Portable Multi-contaminant Detection Instrument for D&D

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Abstract

At Department of Energy sites (especially those scheduled for closure such as Rocky Flats Environmental Technology Site), hundreds of structures comprising millions of square feet must be demolished and removed. Structures range from environmental monitoring stations to uncontaminated office trailers to highly contaminated former plutonium production facilities. Most of the effort will lie in decontaminating and decommissioning (D&D) highly contaminated processing facilities, such as buildings in which plutonium was processed. The cost, schedule, ES&H, and health physics aspects of the D&D activity are all driven by the extent to which the facility is contaminated with radionuclides, RCRA heavy metals, and TSCA organics. The ability to identify these contaminants *a priori* drives the approach to (and therefore cost and schedule of) D&D. When little information is available, a worst-case scenario must be assumed, which results in the most restrictive level of personnel protective equipment (PPE) for workers and thus the lowest possible work efficiency and highest cost.

Under this three-Phase SBIR project, ADA Technologies is developing a portable, qualitative analysis device that can be maneuvered into difficult-to-access locations to determine the nature and levels of contamination prior to the initiation of D&D activities. This device will enable D&D professionals to select the appropriate ES&H/Health Physics approach based on data acquired in the space being treated. The result will be decreased cost, schedule optimization, and waste minimization. The ADA tool will provide visual feedback via a miniature camera, elemental analysis of contaminants using laser-induced breakdown spectroscopy (LIBS), and radiation measurements using solid-state detectors. This novel technology will offer a “go/no-go” decision-making capability that *in real time* will allow the operator to analyze the nature, appearance, and type of contamination in a specific, difficult-to-access location. With this key information available, the operator can then plan and carry out D&D activities that are consistent with the nature of the hazard.

As envisioned, the proposed instrument will be contained in an instrument case of roughly 2.6 cubic feet. The sample probe will have an 8- to 16-foot semi-rigid umbilical to allow investigation of remote and difficult-to-access locations. The probe head will be less than 3.5” in diameter by 8” long, for easy access to the spaces of interest. Inside the probe head will be simple optics to focus an optical fiber-borne laser pulse for generation

of a plasma, a color video camera, light source for visual inspection, radiation detector, and a second optical fiber for plasma-emission transmission to the instrument. The head will have a quick-disconnect from the umbilical to allow easy replacement of the protective shroud and/or disposal of contaminated components. One innovative aspect of this instrument will be the combination of fixed and variable band-span (automated) spectrographs to allow the instrument to quickly identify contaminants that are present and to then refine the determination in subsequent laser pulses.

Under the Phase I project, an ADA Technologies' LIBS instrument (previously developed) was enhanced with a small video camera in the sample wand. Also during Phase I, this instrument was tested to determine the detection limit for many contaminants anticipated at D&D sites or other clean-up sites, such as Superfund sites. Calibration samples for eighteen elements (Ag, As, Ba, Be, Cd, Co, Cr, Cs, Hg, Mn, Ni, Pb, Sb, Se, Ti, U, V, Zn) were prepared in multiple concentrations on various substrates, with and without interferents such as oils. These samples were tested on ADA's wide-band and narrow-band LIBS instruments. Over 5500 spectra were collected and analyzed to determine the detection limits for these materials. From the literature, it is known that over 36 elements are detectable using LIBS instruments that are similar in configuration to the ADA instruments (small, portable). The most notable element for D&D applications is beryllium, which LIBS can detect at very low levels in the field. This is important because beryllium is quite toxic and other fieldable technologies, such as XRF, are not capable of detecting beryllium. One of the most encouraging aspects of the Phase I project was the positive response received by ADA from the D&D community when briefed on the new instrument. The letters of support and the offers to assist in evaluating the Phase II prototype equipment under actual service conditions validated the potential (and clear need) for this technology within the D&D application area.

