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Application and Development of Laser Induced Breakdown Spectroscopy (LIBS) Instrumentation for International Safeguards

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Abstract

Advanced methodologies and improvements to current measurements techniques are needed to strengthen the effectiveness and efficiency of international safeguards[1]. The primary tool employed by the IAEA to detect undeclared processes and activities at special nuclear material facilities and sites still is environmental sampling. This type of environmental sampling is both time consuming and costly since many samples must be collected, packaged, and shipped to an analytical laboratory for analysis which in some cases can take weeks to months to complete. Los Alamos National Laboratory is currently investigating potential uses of LIBS for safeguards applications, including (1) a user-friendly man-portable LIBS system to characterize samples in real to near-real time (typical analysis time are on the order of minutes) 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 hot cells and glove boxes providing relative compositional analysis of process streams for example ratios like Cm / Up and Cm / U, (3) an inspector field deployable system that can be used to analyze the microscopic and single particle samples containing plutonium and uranium, and (4) a high resolution LIBS system that can be used to determine the isotopic composition of samples containing for example uranium, plutonium...etc.

In this paper, we will describe our current development and performance testing results for LIBS instrumentation both in a fixed lab and measurements in field deployable configurations.

Introduction

Laser Induced Breakdown Spectroscopy (LIBS) is a laser based optical method that can be used to determine the elemental composition of liquids, solids, and gases. In the LIBS technique, short pulses (typically 10 nanoseconds) from a laser are focused upon the surface of a sample where a micro-plasma is generated consisting of elements evolved from the surface and the gas above the surface. The emission from the plasma is wavelength resolved and detected using a dispersive device and a detector. The resulting spectrum is analyzed with a computer. The emission spectrum is characteristic of the emitting species in the plasma which are typically atoms, ions, and small molecules. If the spectra are collected and analyzed as a function of the chemical composition of the elements present, calibration curves can be generated from which semi to quantitative information can be determined. LIBS offers several advantages over classical wet chemical analysis techniques; (1) real-time or near real time automated elemental analysis; (2) it is essentially non-destructive (only a few micrograms of material is remove from the sample per laser shot) with little or no sample preparation and handling required; (3) on-line or at-line analysis is possible, and ; (4) remote operation from multiple sites via fiber optics can be achieved. It is also a highly configurable technique meaning that instruments of many different shapes, sizes, and configurations can be designed, constructed, tested, and used to obtain chemical compositional information with varying levels of sensitivity, precision, and deployment (from fixed lab to field deployable systems).

LIBS Instrumentation

Laser Induced Breakdown Spectroscopy better known as LIBS, has been under development and applied to chemical analysis problems at Los Alamos National Laboratory and laboratories around the country and the world for over 40 years [2]. However, rapid development in LIBS was accelerated based primarily upon the pioneering work by Radziemnski, Cremers, and Loree at Los Alamos National Laboratory in the mid-nineteen eighties (1984) [3]. As an example of the maturity of LIBS technology, an instrument based on LIBS is scheduled for deployment to the planet Mars in 2011 for the elemental analysis of remote surfaces and features up a remote measurement distance of 10 meters [4]. There are also national and international meetings devoted to improvements in and the application of LIBS technology to chemical analysis problems [5].

Conceptually, the instrumentation for LIBS can range from simple to complex, depending upon the analytical analysis protocol and the level of precision and accuracy of the desired measurement. A schematic of a LIBS instrument is shown in Figure 1. In this diagram, the output typically from a Nd:YAG laser is focused onto the surface of a sample where a small plasma (typically a few millimeters

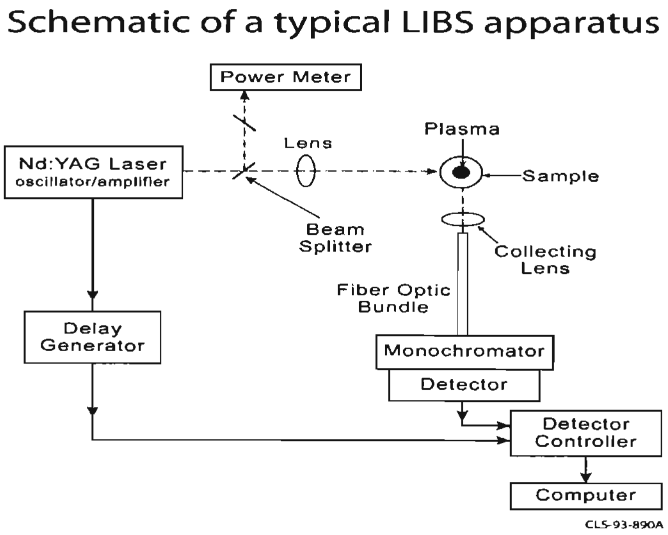
Schematic of a typical LIBS apparatus

Figure1. Schematic of a typical LIBS experimental apparatus is shown.

