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Title: Development of Laser Induced Breakdown Spectroscopy Instrumentation for Safeguards Applications

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Paper Title:
Development of Laser Induced Breakdown Spectroscopy Instrumentation for Safeguards Applications

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Abstract

In September 2006, a Technical Meeting on Application of Laser Spectrometry Techniques in IAEA Safeguards was held at IAEA headquarters (HQ). One of the principal recommendations from this meeting was the need to "pursue the development of novel complementary access instrumentation based on laser induced breakdown spectroscopy (LIBS) for the detection of gaseous and solid signatures and indicators of nuclear fuel cycle processes and associated materials." Pursuant to this recommendation the Department of Safeguards (SG) under the Division of Technical Support (SGTS) convened the Experts and Users Advisory Meeting on Laser Induced Breakdown Spectroscopy (LIBS) for Safeguards Applications. This meeting was held at IAEA HQ from July 7 – 11, 2008 and hosted by the Novel Technologies Unit (NTU). The meeting was attended by 12 LIBS experts from the Czech Republic, the European Commission, France, the Republic of Korea, the United States of America, Germany, the United Kingdom of Great Britain, Canada, and Northern Ireland.

After a presentation of the needs of the IAEA inspectors, the LIBS experts were in agreement that needs as presented could be partially or fully fulfilled using LIBS instrumentation. The needs of the IAEA inspectors were grouped in the following broad categories: (1) Improvements to in-field measurements / environmental sampling; (2) Monitoring status of activity in a Hot Cell; (3) Verifying status of activity at a declared facility via process monitoring; and (4) Need for pre-screening of environmental samples before analysis.

Under the Department of Energy / National Nuclear Security Administration (DOE/NNSA) Next Generation Safeguards Initiative (NGSI) Los Alamos National Laboratory is exploring three potential applications of LIBS for international safeguards. As part of this work, we are developing: (1) a user-friendly man-portable LIBS system to characterize samples across a wide range of elements in the periodic table from hydrogen up to heavy elements like plutonium and uranium; (2) a LIBS system that can be deployed in harsh environments such as gloveboxes and hot cells providing relative compositional analysis of process streams for example ratios like Cm/Pu and Cm/U; and (3) an inspector field deployable system that can be used to analyze the elemental composition of microscopic quantities of samples containing plutonium and uranium.

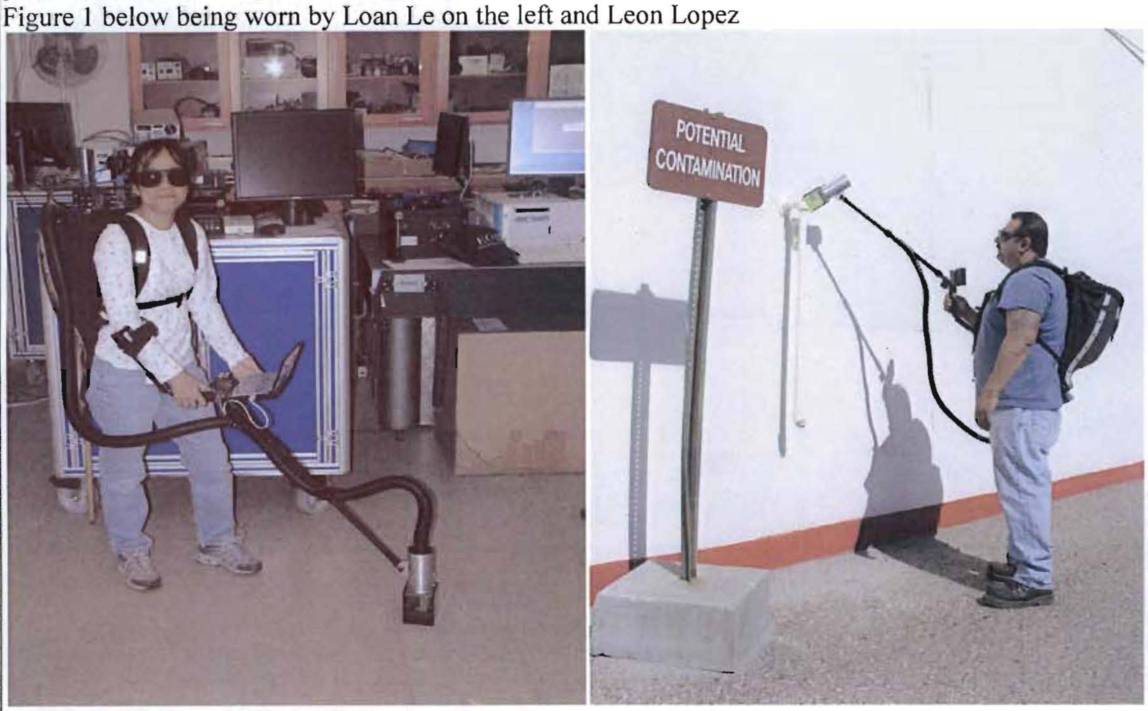
In this paper we will describe our current development and performance testing results both in a fixed lab and measurements in field deployable configurations using LIBS instrumentation developed for applications to international safeguards.