In Phase II, ADA will complete the design and field-testing/validation of this new instrument. Tasks to be addressed in Phase II include: 1) development of several application-specific sample probes, 2) integration of radiation sensors, 3) refinement of user-appropriate software, 4) field evaluation, and 5) modification/optimization of the instrument based on the field evaluation feedback.

ADA will be teaming with Mississippi State University's Diagnostic Instrumentation and Analysis Laboratory (DIAL) to help select and integrate state-of-the-art components into the Phase II prototype LIBS package. DIAL has broad experience in LIBS development and has performed a significant amount of testing in D&D environments. ADA is excited about this teaming arrangement because of DIAL's LIBS experience in other applications coupled with field work at additional D&D sites. The collaboration of ADA and DIAL will facilitate a successful product-development effort. As important as the product itself, the ADA/DIAL team is capable of creating a highly successful product deployment in D&D settings, which presents very real challenges to those unfamiliar with that arena.

Problem

In D&D operations, the selection of cleanup technology is a function of contaminants encountered. The rate of cleanup is dramatically affected by selected technology (level of PPE needed, sophistication of equipment, space preparation and post-treatment demobilization). If an instrument existed that could quickly characterize unknown contaminants found in enclosed and tight spaces, then the efficiency of D&D operations could be greatly improved by allowing selection of appropriate PPE and clean-up technology without having to wait for time-consuming off-site laboratory analysis. ADA's LIBS instrument for D&D operations addresses this need.

Objective

The objective of this project is to develop a field-portable analyzer for use in confined spaces to quickly and reliably identify local contaminants. The information generated by this instrument can then be used to select appropriate PPE and cleanup technologies, thereby reduce cleanup costs by matching technology and PPE to level of contamination.**Approach**

ADA approach to satisfy this objective is to use laser-induced breakdown spectroscopy (LIBS) to identify contaminants. In addition to LIBS, a video camera and monitor will be used to provide a visual feedback of the deposits. Finally a radiation sensing system will be combined with the instrument to provide a rapid and portable assessment tool.

ADA has designed, fabricated and tested several LIBS-based instruments in the past for multiple applications. Experience and expertise from these projects is being used extensively in the design and refinement of the new instrument. Among the improvements that ADA is making to the existing LIBS configuration is the design of multiple task-specific sampling probes as well as implementation of a shorter analysis time. The three compact sampling probes being designed will permit use in tight spaces (internal cavities, ducts & tanks, and at stand-off distances). A conceptual sketch of the instrument is shown in Figure 1.