in spatial dimension) is generated. Typically, the laser operates at 1064 nanometers with a pulse length of 7 – 10 nanoseconds. Depending upon the coupling of the laser light to the sample, a few to several hundred milijoules of excitation energy is required to generate the plasma. The emission is collected with a lens and directed to a spectrometer using a fiber optic bundle. The emission is then analyzed by a computer.

Instrumentation Development and Performance Testing

Backpack Mounted Portable LIBS system

At Los Alamos National Laboratory, a backpack mounted portable LIBS system has been developed and testing is in progress for the detection of the presence of actinides and other elements important to international safeguards. This system consist of a small Nd:YAG laser (Kigre, Inc) operating at 1/3 Hz with an output energy of 25 mj / pulse. The emission from the plasma is collected and directed to three Ocean Optic spectrometers (Model HR200+, with the following wavelength ranges: UV, 200 – 400 nm; VIS, 400 – 600 nm; and NIR, 600 – 1000 nm) using optical fibers. The spectra are detected with a CCD detector and analyzed with a small frame computer (Sony Inc.). The combined system weighs approximately 25 pounds, is completely self-contained, and operated in automatic mode using a battery. Currently the operational lifetime of the system is approximately 3.5 hours. A picture of the backpack LIBS system is shown in Figure2. The technologist in the picture is Leon Lopez of the C-CDE group at Los Alamos National Laboratory. The green / silver unit at the end of the probe and near the wall is the sampling head that includes a small laser and focusing optics used to generate the plasma. This sampling head is also equipped with safety interlocks to protect the user. The green enclosure also prevents the user from coming in contact with dangerous stray reflections from the enclosed Class IV Nd:Yag laser. The black umbilical cord contains fiber optic cables for collecting emission from the plasma and directing it to the spectrometers and power cables for supplying power to the laser. A small form PC is located near Leon's right hand is the master controller for the laser, electronics, spectral collection, and data analysis. The electronic control unit is located in the backpack and contains the laser power supply, Ocean Optics spectrometers, and associated electronics for controlling the system.

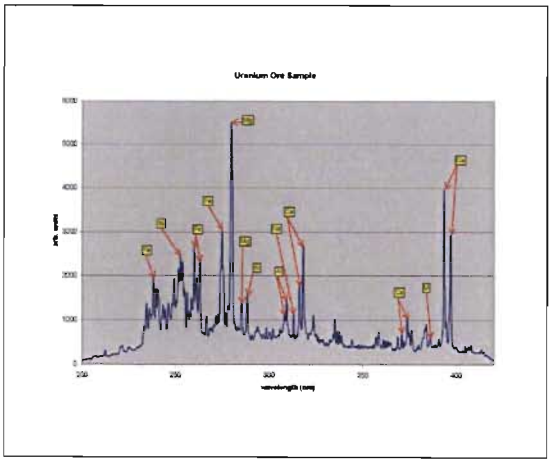

Figure2. A picture of the backpack system is being shown by Leon Lopez. On the right hand side is a typical LIBS spectrum of a sample of depleted uranium in the region 200 – 420 nanometers (nm).

This system has been used to analyze the following sample set: (1) Magnets, AlNiCo, SmCo, and NdFeB; (2)Steels, 350 Marging steel, 250 marging steel, 304L SS, 316 SS, and A36 HRS (hot rolled steel), other steel alloys(carbon steel series 451 – 460); (3) Aluminum alloys, 6061 Al, 7075 Al, and 2024 Al; (4) Carbon fiber or graphite; (5) Aramid rubber; and (6) naturally abundance uranium in SRM 610 (standard reference material from NIST, Washington, D.C., USA), depleted uranium, and uranium ore. A total of 26 samples with a variety of matrices and chemical compositions have been analyzed. The concentration of uranium in the SRM and uranium ore samples was approximately 450 and 7500 ppm respectively.

