LA-UR- 10-03741

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Intended for:

51st INMM Annual Meeting
July 11 - 15, 2010
Baltimore, MD.

Los Alamos
NATIONAL LABORATORY
EST. 1943

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. This need was recognized and discussed at a Technical Meeting on "The Application of Laser Spectrometry Techniques in IAEA Safeguards" held at IAEA headquarters (September 2006). One of the principal recommendations from that 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" also held at IAEA headquarters (July 2008). This meeting was attended by 12 LIBS experts from the Czech Republic, the European Commission, France, the Republic of South Korea, the United States of America, Germany, the United Kingdom of Great Britain, Canada, and Northern Ireland.

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

The primary tool employed by the IAEA to detect undeclared processes and activities at special nuclear material facilities and sites is environmental sampling. One of the objectives of the Next Generation Safeguards Initiative (NGSI) Program Plan calls for the development of advanced tools and methodologies to detect and analyze undeclared processing or production of special nuclear material [1]. 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 elemental composition of microscopic quantities of 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 this 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 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 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 in spatial dimension) is generated. 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, 10 to several hundred milijoules of excitation energy is required to generate the plasma. The emission is collected with a lens and directed to a monochromator using a fiber optic bundle. The emission is then analyzed by a computer.

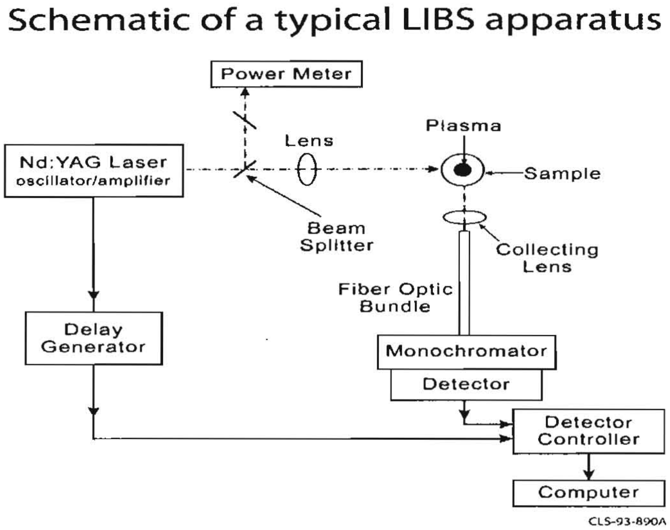
Schematic of a typical LIBS apparatus

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

Instrumentation Development and Performance Testing

Backpack Mounted Portable LIBS system

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+) using optical fibers. The spectra are detected with a CCD detector and analyzed with a pocket computer (OQO, Inc.). The combined system weighs approximately 18 pounds. A picture of the backpack LIBS system is shown in Figure2. The technologist in the picture is Leon Lopez from the Laboratory (C-CDE). The green / silver unit at the end of the probe and near the wall is the sampling head that includes the small laser and focusing optics used to generate the plasma. 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 pocket PC is located near Leon's right hand that services as the master controller for the laser, electronics, spectral collection, and data analysis. The backpack contains the laser power supply, Ocean Optics spectrometers, and associated electronics for controlling the system.