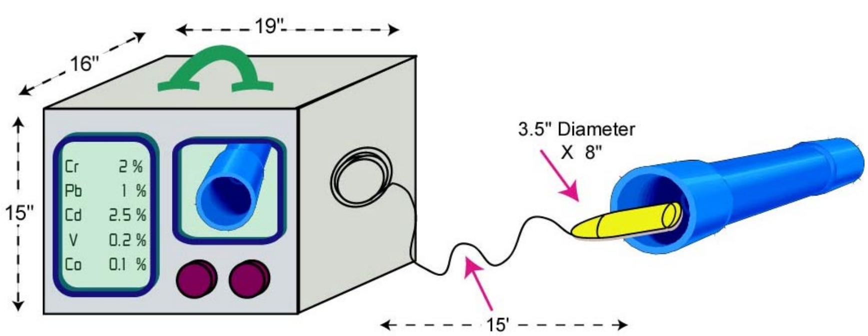

Figure 1: Conceptual sketch of Phase II instrument

As background, laser-induced breakdown spectroscopy (LIBS) is a simple, laser-based technique that can characterize the elemental composition of aerosols, liquids, gases, and solids in real time with a single laser pulse. In many situations, the technique can be quantitative as well as a qualitative. LIBS instruments typically use a short pulse-duration laser (~3-10 nsec in duration and 20-150 mJ of pulse energy) that is focused through a lens onto a surface or into the volume to be analyzed. The high-energy pulse creates a small plasma at the focal point of the system optics during the pulse (see Figure 2). The resulting high-temperature plasma (~ 20,000 K) is sufficient to vaporize, atomize, and electronically excite a small amount (pg to ng) of the sample matter. These excited atoms and molecular fragments decay primarily by emission of photons whose wavelength spectrum is characteristic of the atoms in the plasma. The light from the emitting atoms is collected using standard optical techniques and dispersed in a monochromator or spectrograph, depending on the design of the detector. The resulting emissions frequency spectrum is a fingerprint of the elemental composition of the sample. Through calibration, the intensity of each peak in the spectrum can be related to the relative concentration of the element giving rise to the spectral feature. Beryllium is used as an example in the following discussion of LIBS because of its importance in D&D, but it is important to realize that the process is the same for all the other elements that can be measured using LIBS.

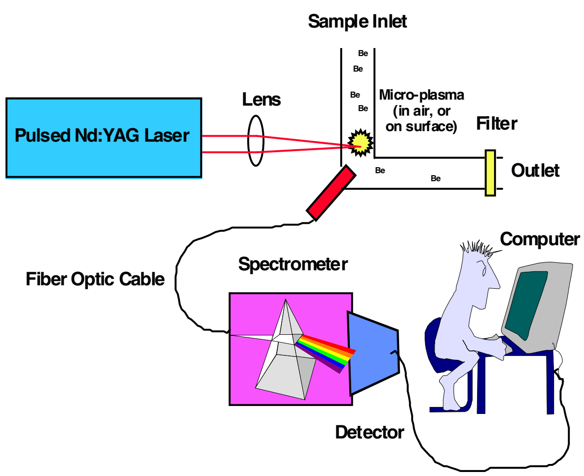

Figure 2: LIBS Operation

Figure 3 presents a series of typical LIBS spectra from the ADA surface/swipe monitor generated from calibration standards of beryllium salts on MCE filter paper. As seen in the graph, the instrument is able to detect beryllium at levels as low as 0.1 µg deposited uniformly as a solution on a 41mm diameter filter, then dried. There are two important features to recognize in Figure 3: 1) beryllium emits photons (at the temperatures of the plasma) at characteristic wavelengths (the 313.1 nm beryllium emissions peak is prominent in the plot), and 2) the height of the peak is proportional to the concentration of beryllium on the filter.