We have identified approximately 30 analysis peaks or unique spectral signatures that can be used to detect the presence of uranium in environmental samples. The peaks that we have identified and assigned for uranium are listed in Table 1 where I and II refer to the neutral and first ionized excited electronic states of uranium atoms. Also we have identified and assigned unique spectral signatures for the magnets (30), aluminum alloys (40), and steel alloys (70). This set of data is similar to the data shown for uranium in Figure 2 above. Since each sample has been analyzed for three spectral regions UV, VIS, and NIR each containing 2048 channels of spectral data, 6144 channels of data are recorded per sample. The complete sample data set was placed in a validated database and then used to provide automatic sample identification for unknown test samples chosen at random from the combined data set without any prior knowledge of the identity of the sample under investigation. Using the algorithms and methodology that we developed, we correctly identified 24 out of 26 samples for a precision of approximately 92 percent. We are currently pursuing an expanded data set with an even wider range of chemical compositions and sample types.

Table1. Uranium peak Assignments from low resolution LIBS spectra.

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

Transparent automatic user friendly analytical analysis functionality has also been integrated into this system. A view of this user friendly interface is shown in Figure 3 below.

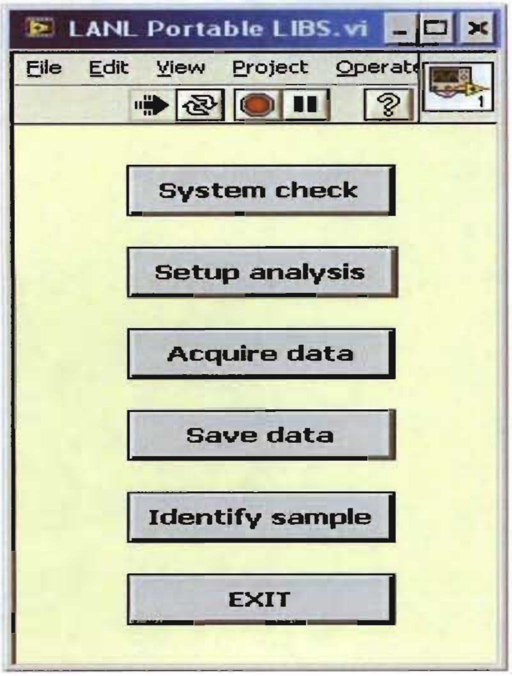

Figure 3. In this figure a transparent user friendly interface for controlling the backpack system, collecting and analyzing data is shown.

This interface allow the user to:(1) perform a system check to verify that the system is operating correctly;(2) set the configuration for making a sample measurement;(3) acquire data;(4) save the data for further analysis;(5) perform sample identification by comparison to the sample data in the validated database; and finally exit or repeat the procedure for analyzing other samples. The transition and performance testing of this system from the laboratory to the field is in progress. System improvements and testing will continue in the laboratory in parallel using a duplicate system. We also are in the process of developing a user manual and training for the safe and efficient use of this system. The intent is for the user to safe and efficient performing sample measurements with this system. To this end we have also designed and installed appropriate safety interlocks to minimize or prevent the user from being exposed to Class IV invisible laser beams which can cause severe skin and eye damage.

Cart / Rack Mounted Field Deployable High Resolution LIBS System Development

We have designed, assembled, and testing is in progress for a high resolution LIBS system that includes an echelle spectrograph (LLA Instruments, Berlin, Germany). The spectrograph has a resolution of approximately 20,000 (wavelength / shift in wavelength). The emission is detected with an ICCD detector within the spectral range of 200 to 780 nm. The excitation source is a Quantel Nd:YAG laser operating at 20 Hz with a 9 nanosecond pulse width and maximum output energy of 100 mj / pulse. The system is controlled by an industrial computer operating on the windows XP platform. This system has the capability to be operated in one of three modes: (1) ***In situ*** with measurements distances of a few inches in a sampling chamber attached to a mobile platform; (2) remote measurements using direct optical access through the containment windows of hotcells or gloveboxes using a variable 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.

The remote functionality of this system in principle will allow monitoring and control of nuclear materials and processes at nuclear facilities in real to near-real time in a continuous and un-attended mode. Therefore any attempt to clandestinely remove or modify materials and nuclear facilities will be immediately detected. This system also can be used to provide isotopic and ratio analysis of samples of actinides (for example, isotopic measurements on samples of uranium, and important ratios that include U / Cm, Pu /, Cm, etc).