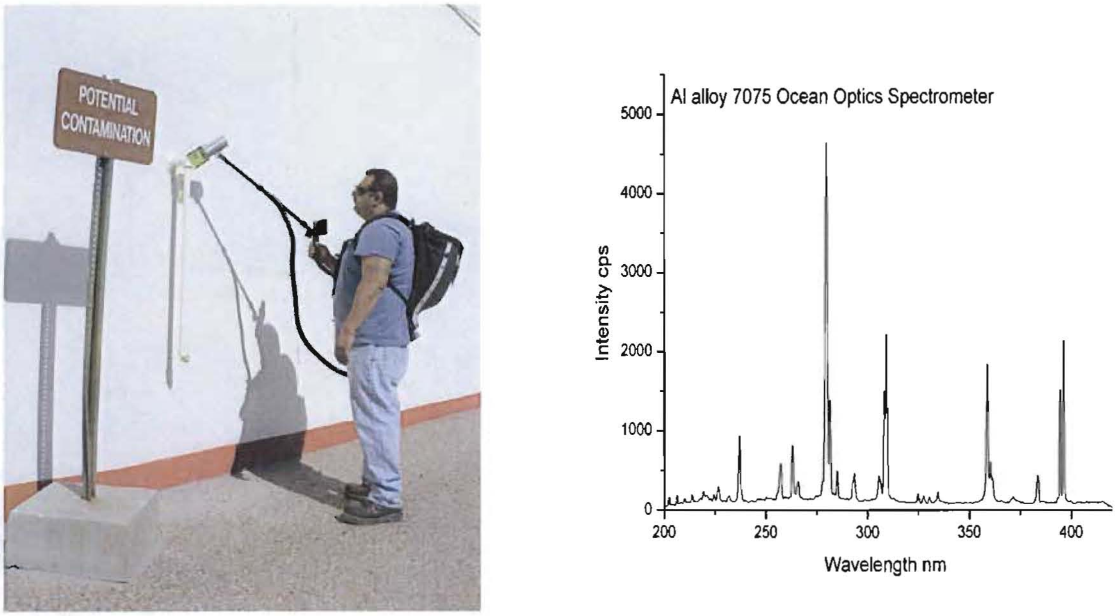

Figure2. A picture of the backpack system is being shown by Leon Lopez. On the right hand side is a typical LIBS spectrum of an aluminum alloy (Al 7075) sample in the region 200 – 420 nanometers (nm).

This system was used to analyze the following samples: (1) Magnets, AlNiCo, SmCo, and NdFeB; (2)Steels, 350 Marging steel, 250 marging steel, 304L SS, 316 SS, and A36 HRS (hot rolled steel); (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) and uranium ore. The concentration of uranium in the SRM and uranium ore samples was approximately 450 and 7500 ppm respectively.

We have used multivariate analysis or MVA to analyze spectral data collected from the samples listed above. The spectra collected and analyzed are similar to that shown in Figure 2 for Al 7075.

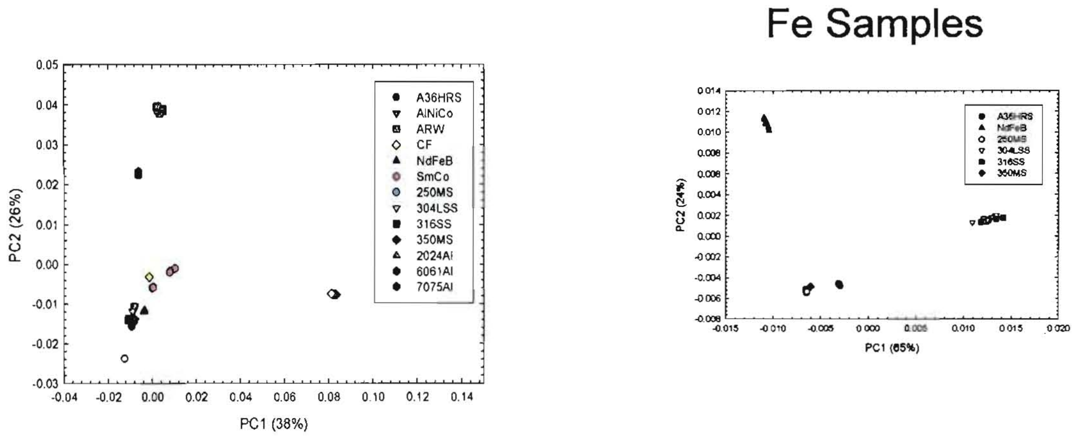

Figure3. MVA analysis of LIBS spectra for samples listed above showing clustering according to sample type on the left hand side. On the right hand side MVA analysis is shown for only the samples containing Fe.

