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Intended for:

INMM 50th Annual Meeting
July 12 - 16, 2009
Tucson, Arizona

Los Alamos
NATIONAL LABORATORY
EST. 1943

Potential Application of LIBS to NNSA Next Generation Safeguards Initiative (NGSI)

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Abstract

In a climate in which states and nations have been and perhaps currently are involved in the proliferation of nuclear materials and technologies, advanced methodologies and improvements in current measurement techniques are needed to combat new threats and increased levels of sophistication. The Department of Energy through the National Nuclear Security Administration (NNSA) has undertaken a broad review of International Safeguards. The conclusion from that review was that a comprehensive initiative to revitalize international safeguards technology and the human resource base was urgently needed to keep pace with demands and increasingly sophisticated emerging safeguards challenges.

To address these challenges, NNSA launched the Next Generation Safeguards Initiative (NGSI) to develop policies, concepts, technologies, expertise, and infrastructure necessary to sustain the international safeguards system as its mission evolves for the next 25 years. NGSI is designed to revitalize and strengthen the U.S. safeguards technical base, recognizing that without a robust program the United States of America will not be in a position to exercise leadership or provide the necessary support to the IAEA (International Atomic Energy Agency). International safeguards as administrated by the IAEA are the primary vehicle for verifying compliance with the peaceful use and nonproliferation of nuclear materials and technologies.

Laser Induced Breakdown Spectroscopy or LIBS has the potential to support the goals of NGSI as follows: by providing (1) automated analysis in complex nuclear processing or reprocessing facilities in real-time or near real-time without sample preparation or removal, (2) isotopic and important elemental ratio (Cm / Pu, Cm / U, …etc) analysis, and (3) centralized remote control, process monitoring, and analysis of nuclear materials in nuclear facilities at multiple locations within the facility. Potential application of LIBS to international safeguards as outlined in the NGSI will be discussed.

Introduction

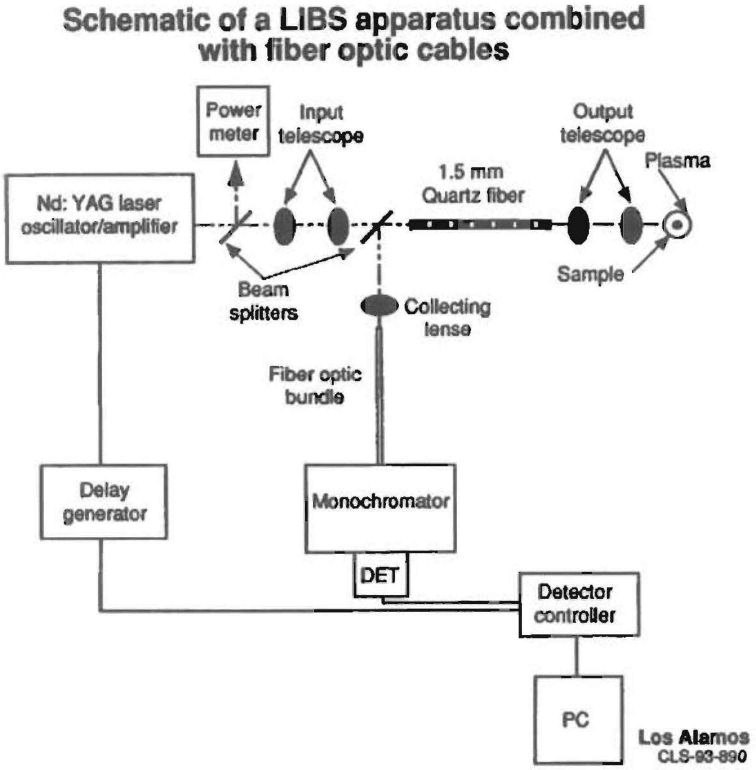
Laser-induced breakdown spectroscopy (LIBS) is a laser based optical method that can be used to determine the elemental composition of liquids, solids, and gases. In some cases small molecules can also be analyzed using LIBS. In the LIBS technique, short pulses from a laser are focused upon the surface of a sample and 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 originating from the surface and the gas above the surface. If the spectra are collected and analyzed as a function of the chemical composition of the elements present in samples of interest, calibration curves can be generated from which semi to quantitative information can be determined from samples of similar chemical composition. Sample analysis times using LIBS are on the order of a few minutes, very little if any sample preparation is required, and only a few micrograms of sample is remove per analysis. Thus analysis using LIBS can be considered essentially nondestructive, near real time, and waste free.