A prototype version of this system is shown in Figure 4. The picture on the left shows the sampling head (blue box mounted on a tripod) that contains the laser excitation source and optics for directing and focusing the laser beam through a window of a hotcell or glovebox. The sampling head also includes

Figure4. In this picture is shown a general view of the Cart / Rack mounted LIBS system on the left and the system coupled to a 50 meter fiber optic cable illuminated with a green alignment laser for visual effects on the right hand side.

optics for collecting the emission from the plasma and directing it to the spectrograph (black box to the left of the first level below the top of the platform) via a fiber optic cable. The blue box on the top of the platform with the access door open is the ***in situ*** sampling chamber. The light beige box also located on the first shelf below the top is the industrial computer used to control the system. The vertical light colored box on the bottom shelf is the power supply for the Nd:YAG laser. The picture on the right side of Figure 4 shows the system coupled to a 50 meter fiber optic cable that was illuminated with a green alignment laser for visual effects. We have used this system to collect LIBS spectra through 2, 5, 20, and 50 lengths of fiber optic cables. A typical LIBS spectrum collected from a sample of depleted uranium is shown in Figure 5. A LIBS spectrum of thorium oxide in a steric acid binder is shown in Figure 6 below.

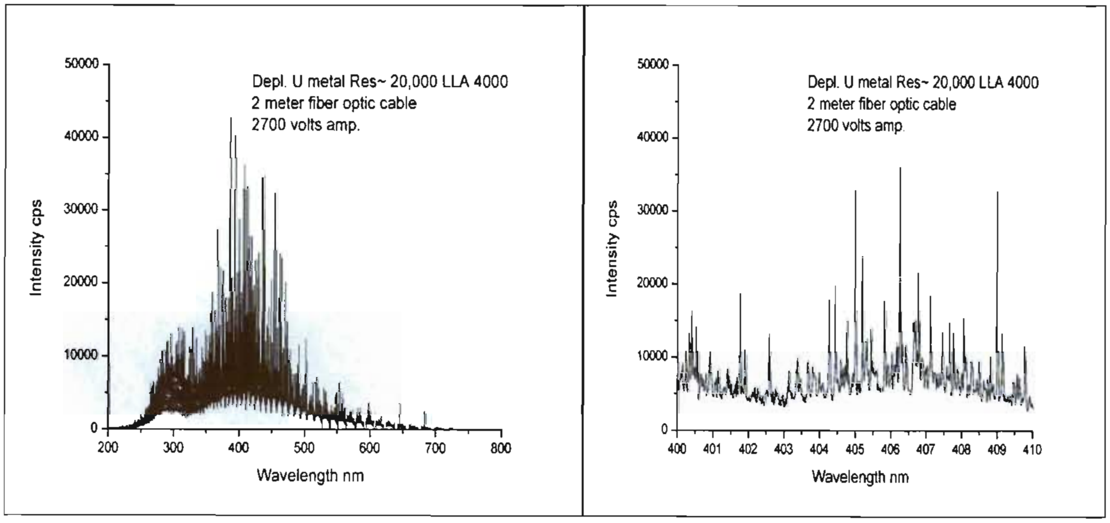

Figure5. In this Figure we show a high resolution spectrum of a sample of depleted uranium between 200 and 800 nanometers. On the right hand side is shown a 10 nanometer section of the full spectrum.