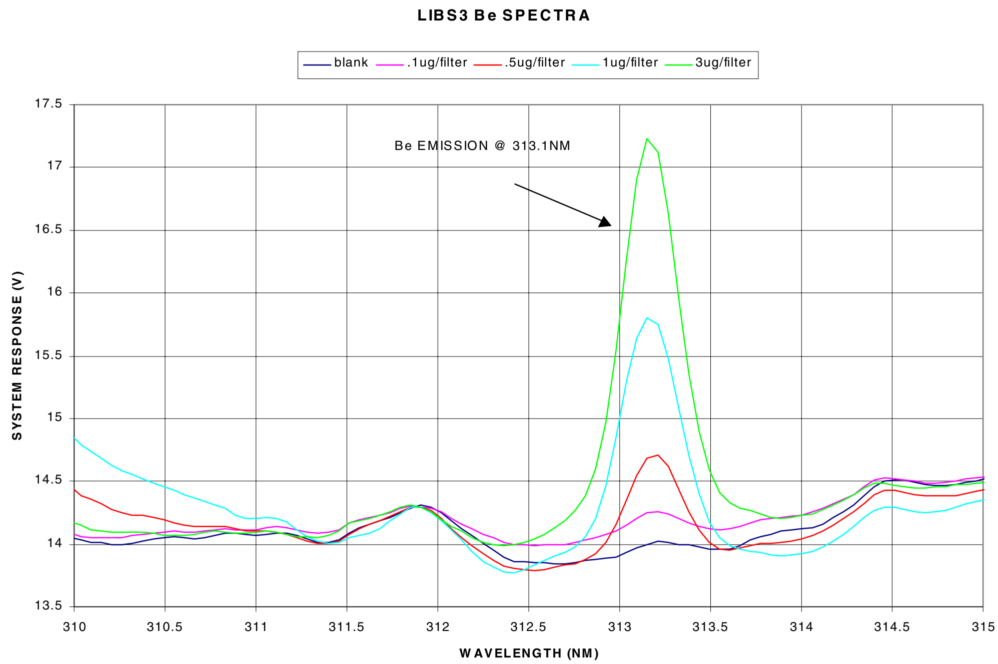

Figure 3: Beryllium spectra collected with ADA Surface/Swipe LIBS Instrument (Each curve represents a spectrum collected from a single laser pulse)

Once the data has been collected, specialized techniques to extract the signals of interest from the spectral data are used. The calibration techniques for LIBS are varied and several are proprietary.

During the Phase I program, an existing field-portable ADA LIBS instrument was used to measure a series of materials anticipated in D&D environments on various substrates (filter paper, wallboard, carbon steel, stainless steel) with differing interferents such as grease and machine oil. These tests were designed to determine the detection limits of the technology for the materials of interest at various D&D sites under typical field conditions. The instrument used for these tests is shown below along with the sample carousel.

One limitation of LIBS technology is that the actual sample volume from a single laser pulse is quite small. This can be accommodated by designing an instrument with a rapid repetition rate for the pulsed laser. Elements present in low concentrations and not uniformly distributed can be readily detected by collecting spectral data for a few hundred laser pulses spread over the area of interest. The upgraded operating software will be able to accrue spectral data from a series of laser pulses and apply specialized techniques to extract meaningful signals from the noise and to find statistical significance in results from the processed data.

Figure 4: Existing ADA LIBS instrument used in Phase I project

The following table shows the detection limits of the instrument as determined Phase I. These detection limits are based on 100 individual laser pulses.

Table 1: Phase I detection limits

Metal	Wavelength (nm)	Detection Limit (i g/cm^2)	Detection Limit (ppm)
Silver (Ag)	328	0.039	6.0
Arsenic (As)	193	4.363	750
Barium (Ba)	229, 232	0.186	32
Beryllium (Be)	313	0.002	0.36
Cadium (Cd)	226.8	0.361	62
Cobalt (Co)	345	1.835	320
Chromium (Cr)	520	0.453	78
Mercury (Hg)	253.7	1.445	250
Manganese (Mn)	402.8	1.927	330
Nickel (Ni)	342	7.707	1300
Lead (Pb)	405.8	0.326	56
Thallium (Tl)	535	0.373	64
Uranium (U)	bands at 260 and bands at 370	NA	NA
Vanadium (V)	249, 265, 280	0.051	8
Zinc (Zn)	204, 207	0.09	16

Also during the Phase I program, one of the planned sample probes was designed and fabricated. This sample probe included the camera but did not incorporate the radiation sensor. The following figure shows the sample probe design and a photograph of the Phase I unit. Please note that the red dot on the pipe is a laser beam from a commercial pocket laser pointer which the operator can use to aim the more powerful plasma-generation laser.

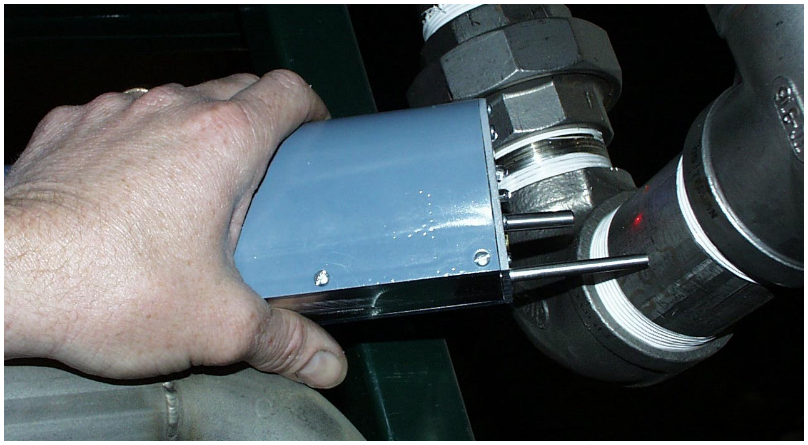

Figure 5: Phase I sample wand

In addition to the sample probe shown above, two additional samples probes will be developed during the course of the Phase II program. These probes are shown in the following figure.