Again the capabilities of LIBS that can be used to support the goals of the NGSI in the area of technology development are : (1) real-time or near real-time automated elemental analysis, (2) essentially non-destructive elemental analysis with little or no sample preparation or handling, (3) on-line or at-line capabilities, and (4) remote operation in multiple sites via fiber optics. Potential safeguards applications to NGSI using LIBS will be addressed in this paper.

LIBS Technique

LIBS has been under development and applied to many chemical analysis problems at Los Alamos National Laboratory and laboratories around the country and the world for over 40 years [1]. As an example of the maturity of LIBS technology, a LIBS instrument is scheduled for deployment to Mars in 2011 for the elemental analysis of remote surfaces and features up to remote measurement distance of 10 meters [2]. There are also national and international meetings devoted to the application of LIBS technology to chemical analysis problems [3]. LIBS is a highly configurable technique meaning that instruments of many different shapes, sizes, and configurations can be designed, constructed, and tested with varying levels of sensitivity, precision, and deployment (from fixed lab to field deployable systems).

Conceptually, the instrumentation for LIBS type analytical analysis can range from simple to complex, depending upon the analytical protocol and the level of precision and accuracy desired. A schematic of a typical LIBS apparatus coupled to the sample using a fiber optic cable is shown in Figure 1 below. In this diagram, the output from a Nd:YAG laser is focused onto the surface of a sample where a small plasma is generated. The laser operates at 1064 nm and the pulse length is 7 – 10 nanoseconds. Depending upon



Schematic of a LIBS apparatus combined with fiber optic cables

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Figure1. In this schematic a LIBS experimental apparatus is shown coupled to the sample using a fiber optic cable.

the coupling of the laser light to the sample, 10 to several hundred milijoules of excitation energy is used to generate the micro-plasma. When using a fiber optic cable, the excitation laser beam is coupled into the fiber optic cable by a telescope. The excitation energy is then coupled onto the surface of the sample by an output telescope. The emission from the plasma is then re-imaged back down the optical fiber to a beam splitter where it is reflected and collected by a lens and a fiber optic bundle. The output from the fiber optic bundle is imaged onto the slit of a spectrograph, where it is detected and analyzed by a PC. An alternative method is to use a second fiber optic cable to transport the emission from the plasma back to the spectrograph for collection and analysis.

In Figure 2, the analysis end of a LIBS fiber optic probe is shown inside a glovebox where the analyst is analyzing a solution containing plutonium. The probe tip is positioned a few centimeters from the liquid surface. The tip-to-liquid distance can be increased up to several inches without significant loss in sensitivity. On the right hand side of the figure another fiber optic probe is shown where a plasma is generated on the surface of a rock. The small white spot beneath the probe is an image of the microplasma. In safeguards applications the optimum distance will be determined by (1) the sensitivity required, (2) space available, (3) ease of replacement, and (4) isolation of the tip from aerosols or liquid droplets generated by the focused laser beam pulse that could reduce transmission.

Figure 2. On the left hand side of this figure is shown the end of a LIBS fiber optic probe where the analyst is analyzing a solution containing plutonium. On the right hand side of this figure is shown another fiber optic probe directed onto the surface of a rock for analysis. The small white spot is the plasma being generated on the surface of the rock. In both cases, the probe contains the telescope optics for focusing the laser and collecting the emission from the plasma.