The data presented in Figure 3 indicates that MVA analysis of LIBS data can be used to classify samples of similar types ^{6}. There is clustering of the samples when a wide range of sample types are used in the analysis. When only the samples containing Fe are analyzed, there is further clustering of different sample types but the concentration of the trace elements are too close to effect a significant separation for the stainless and the marging steel samples. A significant issue in this type of analysis is the low resolution (approximately 2000 -3000) of the spectral data acquired with the Ocean Optic spectrometers. An example of a spectrum of a 304 stainless steel sample is shown in Figure 4. There is significant overlap between the complex spectral signatures of Fe and the trace elements. The spectral signatures for the aluminum alloy sample shown in Figure 2 are much less congested or are reasonably well separated allowing for more accurate assignments. We are continuing to perform statistical analysis on this type of low resolution LIBS spectral data to determine the degree of sample classification possible.

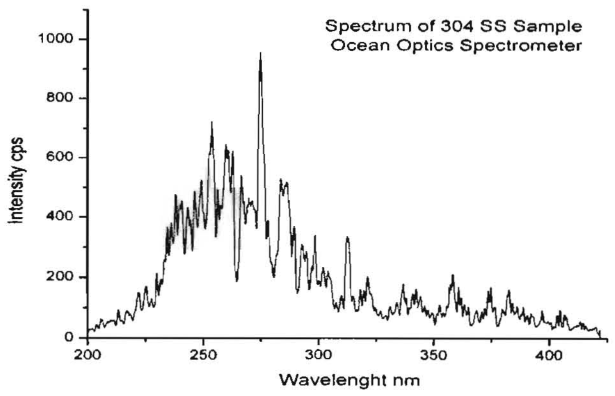

Figure4. A low resolution spectrum of a 304 stainless steel sample is shown.

We have also used this system to obtain LIBS spectra from samples of natural abundance uranium in different matrices (uranium ore, KBr pellets, and standard reference materials (SRM from NIST)). A typical low resolution LIBS spectrum of a natural abundance uranium ore sample is shown in Figure 5 between 200 and 420 nanometers along with some preliminary assignments.

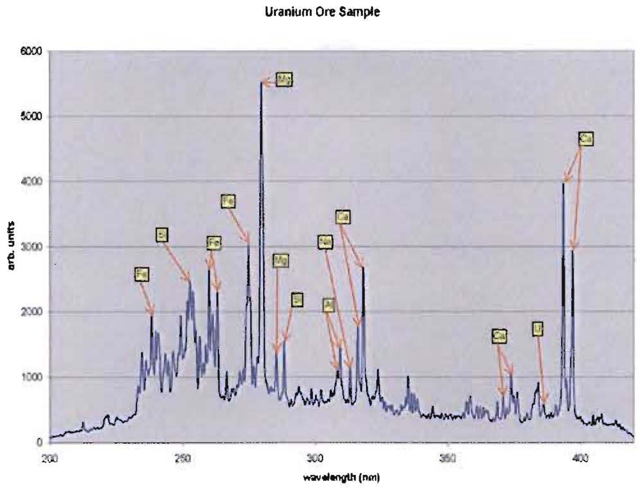

Figure5. A low resolution LIBS spectrum of a sample of natural abundance uranium ore is shown between 200 and 420 nm.