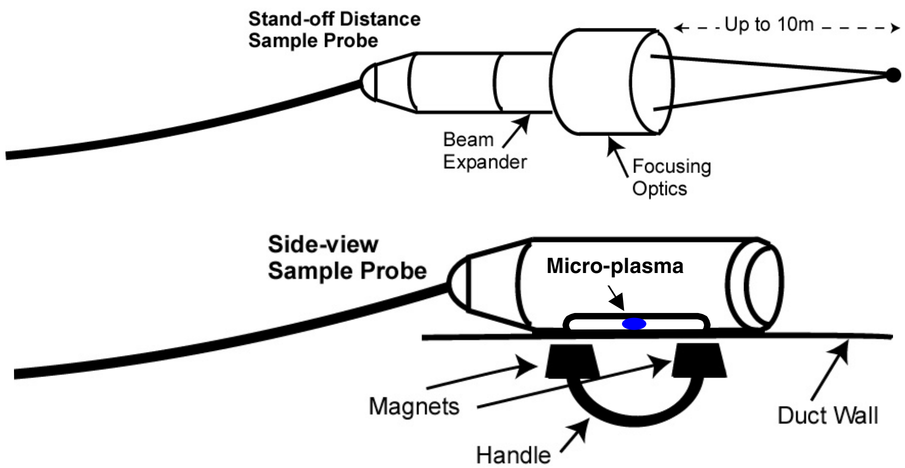

Figure 6: Other planned sample probes

Phase II Program

In the Phase II program, a number of improvements are being made to the instrument, both hardware and software. The following list shows the tasks planned in Phase II program:

1) Design Phase II prototype instrument

2) Build prototype instruments

3) Calibrate prototype systems

4) Complete arrangements with DOE sites to conduct field trials on D&D projects

5) Perform field trials with prototype instruments

6) Develop retrofit kits

7) Perform second round of field trials

8) Project management and reporting

The following bulleted list shows some of the important project milestones:

- Project start 6/2001
- Prototype design complete 1/2002
- Prototype fabrication complete 3/2002
- First round of field-tests start 3/2002
- Second round of field-tests start 7/2002
- Project ends 6/2003

In Phase II, the project team was expanded to include:

Eberline Services : Eberline will provide important field evaluation at their on-site laboratory at Rocky Flats.

DIAL at Mississippi State : DIAL will provide consulting on the Phase II LIBS instrument design, and assistance in development of calibration routines.

Phase II Results to date

The Phase II program started in mid-June of 2001 and as of the middle of October the following accomplishment had been achieved:

- A successful Beryllium field-test of the Phase I equipment in a CDC laboratory by Dr. Mark Hoover.
- Identified and purchased a higher power/faster repetition rate laser
- Identified and purchased lastest-generation detectors and spectrometers
- Identified radiation sensor system
- Started designing a more compact sample probe in cooperation with DIAL, where the laser head is external to the probe, with the laser pulse transmitted to the probe via fiber optic cable.

Phase II next steps

The next steps in the Phase II project include:

- Firming up the arrangements with the initial field tests sites;
- Identifying additional field test sites;
- Completing the design and fabrication of the new prototype instrument;
- Installing instrument #1 at Eberline services' RFETS on-site laboratory.

For further information, or to discuss potential for testing at a DOE site, please contact the Principal Investigator, Patrick D. French at ADA Technologies, Inc.