Instrumentation Development and Performance Testing

Backpack Mounted Portable LIBS System

A backpack mounted portable LIBS system has been developed to detect the presence of actinides and analyze samples important to international safeguards and NNV activities. This LIBS 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 HR2000+) using optical fibers. The spectra are detected and analyzed using a pocket PC. The combined system weighs approximately 30 pounds. A picture of the backpack LIBS system is shown in Figure 3 below. The technologist in the picture is Leon Lopez from the Laboratory. The green / silver unit at and near the wall is the sampling head of the probe that contains the small laser and focusing optics used to generate the plasma on the surface of the sample. The black umbilical cord contains a fiber optic cable for collecting emission from the plasma and directing it to the spectrometers and power cables for supplying power to the laser. Near the right hand of Leon is the location of the pocket PC which serves as the master controller for controlling the laser and analyzing the spectral data from the spectrometers.

Figure3. Picture of the backpack mounted LIBS system being shown by Leon Lopez. On the right side is a typical LIBS spectrum taken with the backpack system and displayed on the pocket PC..

This system was used to collect and analyze samples important to safeguards and NNV activities. The samples analyzed include, (1) Magnets, AlNiCo, SmCo, and NdFeB, (2) Steels, 350 marging steel, 250 marging steel, 304L SS, 316 SS, 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 occurring Uranium in SRM 610 (standard reference material from NIST, Washington, D.C., USA) and uranium ore. The concentration of uranium in the SRM was 450 ppm and approximately 7500 ppm in the ore samples. A typical LIBS spectrum of a uranium ore sample is shown in Figure 4 below. Similar spectra was collected and analyzed for all of the other samples analyzed.

It is interesting to note that the strongest peaks in the spectrum shown in Figure 4 below are not due to uranium transitions. 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 available for emission. Thus electronic transitions involving such states are generally weak compared to 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 of actinide elements very challenging using laser induced emission spectroscopy or LIBS.

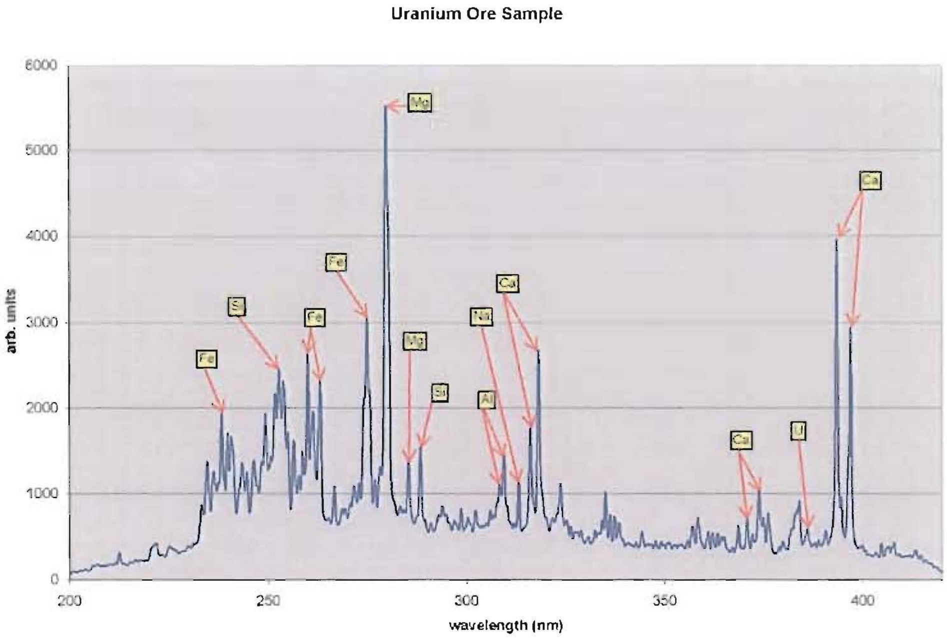

Figure 4. LIBS spectrum of a sample of naturally occurring uranium ore indicating peak assignments for the elements listed.