It is interesting to note that the most intense peaks assigned in the spectrum shown in Figure 5 above are not due to uranium transitions. The uranium ore sample or BL-5 is a low grade concentrate from Beaverlodge, Saskatchewan, Canada. The major mineralogical components are, in decreasing order of abundance: plagioclase feldspar ($Na_{65}K_{10}Ca_{25}$), hematite (Fe_2O_3), quartz (SiO_2), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), chlorite ($(Mg,Fe,Al)_3(Si,Al)_4O_{10}(OH)_2(Mg,Fe,Al)_3(OH)_6$), and muscovite ($KAl_2AlSi_3O_{10}(OH,F)_2$); uraninite ($UO_2$) is the main uranium-bearing mineral. The approximate chemical composition of the major elements in this standard sample in weight percent are: Si (22.0), U (7.09), Al (6.0), Fe (5.9), Ca (4.0), Na (3.6), C (1.9), Pb (1.5), Mg (1.5), K (0.4), Ti (0.4), S (0.3) and V (0.1) [7]. The density of states for uranium and other actinides is very high compared to elements like calcium, iron, magnesium, silicon, aluminum, and sodium. In the case of uranium in the sample, the excitation energy must be shared among the high density of states that are available for emission. Thus electronic transitions involving such states are generally weak when present with other elements with less complicated electronic state distributions. This along with the more complicated quantum physics and photo-dynamics associated with emission from excited states in actinide elements makes analysis very challenging using LIBS.

However, we have identified several low resolution analysis peaks that can be used to detect the presence of uranium in environmental samples. The peaks that we have tentatively 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.

Table1. Preliminary Uranium peak Assignments

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

Currently this system can be operated in a completely stand-alone mode for approximately 1.5 hours using battery power. We are investigating a more efficient and compact battery power system that should increase the operational analysis lifetime to approximately 3 hours and reduce the overall weight from 18 to 15 pounds. Transparent automatic user friendly analytical analysis functionality is also being integrated into this system. The transition of 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.

Cart / Rack Mounted Field Deployable High Resolution LIBS System Development

We are in the process of designing, assembling, and testing a high resolution LIBS system that includes a high resolution echelle spectrograph (LLA Instruments, Berlin, Germany). The high resolution 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 and 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 will have 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 6. 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 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.

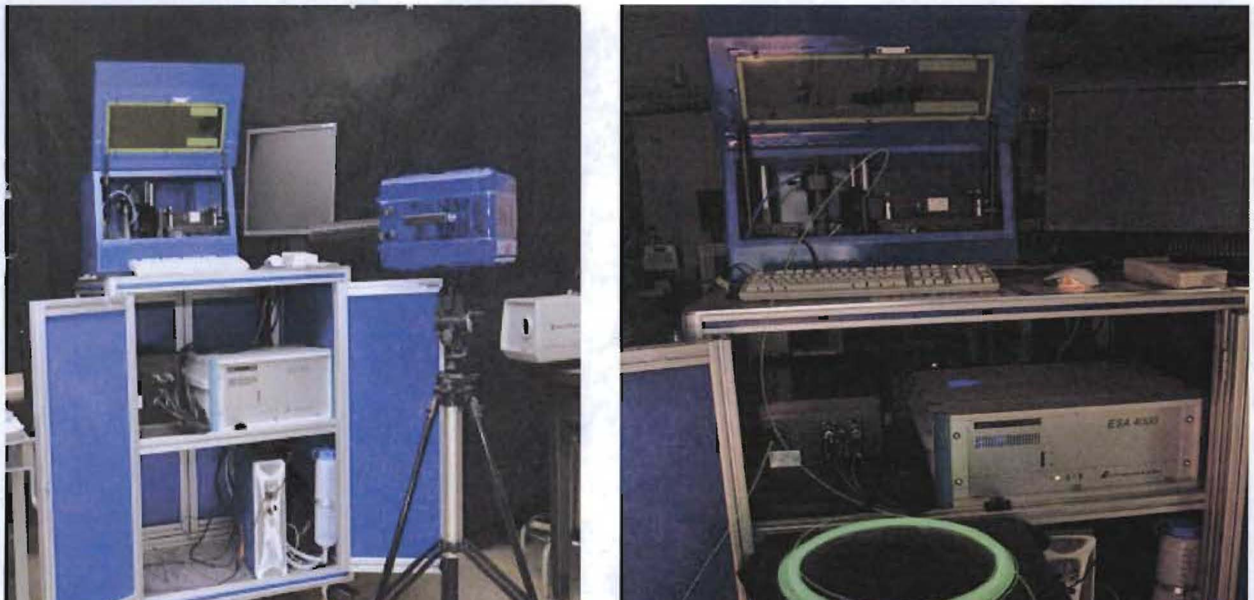

Figure6. In this picture is shown a general view of the Cart / Rack mounted LIBS system on the left and the system coupled to a 50 meter fiber optic cable illuminated with a green alignment laser for visual effects.

