W, Ti, Ti/W, and Zr were used to determine if the provenance of the columbite-tantalite samples, all with quite similar LIBS spectra, could be discriminated using advanced multivariate statistical techniques.

## Analysis of Silver Coins by Laser-Induced Breakdown Spectroscopy (LIBS).

Alyssa M. Kress[1], Lucille J. East[2], Richard R. Hark[1], Jhanis Gonzalez[3]

[1]Department of Chemistry, Juniata College, Huntingdon, PA 16652, USA

[2]A3 Technologies, LLC, Aberdeen, MD 21001, USA;

[3]Applied Spectra, Inc., Fremont, CA 94538, USA

**Abstract:** Silver coins were first struck in the United States in 1794 when banks and merchants brought metals to the Philadelphia Mint for coinage. These metals mostly originated from foreign coins, as well as bullion from mines and refineries. Initially, the depositor was able to request the denomination to be minted. This led to erratic production because depositors favored large denominations causing the smaller denominations to become essentially worthless and obsolete. With the Coinage Act of February 21, 1853, the government placed regulations on silver coinage and defined values for the coins regardless of composition. This arrangement later lead to disputes over face value that persisted until the use of silver for coinage was discontinued in 1970.

Some numismatists choose to accumulate their collection on the basis of a coin's metallurgical composition, such as only collecting gold, silver, copper, or platinum coins. For these collectors especially, accurately knowing the chemical make-up of a coin is important to verify authenticity. However, a main concern for collectors is that many analytical techniques applicable for analysis of coins are unacceptably destructive which lowers the value of the coin.

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has successfully been applied to the analysis of coins without significant damage and at very low detection limits for trace elements. Unfortunately, this technique requires specialized training and involves expensive instrumentation. Laser-induced breakdown

spectroscopy (LIBS) has the potential to distinguish coins based on their chemical composition and trace elements more quickly and cost effectively, without causing considerable damage. Coins from the United States and foreign mints, dating predominantly from the mid-nineteenth to mid-twentieth centuries and containing varying amounts of silver (Figure 1), were studied using an RT100-HP LIBS instrument

## Discrimination of Biological and Chemical Threat Simulants in Residue Mixtures on Multiple Substrates

Jennifer L. Gottfried1. Kimberly Weber[2], Dana Short[2], Tyler Goralski[2], Stephanie McCaslin[2], Rich Rossman[2]. Diane Wong[3]
[1]U.S. Army Research Laboratory.
[2]Battelle.
[3]A3-Technologies

Laser-induced breakdown spectroscopy (LIBS) is a promising technique for detection of chemical and biological warfare agents in the field by military or first responder personnel. LIBS can be used to probe both the organic and inorganic constituents of solid/liquid/aerosol samples in realtime with no sample preparation, and therefore has the potential to serve as an early warning system to trigger analysis by confirmatory, but more time-consuming sensors. Our laboratory, as well as many others, has generated increasingly promising results with regards to chemical and biohazard detection and identification.1-3 Much of the progress is due to the improvements in the use of advanced chemometric techniques, which have converted LIBS from just an “elemental detector” to a versatile molecular and biomaterial sensor.

Residue samples of biological and chemical threat simulants were prepared on polycarbonate, stainless steel, and aluminum foil by Battelle Eastern Science and Technology Center. LIBS spectra were collected by Battelle on a LIBS Pelicase (PL100-GEO) instrument developed by A3 Technologies. In this paper, the chemometric analysis of the Battelle data at the U.S. Army Research Laboratory (ARL) will be presented. The simulant samples tested include *Bacillus atrophaeus* spores, *Escherichia coli*, MS-2 bacteriophage, _-Hemolysin from *Staphylococcus aureus*, 2-chloroethyl ethyl sulfide (CEES), and dimethyl methylphosphonate (DMMP). Luria broth, Phosphate Buffered Saline (PSA) with 1% Bovine Serum Albumin (BSA) and Chloroform served as inoculation controls. Models based on partial least squares discriminant analysis (PLSDA) were developed based on the full broadband spectra and on input variables derived from only the relevant emission lines. The performance of the two types of models for individual substrates and multiple substrates will be compared.

In addition, mixtures of the simulants and controls with two interferents, dolomitic limestone and ovalbumin, were tested against the models.

ASTM-Symposium on Surface and Dermal Sampling. October 14-15. San Antonio. Texas. 2010.

## Semi-Qualitative Beryllium analysis by Laser Induced Breakdown Spectroscopy (LIBS)

Jhanis J. Gonzalez, Jong Yoo, Chunyi Liu, and Richard E. Russo.

Applied Spectra, Inc. Fremont. CA, 94538

In recent years, there has been an increased awareness in the health risks associated with toxic metal species as Cadmium (Cd), Lead (Pb), Mercury (Hg), and Beryllium (Be). Due to increasing health risk associated with a certain class of toxic elements, the U.S. Occupational Safety and Health Administration (OSHA) has set a maximum legal limit for employees at the work place to be exposed to these chemical substances. A simple and effective analytical method for both qualitative and quantitative analysis of these toxic metals in ambient air, on surfaces, and in bulk materials is increasingly sought after by health policy regulators, health professionals as well as analytical service labs. In particular, laser ablation as a method to perform solid sampling has received tremendous interest due to its ability to analyze diverse samples without laborious acid dissolution process and generation of toxic acid waste. LIBS (Laser Induced Breakdown Spectroscopy), which is based on emission spectroscopy of the laser ablation generated plasma, has been studied and developed for trace element analysis in various types of solid materials as a rapid, *in situ*, multi-elemental technique.

The focus of the current work is to develop LIBS for the detection of Beryllium (Be). It has been documented that the inhalation of Beryllium-containing dusts can produce a direct corrosive effect on healthy tissues and may cause a chronic, life-threatening allergic disease called Berylliosis. A test method for determining Beryllium content in soils, rocks, sediments, and fly ashes has been developed by the American Society for Testing and Materials (ASTM) using Ammonium Bifluoride extraction and fluorescence detection[1]. However, one main drawback of such approach for Be analysis is the laborious and time-consuming sample preparation steps, in addition to the generation of chemical waste from processing samples. LIBS has been tested as an analytical method for determination of Be in air[2] and in particle filters[3]. The results of these studies indicated that LIBS is an appropriate technique for both qualitative and quantitative determination of Be if an appropriate sampling protocol can be developed.

In the current study, the use of commercial LIBS system (RT100-HP, Applied Spectra, Inc., Fremont, CA) was assessed as a screening tool for quick identification of the surface Beryllium (Be) presence above the controlled limit. The surface areas of potential Be contamination were swiped with cotton swabs to collect Be particles. The swabs were then analyzed with a certain set of laser ablation sampling pattern using RT100-HP LIBS instrument. The goal was to determine whether Be signal can be detected from these samples and subsequent correlation of LIBS intensity can be made with concentration values obtained from ICP-OES analysis. A special attention was paid to developing a proper LIBS sampling protocol and data reduction scheme to differentiate samples that has Be concentration above the OSHA limit from those that are safely below it. Along with optimization of laser and detection parameters, other important sampling parameters for establishing LIBS as an effective Be screening method include the pattern of sampled locations on the swab surface, signal averaging scheme, and a number of laser pulses applied per sampled spot.

## Appendix (4)

## ASI Patents

1. COMBINATION LIBS AND RAMAN ABLATION SYSTEM (Standoff Apparatus)

2. COMBINATION LIBS AND RAMAN ABLATION DATA COLLECTION SYSTEM AND METHOD

Disclosure No: 61/321678

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