An expanded region of the uranium spectrum between 340 and 392 nm is shown in Figure 5 below. In this spectral region we show four independent data collections (col.1-4) that are the sum of 10 spectra averaged together. The peaks / features in the data collections are extremely reproducible except for small shifts in intensity indicating that the features are due to spectral transitions from elements in the sample and not random noise. Several small features assigned to uranium transitions with excited state designations are indicated. The largest feature assigned to uranium at 385.89 can be used for semi quantitative analysis for samples containing uranium. Because of the limited resolution of the spectrometers (approximately 0.1 nanometers) used to collect and analyze the spectral emission, this spectral feature actually is the combination of more than one peak. Thus this is a fundamental limitation of this type of low resolution device in the analysis of complex elements like actinides. Such a device can be used to detect the presence of actinides and in some cases provide limited semi quantitative analysis depending upon the sample matrix. The real merit and benefit of such a device is that it can be used as a screening tool to potentially provide real time rapid site characterization without sample removal, packaging, and shipping for further analysis.

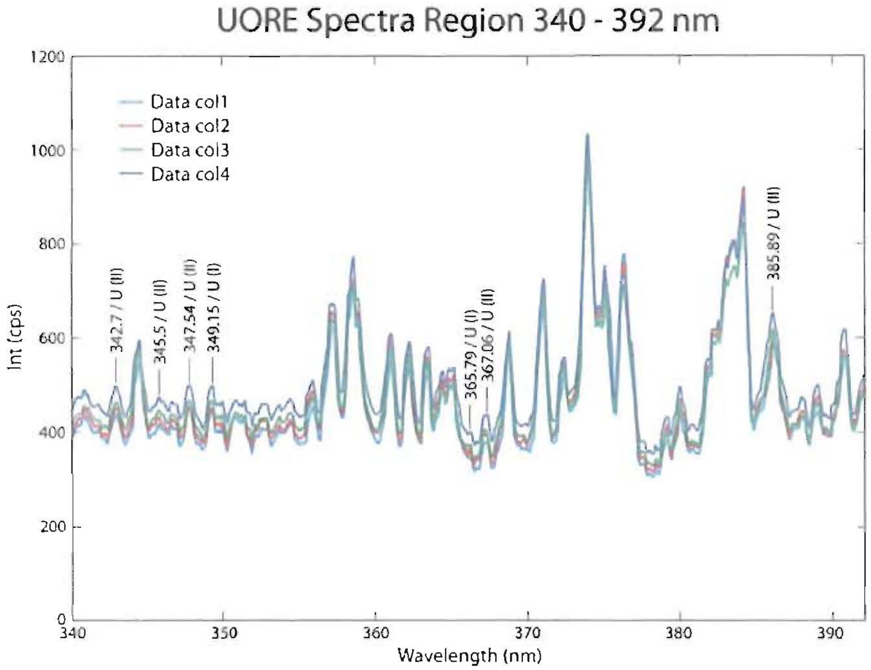

Figure 5. Shown is an expanded view of the spectral region 340 to 392 nm from the spectrum in Figure 4.

This device has also been used to analysis a suite of samples important to safeguards and NNV (Nuclear Nonproliferation and Verification) activities. The spectra collected and analyzed are similar the spectra shown in Figure 4. We have used multivariate analysis or MVA to analyze spectral data collected for the samples important to safeguards and NNV listed above. A preliminary analysis of the data is shown in Figure 6 below. The data presented in this plot give the indication that this type of statistical analysis can potentially be used to classify sample types using LIBS spectra. There is indication of clustering among samples of the same type except for the steel samples. We are in the process of further testing this type of statistical analysis method to see how well it can be used to classify or identify sample types from LIBS spectra [4].