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 6 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 316 stainless steel is shown in Figure 7. This type of spectra can be used to determine elemental ratios of samples of special nuclear material. By contrast, it would be very difficult to use the low resolution spectra shown in Figure 4 (spectrum of a sample of 304 stainless steel), acquired with an Ocean Optics spectrometer to perform elemental ratio analysis of complex elements like the actinides.

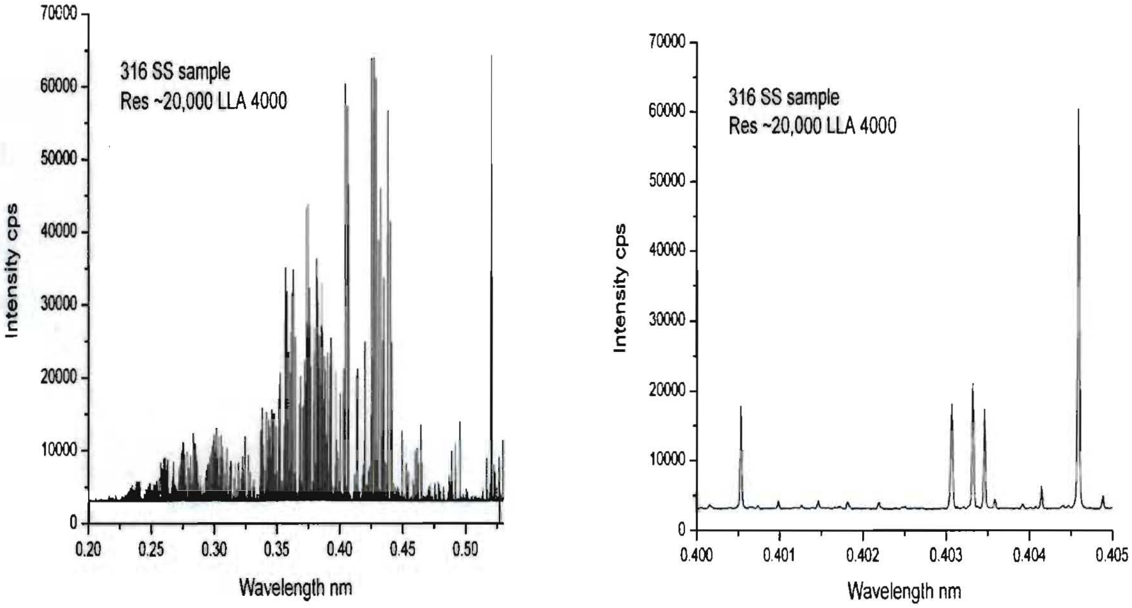

Figure7. Shown are high resolution sections of a 316 stainless steel sample collected through a 2 meter fiber cable. On the left hand side is a broad view of the spectrum covering approximately 300 nanometers. On the right hand side is a 5 nm section showing very good signal to noise.