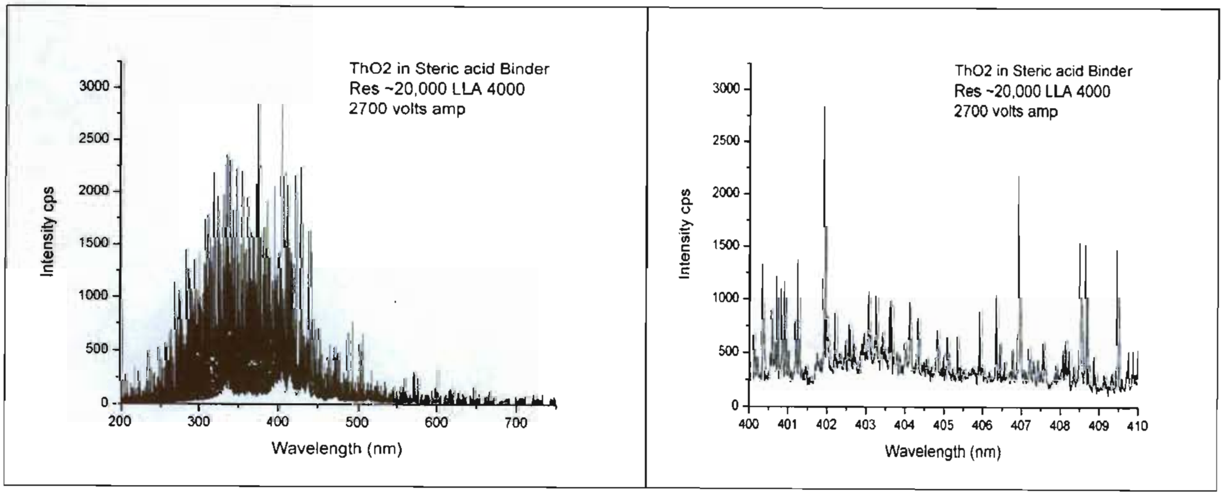

Figure 6. In this figure we show a full LIBS spectrum of thorium oxide on the left hand side between 200 and 750 nanometers. An expanded view of a 10 nan0meter section is shown on the right hand side of the figure.

A careful and detailed review of the data shown in Figures 5 and 6 indicate that this type of spectra can be used to perform actinide ratio measurements on samples containing mixed actinides with a 20,000 resolution echelle based spectrograph. By combining the uranium and thorium spectra, many peak or line pairs or high order peak sets can be used to analysis mixed actinide samples. By contrast, it would be very difficult to use the low resolution spectra shown in Figure 2 (spectrum of a sample of depleted uranium), acquired with an Ocean Optics spectrometer to perform elemental ratio analysis of complex elements like the actinides.

High Resolution LIBS Isotopic System Development

We are developing an even higher resolution LIBS system for isotopic and ratio analysis for samples containing actinides. The core of this system is a high resolution echelle spectrograph with a resolution of 75,000 (wavelength / shift in wavelength). The resolution required to analyze enriched samples of uranium and plutonium is approximately 16,000 and 47,000 respectively. Thus this system can be used to perform isotopic analysis on samples of uranium and plutonium[6]. This is a much smaller compact spectrograph (approximately ¾ meter path length) compared to those used previously to perform isotopic measurements on samples of plutonium and uranium. For the plutonium measurements, a 2 meter scanning spectrograph operated in double pass mode was used. For the uranium isotopic measurements, a 1 meter scanning spectrograph was used. The compact high resolution spectrograph along with an approximately 2 nanometer wide spectrum of a sample of depleted uranium is shown in Figure 7 below. The 424.3 nanometer line for uranium (the next line to the right of the marked line) was used to perform isotopic analysis on samples of uranium (U-238 / U-235).

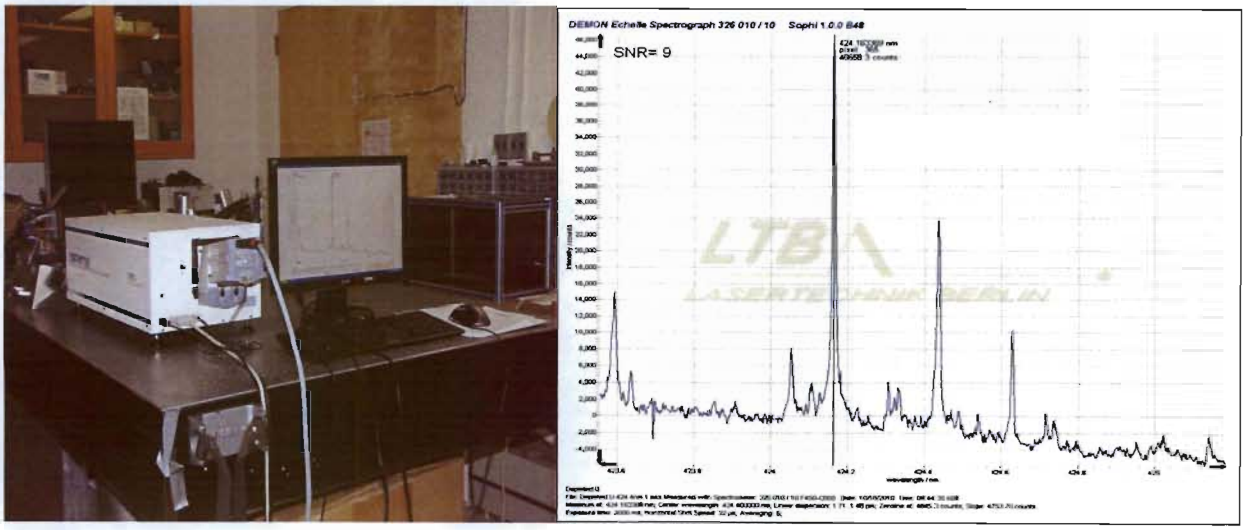

Figure7. In this figure we show a high resolution spectrograph (75,000). A spectrum of an approximately 2 nanometer section for a sample of depleted uranium is shown on the right hand side.