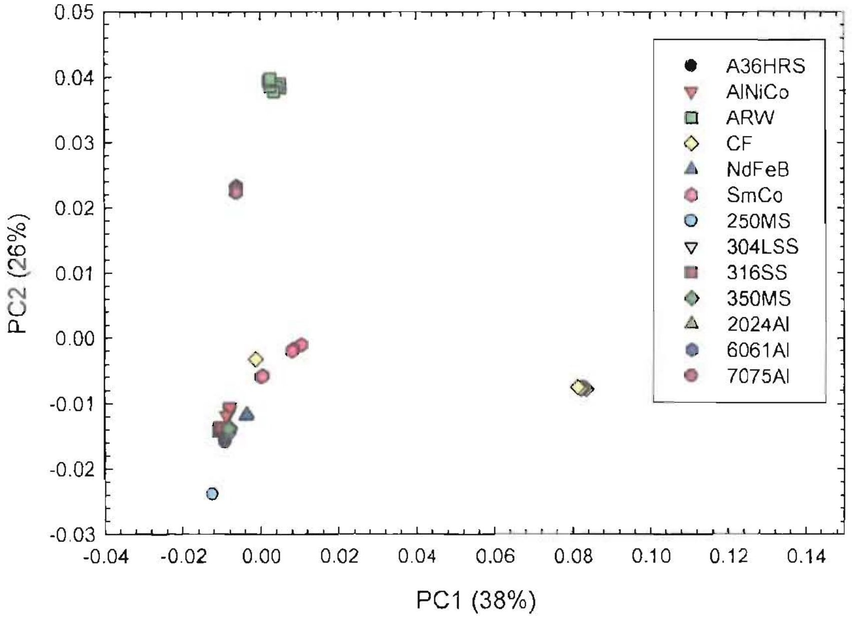

Figure 6. MVA analysis of samples important to safeguards and NNV activities is shown in this graph.

High Resolution Isotopic Sensitive Fixed Lab LIBS Instrument

We have an operational high resolution fixed lab LIBS system located in a nuclear facility here at Los Alamos National Laboratory. This system consists of a high resolution (approximately 155,000 in single pass mode) 2 meter McPherson Czerny Turner design spectrometer that can be operated in double pass mode. The excitation source is a Continuum Surelite I Nd:YAG laser operating at 10 Hz with a pulse width of approximately 5 nanoseconds and energy output to 400 mJ per pulse. The emission signal is detected by a Princeton Instruments ICCD detector and analyzed by a Micron 266 MHz PC running Windows NT v4.0. A picture of this high resolution LIBS system is shown in Figure 7 below. This system was used to analyze a sample of plutonium oxide containing a 49 / 51 mixture of Pu (239 / 240) [5]. LIBS has also been used to perform isotopic analysis on samples of uranium [6]. A LIBS spectrum of this plutonium sample is shown in Figure 8 below.

This is a scanning system so obtaining survey spectra between 200 and 850 nanometers is very difficult and time consuming. We are in the process of modifying and upgrading this system such that medium resolution survey type LIBS spectra can be obtained. This modification includes the addition of a medium resolution echelle spectrograph from LLA Instruments GmbH Berlin Germany. This spectrograph has a resolution of approximately 20,000 and is equipped with an ICCD detector. With this spectrograph we will also be able to collect spectra in single shot mode between 200 and 780 nanometers.