Spectra of a 316 stainless steel sample collected through a 50 meter 800 micrometer core diameter fused silica fiber with silicon cladding is shown in Figure 8. There are significant losses in the overall intensity of spectral lines between 200 and 530 nanometers. More importantly, below approximately 390 nanometers spectral line intensities are essentially zero. The loss of spectral transmission between 200 and 390 nanometers is a significant problem since there are many useful analytical lines for most of the elements in the periodic table that occur in this region. The specification for the fibers that we have and are testing indicates that there should be transmission down to 200 nanometers but this is not consistent with the data. There is no apparent decrease in the resolution or fidelity of the spectral data shown in Figure 8. However, the overall spectral intensity is decreased by approximately 60 to 70

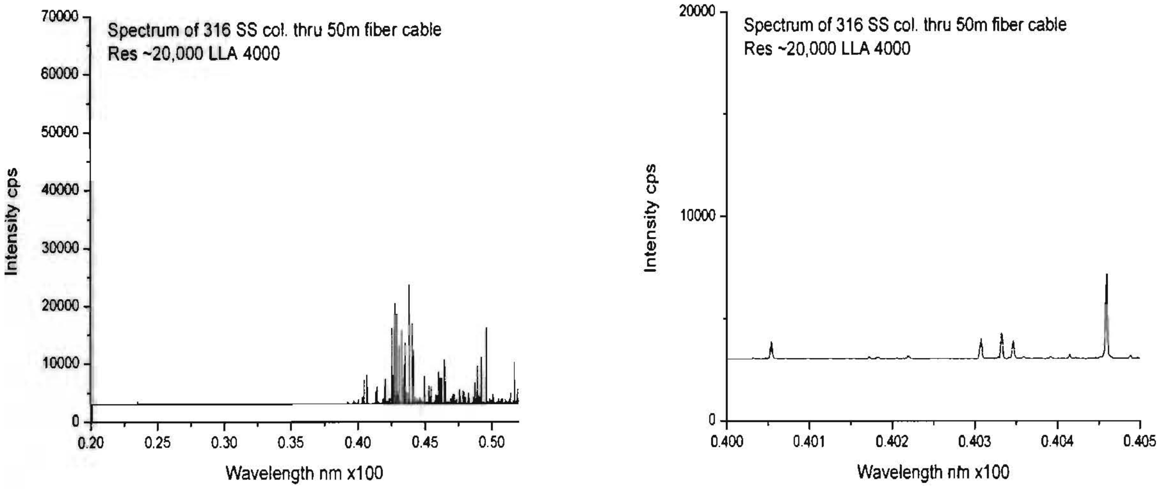

Figure8. Shown are sections of LIBS spectra of a 316 stainless steel sample collected through a 50 meter fiber optic cable.

percent. This is not necessarily a significant problem since this instrument contains a high gain detector system. We can make up for most if not all of the loss in overall spectral intensity by increasing the gain on the detector. However, the loss of transmission below 390 nanometers for the 5, 20, and 50 meter fibers is a significant problem and a solution must be found. The 2 meter fiber from a different company does have transmission down to 200 nanometers. We are currently reviewing spectral transmission data from other manufacturers of optical fibers in hopes of finding a solution to this problem.

Data from the initial performance testing of the Cart / Rack mounted high resolution LIBS system indicates that the system is working very well for the ***in situ*** sample chamber configuration. Performance testing using the variable focusing sample head and fiber optic cable configurations are in progress. As part of this performance testing plan, we will be testing a fiber optic coupled systems at a nuclear facility at Los Alamos and Oak Ridge National Laboratories in the near future.

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. The backpack LIBS system can be used to provide real time analysis in the field thereby significantly reducing the number and therefore the cost associated with the collection, packaging, and shipping of samples for further analysis. The burden and sample loading on analytical labs like the safeguards analytical lab will also be significantly reduced as well. Combining LIBS with fiber optic probes from multiple locations within nuclear material processing facilities has the potential for process monitoring and control in a continuous and unattended fashion. Thus any clandestine attempt to divert or remove material from nuclear facilities will be reduced.

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The author would like to acknowledge support of this work from DOE/NNSA (Program Offices NNSA 241 and 242), Mars Instrument Development Program (NASA), and the 94-1 Material Identification and Surveillance Program (PMT Division, Los Alamos National Laboratory). Los Alamos National Laboratory is operated by Los Alamos National Security, LLC for the United States Department of Energy under contract No. DE-AC52-06NA25396.