We hope to begin isotopic measurement on samples of uranium and plutonium soon using this spectrograph.

Single Particle LIBS Microscope Development

Finally, we are also developing a LIBS microscope system that can be used to analyze single particles of samples important to international safeguards. This tool can be used by inspectors that take swipe samples and want to make measurements in a field setting to determine if actinide elements are present. An image of this system along with a re-designed compact version is shown in Figure 8 below.

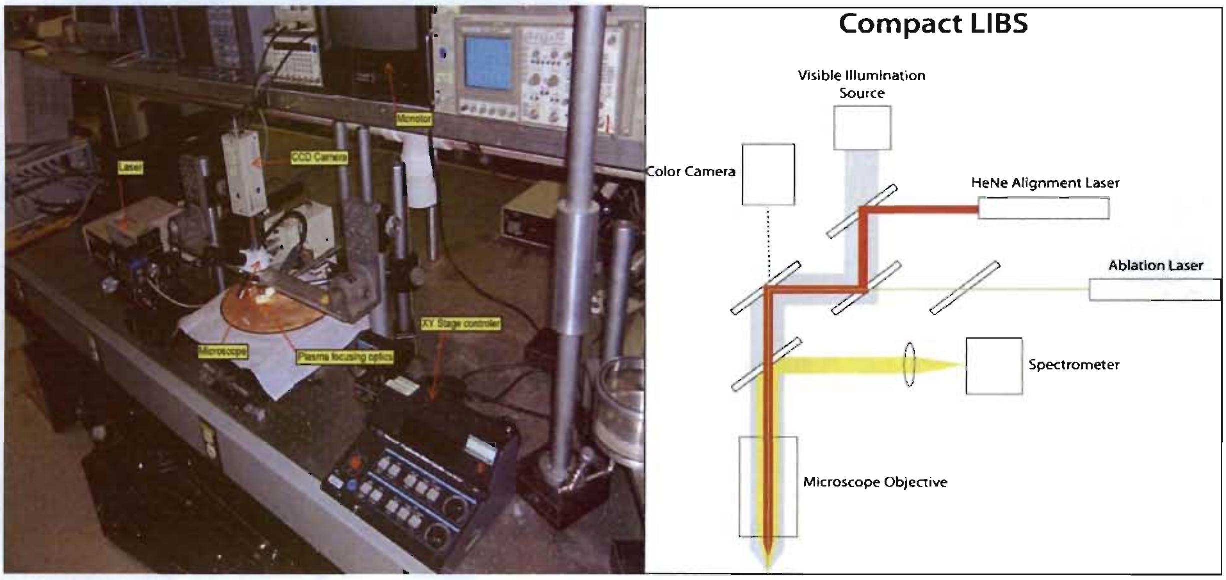

Figure 8. We show an image and a schematic of a compact version of the LIBS microscope in this figure.

This LIBS microscope can be used to analyze single particles on swipe media currently with a spatial resolution of approximately 100 microns. This tool has been used to analyze approximately 100 micron single particles of aluminum. A single particle LIBS spectrum of an aluminum particle is shown in figure 9 below.