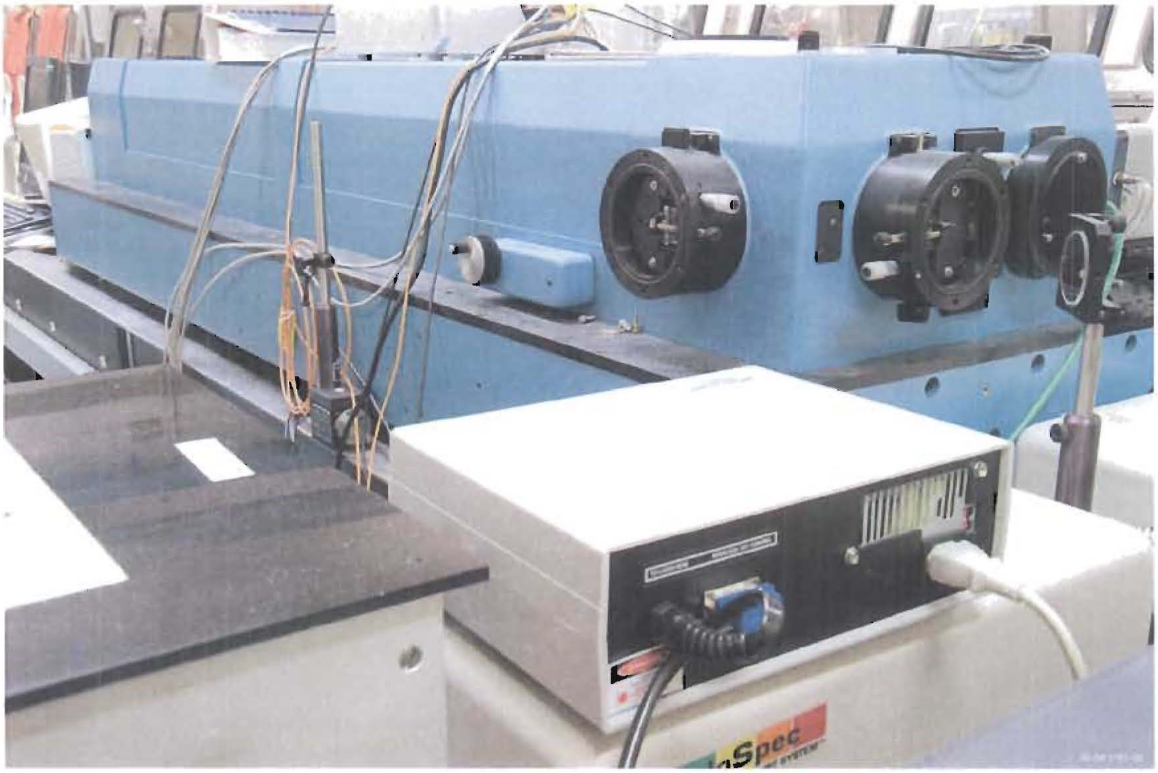

Figure 7. A picture of a High resolution fixed lab LIBS system in a nuclear facility here at Los Alamos National Laboratory is shown in this figure.

Thus single particle and elemental ratio analysis of samples of actinides will in principle be possible as well as elemental ratio analysis of samples of spent nuclear fuel or SNF.

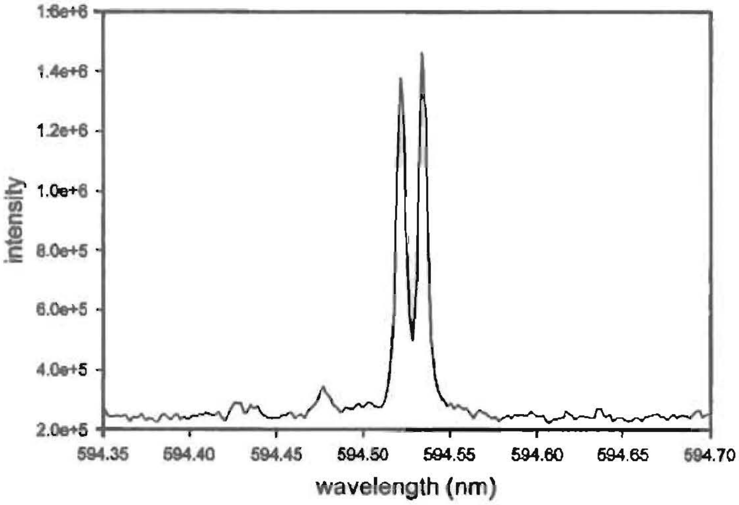

Figure 8. LIBS spectrum of a plutonium oxide sample with isotope ratio for Pu-239 to Pu-240 of 49:51 is shown. The Pu-239 transition is located at 594.52202 nm and the Pu-240 transition is located at 594.53457 nm. The isotopic ratio was also determined by standard gamma-ray spectroscopy.

Cart / Rack Mounted Field Deployable High Resolution LIBS System

We are also in the process of designing, constructing, and testing a high resolution LIBS system that contains a high resolution echelle spectrograph. The high resolution spectrograph has a resolution of 60,000 in single pass or 120, 000 in double mode. The emission is detected with a ICCD that has a minimum gate width of 16 nanoseconds and the spectral coverage is 200 to 780 nm. The excitation source is a Quantel USA Nd:YAG laser operating at a rep rate of 20 Hz, 9 nanosecond pulse width and an output energy of up to 330 mJ / pulse. This system will have the capability to be operated in one of three modes: (1) ***in situ*** measurements with measurement distances of a few inches in a sampling chamber near the mobile platform, (2) remote measurements using direct optic access through the windows of hot cells or gloveboxes using a variable focused sampling head, and (3) remote measurements using fiber optic cable coupled probes at measurement distances up to approximately 100 meters both inside and outside hotcells and golveboxes.