1. Introduction

We continue to make progress on the design, assembly, and testing of LIBS systems to address the needs of environmental sampling and analysis for international safeguards. Progress in all areas of our development work plan has been made including: (1) a backpack mounted portable system, (2) a cart / rack mounted medium resolution system, (3) a high resolution isotopic sensitive system, (4) fiber optic probe development, and (5) LIBS microscope / imaging probe development.

2. Backpack Mounted LIBS System

The backpack mounted LIBS system is operational in a fully standalone and automatic mode under computer control using only battery power. Currently we can operate this system for approximately 1.5 hours in this mode. The mini computer controls the firing of the laser, control and data collection for the spectrometers, emission peak assignments, and storage of the spectral data. This system has been operated outside the laboratory at TA-35 in a field test in a fully integrated and standalone mode for an analysis time of approximately 1 hour and 20 minutes. Approximately 40 sampling areas were analyzed during this initial field test. The sampling areas included asphalt in the parking lot, metal samples, paint, concrete, dirt / soil, plastics, sand, and a depleted uranium metal sample. Pictures of the current backpack system are shown in Figure 1 below being worn by Loan Le on the left and Leon Lopez



Fugure1. Pictures of the LIBS backpack system.

on the right hand side. Loan and Leon are two members of our LIBS international safeguards instrumentation development team. The picture on the right hand side also shows one of the areas sampled during our initial outside field test exercise. This system has been used to analyze samples of depleted uranium in an ore and a metal sample. Preliminary peak identifications and assignments for uranium emission line are shown in Table 1 below.

Table1. Preliminary Uranium peak identification and assignments are shown below.

Wavelength nm	Ionization State	Wavelength nm	Ionization State
268.37	U II	389.4	U II
270.63	U II	399.82	U II
277.00	U II	401.78	U II
278.44	U II	409.19	U II
295.63	U II	411.61	U II
302.22	U II	415.4	U II
310.24	U II	424.3	U II
311.16	U II	436.1	U I
339.47	U II	462.7	U II
350.76	U I	547.5	U II
353.4	U II	548.01	U II
367.01	U II	556.4	U II
385.9	U II	597.6	U I
387.4	U II	682.8	U I

We have identified and assigned 28 peaks for uranium emission lines using the backpack system.. Currently we envision adding several user friendly features and operational guides to this system that include: (1) a heads up display for better operational comfort and efficiency in outdoor lighting conditions, (2) addition of a lithium ion battery to increase the operational lifetime of the system to approximately 3 hours and a weight reduction of 4 pounds, (3) a safety interlock system for the sampling head, (4) development of a validated library of spectral data on samples of interest, (5) an expanded set of field test at LANL and other site yet to be determined, (6) additional of a geo registration (GPS) feature to the system such that if a sample of high interest and sensitivity is found, the location can be relocated precisely for further analysis, and (7) development of a user friendly operational manual. A second backpack LIBS is being assembled and testing will soon begin. The additional of the second backpack LIBS system will improve the efficiency of our performance testing and system improvements while expanding our field testing exercises.

3. Cart / Rack Mounted LIBS System

A medium resolution spectrometer was received (form LLA Instruments, Berlin, Germany) and installed on February 25-26, 2010. We also have an older version of this system that was also checked out and put into operation. Thus we currently have two operational cart / rack mounted LIBS system. Our intent is to take one of the systems to the nuclear facility here at LANL and the other one to Oak Ridge National Laboratory (or other locations of interest) for measurements hopefully soon. We have been in the process of testing both systems and both are operating very well providing good quality and high fidelity emission spectra. Again, the cart / rack mounted systems can be operated in three modes: (1) ***in situ*** measurements with measurement distances of a few inches in a sampling chamber attached to the mobile platform, (2) remote measurements using direct optical access through the windows of hotcells and gloveboxes using a focusing head, and (3) remote measurements using fiber optic coupled probes at measurement distances up to approximately 100 meters both inside and outside hotcells and gloveboxes. Theoretically, these systems can be used to performed isotopic analysis on samples of uranium since the resolution required for uranium is approximately 16,000 and the resolution of the spectrometer is 20,000. These systems can be used to perform trace element and ratio measurements on samples of actinides for example U / Cm, Pu /Cm, etc. Pictures of the newest version of a cart / rack mounted LIBS system are shown in Figure2 below. On the left hand side we show a general view of the system consisting of: (1) blue box on top of the tripod is the sampling unit for directing the laser beam through