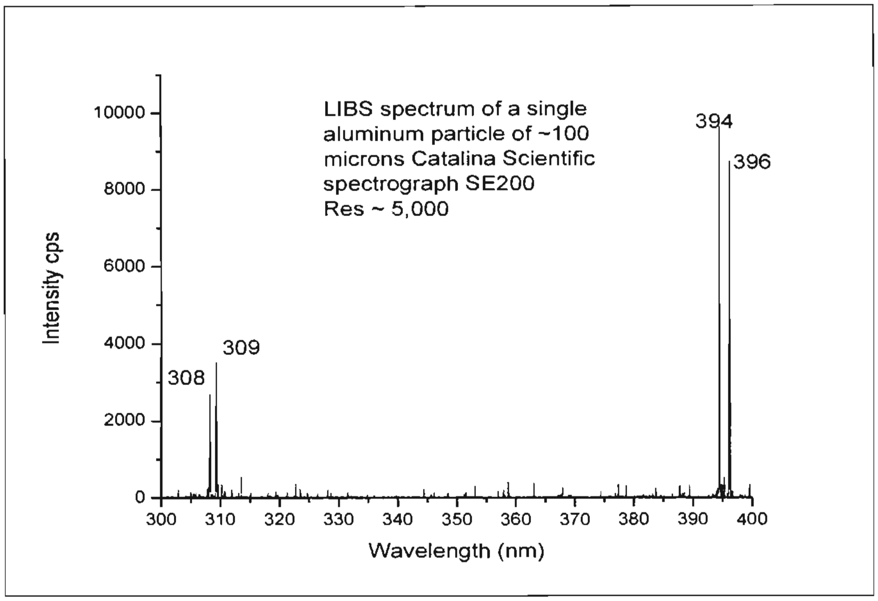

Figure9. Shown is a LIBS spectrum of an approximately 100 micron particle of aluminum.

We are currently in the process of using this system to analyze single particles of depleted uranium and thorium. The results of this investigation will be the subject of future reports.

Conclusions

In this paper we have described some of our current development and performance testing results for LIBS systems designed to address the needs of the IAEA inspectors, the goals of DOE /NNSA's NGSI, and International Safeguards. The goals and needs will be supported by providing (1) improvements in the analysis times for special nuclear materials (typical analysis times on the order minutes can be achieved), (2) performing real-time process monitoring and control in nuclear facilities in a continuous and unattended mode, and (3) performing in-field, prescreening and analysis of environmental and nuclear material samples. All of the LIBS system that we have developed can be deployed in a field setting thereby significantly reducing the number and therefore the cost associated with the collection, packaging, and shipping of samples for further analysis.

References:

1. "NGSI Program Plan: FY2009 – FY2013," Office of Nonproliferation and International Security, NNSA / DOE, November 2008.

2. D.A. Cremers and L. J. Radziemski, "Handbook of Laser-Induced Breakdown Spectroscopy", (John Wiley&Sons, England, 2006); Jagdish P. Singh and Surya N. Thakur (Editors), "Laser-Induced

Breakdown Spectroscopy", (Elsevier B. V. 2007); Andrzej W. Miziolek, Vincenzo Palleschi, and Israel Schechter (Editors), "Laser-Induced Breakdown Spectroscopy (Fundamentals and Applications)", (University Press, Cambridge 2006).

3. D. A. Cremers, L. J. Radziemski, and T. R. Loree, App. Spectrosc., 38 (1984), 721-729.
4. J. R. Thompson, R. C. Wiens, J. E. Barefield, D. T. Vanniman, H. E. Newsom, and S. M. Clegg, "Remote Laser Induced Breakdown Spectroscopy (LIBS) Analysis of DaG 476 and Zagami Martian Meteorites", Journal of Geophysical Research, Vol. 111, E05006, doi: 10.1029/2005JE002578, 2006;R. C. Wiens, R.E. Arvidson, D. A. Cremers, M. J. Ferris, J. D. Blacic, F. P. Seelos, and K. S. Deal, "Combined remote mineralogical and elemental identification from rovers: Field and laboratory test using reflectance and laser-induced breakdown spectroscopy, *J. Geophys. Res.-Planets* **2002**, 107, 8003, doi:10.1029/2000JE001439.
5. NASLIBS (North American Symposium on LIBS held yearly) and an International Conference on LIBS held every two years at locations around the world.
6. C. A. Smith, M. A. Martinez, D. K. Veirs, and D. A. Cremers, "Pu-239/Pu-240 isotope ratios determined using high resolution emission spectroscopy in a laser-induced plasma" *Spectra. Acta. Pt. B-Atom. Spectr.* **2002**, 57, 929-937.; W. Pietsch, A. Petit, and A. Briand, "Isotope ratio determination of uranium by optical emission spectroscopy on a laser –produced plasma plasma-basic investigations and analytical results", *Spectrosc. Acta Pt. B-Atom. Spectr.* **1998**, 53, 751-761.
7. The source for the uranium ore sample can be found at the following URL: http://www.nrcan.gc.ca/mms-smm/tect-tech/ccrmp/cer-cer/bl-5-eng.htm.

Acknowledgements

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