The remote measurement capability in principle will allow remote monitoring and control of nuclear materials and processes in nuclear facilities in real to near-real time in a continuous mode. Thus the safeguarding of nuclear materials and processes can be rapidly monitored and verified in real time. Therefore any attempt to clandestinely remove or modify processes in nuclear facilities will be immediately detected. A major improvement in the ability to safeguard processes and nuclear materials in nuclear facilities could be realized. The threat to the proliferation of nuclear materials and technologies can be significantly reduced using this system. The detection of undeclared activities can also be realized using this system since the system is field deployable, mobile, and can be operated in several modes. The system can also be used to perform isotopic, elemental ratio analysis, major, minor, and trace elemental analysis.

A prototype version of this system is shown in Figure 9 below. The picture on the left shows the sampling head (blue box mounted on a tripod) which contains the laser excitation source and optics for directing and focusing the laser beam through the window in the hotcell to the sample where a plasma is generated. The sampling head also contains optics for collecting the emission from the plasma and directing it to a spectrograph via a fiber optic cable. Although the contrast is not optimized one can see sampling containers inside the hotcell from which samples could potentially be analyzed. A LIBS spectrum of a copper target is visible on the computer monitor. The right hand side of the Figure shows the mobile platform containing the power supply module for the laser that sits to the left on the same level as the computer screen. The top shelf contains the computer on the right hand side, a pulse timing controller in the middle, and the detector (light blue box0 and the spectrograph (the vertical black box). This system is being used to perform concept design and testing. For the high resolution version, the computer, detector, and spectrograph will be replaced with a high resolution spectrograph, detector, and computer system. Fiber optic probes that can be coupled to the high resolution LIBS are also under development.

Figure 9. A prototype version of a field deployable high resolution LIBS system is shown in this picture.

Conclusions

In this paper we have described the development efforts in our laboratory that have been used to design, construct, and test LIBS systems which can be used to support the goals of NGSI. The LIBS systems described will support the goals of NGSI by providing (1) improvements in the speed of nuclear material measurements, (2) performing real-time process monitoring and control in nuclear facilities in a continuous and unattended fashion, and (3) performing in-field, prescreening and analysis of environmental and nuclear material samples. The backpack mounted portable LIBS system can be used to provide real time sample analysis of environmental and nuclear material samples in the field thereby significantly reducing the cost associated with the collection, packaging, and shipping of uninteresting samples for further analysis. By using this prescreening approach only those samples needing further analysis will be collected, packaged, and shipped. The burden and sample loading on analytical labs like the safeguards analytical lab will also be significantly reduced. Since LIBS can be combined with fiber optic probes to measurement distances of approximately 100 meters the potential exists to design and construct a system that can be used to monitor and control processes in nuclear facilities in a continuous and unattended manner in real time. Thus any clandestine attempts to divert material from nuclear facilities will be reduced or eliminated thereby reducing the probability of the proliferation of nuclear materials. The ability to safeguard nuclear materials will be improved. Most LIBS measurements can be obtained on a time scale of minutes which will result in an improvement in the speed of nuclear material measurements. One final attribute of LIBS measurement systems is that all of the elements in the periodic table can be analyzed. Thus composition of system components can also be analyzed. For example, the required specifications on material of construction for containment systems (for example, alloys, metals, and welds) can be determined. Also, by monitoring elements in process streams associated with the presence of corrosion (Cr, Fe, and Ni) in stainless steel for example, the potential onset of corrosion can be detected and remediated. In a way the health of containment systems in nuclear facilities can also be potentially monitored in real time using LIBS systems.

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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.