Figure2. Shown are pictures of cart / rack mounted LIBS system.

the windows of gloveboxes and hotcells, (2) the small blue box located on the top of the rack with the door open is the in situ sampling chamber containing the excitation laser and optics for generating the plasma and collection optics for directing the emission to the spectrometer, and (3) the rack with the doors open showing the spectrometer (back box), computer (light colored box) and the power supply for the laser located on the bottom rack of the system. On the right hand side of this picture is shown the rack mounted LIBS system coupled to a 50 meter fiber optic cable. We have used the cart / rack mounted LIBS systems to collect and analyzes samples of magnets, steels, aluminum alloys, carbon fibers, and depleted uranium. LIBS spectra of a depleted uranium metal sample are shown in Figure3 below.

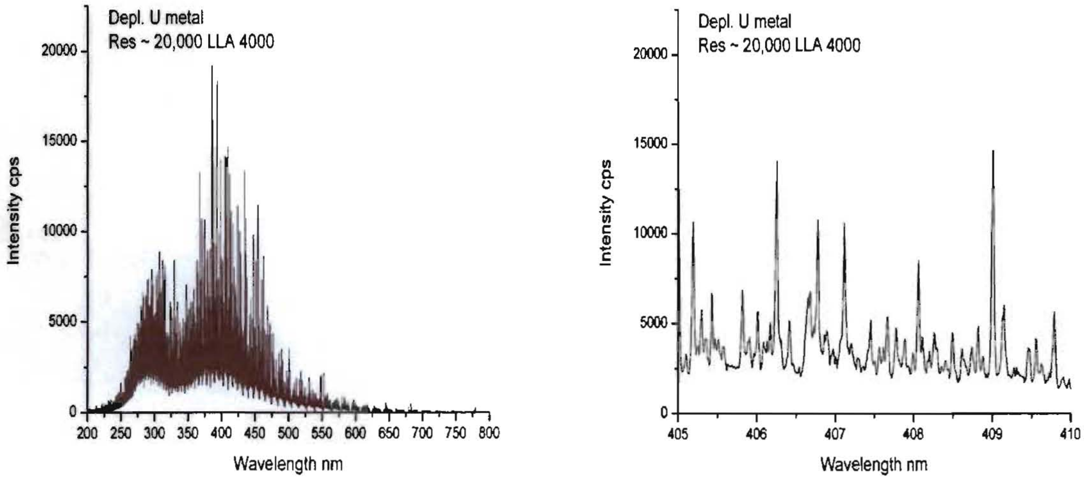


Figure3. Shown are LIBS spectra of a sample of depleted uranium metal sample.

Atomic emission spectra of the actinide elements arise from complicated excited state quantum physics and photo dynamics and a very high density of states resulting from complex electronic configurations. The result is a complex overlapping emission spectral profile as shown on the left hand side of Figure3. Even with a spectral resolution of 20,000 and temporal resolution of a few hundred nanoseconds, the spectra still seems congested. However, taking a 5 nanometer section of the spectra on the left and expanded it, there are distinct spectral signatures or peaks that can be identified and assigned to electronic transitions from excited states of uranium atoms. Using the spectra shown in Figure3, we have identified and assigned approximately 320 unique uranium spectral lines that can be used in the analytical analysis of samples containing uranium. We are currently continuing to analyze samples containing depleted uranium using this system. However, preliminary analysis indicates that we can use this system to perform trace and elemental ratio analysis. Complete performance testing of these systems will be the subject of future technical reports.

4. High Resolution Isotopic LIBS System

We took delivery of a high resolution (resolution approximately 75, 0000) spectrometer system from LTB Instrument also from Berlin Germany on July 1-2, 2010. This spectrometer system has resolution sufficient to perform isotopic analysis on samples of plutonium and uranium. Currently we are in the initial performance testing phase using this system. Results from performance testing using this system will be forth coming in future reports and presentations.

5. Fiber Optic probe Development

Again, we have coupled 2, 5, 20, and 50 meter fiber cables to a cart / rack mounted medium resolution LIBS system. A picture of a cart / rack mounted LIBS system coupled to a 50 meter fiber optic cable is shown on the right hand side of Figure2. A LIBS spectrum of a sample of stainless steel collected through the 50 meter fiber optic cable is shown in Figure4 below.

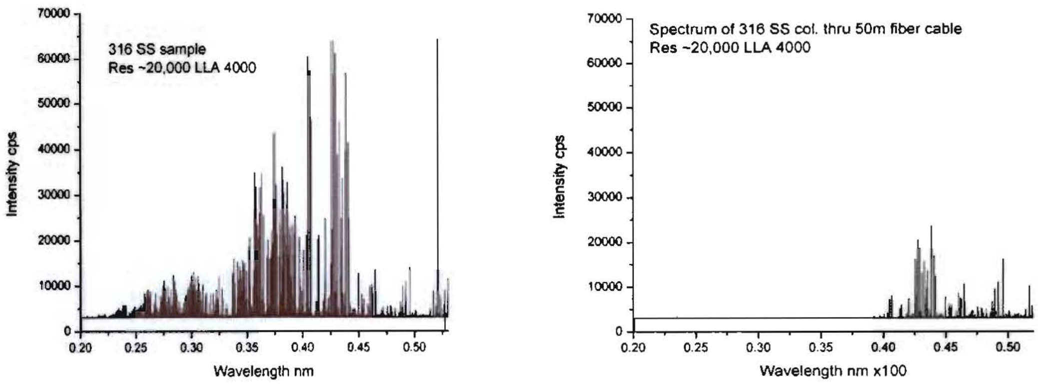


Figure4. A LIBS spectrum of a sample of Stainless collected through a 2 meter and a 50 meter fiber cable is shown in this figure.

There is a significant decrease in the intensity of the spectral lines which is not necessarily a serious problem since the detector in this system is a high gain intensified charge coupled device (ICCD). Most if not all of the decrease in the spectral intensity can be recovered by increasing the gain on the detector. However, a more serious problem is the lost of spectral intensity below 400 nanometers. This is a serious problem since a lot of good analytical emission lines are observed in this region. We have ordered a new set of fibers from a different company the specifications of which seem to indicate significant transmission down to 200 nanometers. Performance testing of the fibers as soon as we receive them will begin.

6. LIBS Microscope / Imaging Probe Development

A LIBS Microscope has been designed and assembly is in progress to be followed by performance testing. A picture of an early breadboard version of this system is shown in Figure5 below.

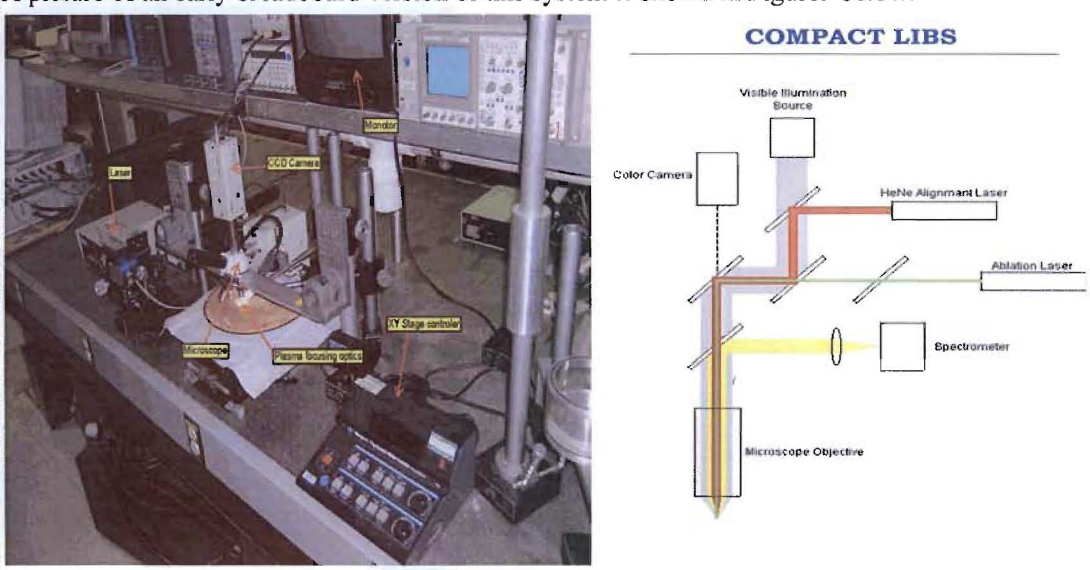


Figure5. A picture and a current schematic of a LIBS microscope / imaging probe are shown in this Figure.

On the right hand side of this figure is a current schematic of this system. This is a smaller compact version of the breadboard system. We have shown that we can perform single shot analysis with a spatial resolution of 80 microns with the earlier version of this system. Our intent is to begin with approximately 80 micron metal particles and perform single shot analysis. We believe that we can use this system to analyze particle on the order of 10 to 20 microns in spatial dimension. John Jolin has joined our LIBS safeguards development team and has been assigned to work on this system. Again, the results of this development effort will be forthcoming.

7. Acknowledgements

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