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Field-testing for environmental pollutants using briefcase sized portable LIBS system

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The integration of miniature fiber optic spectrometers with small high peak power laser transmitters has lead to the development of a portable analytical instrument capable of real-time qualitative analysis. LIBS, (Laser Induced Breakdown Spectroscopy) systems are now assembled with commercial off the shelf (COTS) components to produce portable briefcase size elemental analyzers that are capable of sustained battery operation in remote field environments. In a typical LIBS system, a high peak power pulsed 1064nm Nd:YAG laser is focused on a targeted material. The pulse power, which is several MegaWatts, generates a plasma from which the elemental line spectra of the sample is then created, collected and analyzed for the elements present. The analysis of the LIBS data occurs in under a second using any laptop computer with virtually no sample preparation. In this work we perform environmental analysis in field conditions with a low-cost portable LIBS system to determine the presence of hazardous and other elements in various samples. The reliability of quantitative data from spectral analysis is also examined.

1. INTRODUCTION

The existence of elemental emission lines was proposed over 140 years ago[1]. From this theory, emission line spectroscopy was born, and latter explained through "quantum" theory. Laser Induced Breakdown Spectroscopy, LIBS, is a relatively new version of this form of spectroscopy made possible with the advent of the laser. One of the first laser induced plasma systems used was demonstrated with a Q-switched Ruby laser at Cornell Aeronautical Laboratories in 1964[2]. The first neodymium LIBS system for solid material analysis was developed in 1967[3]. Neodymium doped **Y**ttrium **A**luminum

Garnet or Nd:YAG lasers are currently the most common laser system used in LIBS. This is because the pulsed solid–state Nd:YAG crystal laser is easily configured to produce the megawatt peak power levels required for reliable laser induced plasma formation.

Homeland security and the war on terror have sparked recent interest in LIBS as a promising technology for the remote detection of explosives, landmines, biological weapons and chemical contaminates [4] . With respect to chemical contaminates, LIBS has also been shown to have many advantages related to field testing for environmental pollutants; the primary advantage being LIBS' ability to provide rapid, reliable, multi-elemental in-situ analysis with virtually no sample preparation.

To date, many researchers have explored the development and use of portable LIBS systems as evidenced by the body of research reported in the 1990s[5,6,7,8,9]. These include a US Army LIBS cone penetrometer system for subsurface in-situ soil classification and the detection of heavy metal contaminates in wells. The US Army's field-portable LIBS system included a compact probe containing of a small customized 1.25" diameter x 14" long 17-Megawatt Nd:YAG laser head. Los Alamos National Labs, (LANL) developed a portable LIBS system designed for a truly remote application; profiling the surface of Mars. The LANL Martian Rover LIBS system is an alternative to the x-ray fluorescence system used on the last two Mars missions. It was recently discovered that the current Mars Rover's x-ray analysis system is not able to provide data on Mars' rock formations due to a thin dust layer that coats everything on the Martian surface. It is suggested that the Los Alamos developed LIBS system will be capable of penetrating the dust coatings and analyzing the Martian substructure.

While some researchers have identified applications, such as those listed above, for which LIBS has been shown to be economically feasible, many more have struggled to justify the use of LIBS for their specific applications due solely to the cost of the hardware.

The purpose of the present study has been to establish the viability of a low-cost, light weight portable LIBS system for remote applications. While the study focused on qualitative as apposed to quantitative results, in order to prove the viability of the technology, from the data presented, those researchers familiar with quantitative LIBS analysis should conclude that the system has the stability to perform quantitative measurements.

2. EXPERIMENTAL

Long and even short term exposure to small quantities of heavy metals such as lead (Pb), Cadmium (Cd), Nickel (Ni), Arsenic (As), Beryllium (Be), Mercury (Hg), Chromium (Cr), Nickel (Ni) and Antimony (Sb) can lead to long-term health consequences, for these elements have exhibited a propensity to accumulate in the human body, causing irreversible damage.

Unfortunately, environmental monitoring of these common toxic materials has traditionally been both expensive, and time consuming.

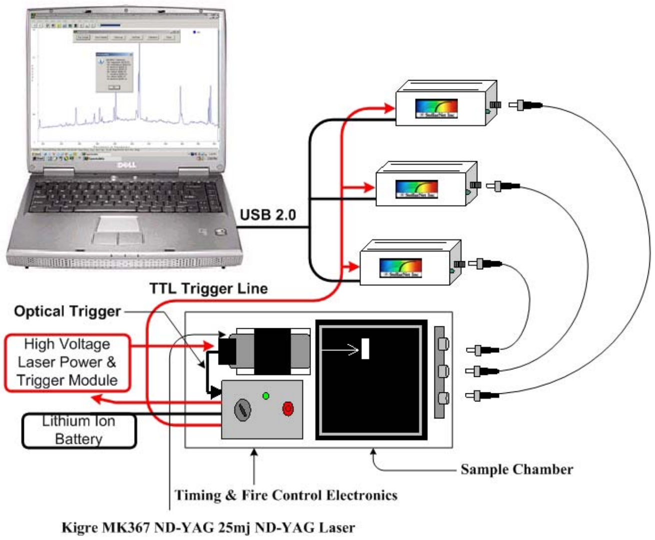


Figure 1. Schematic of the LIBS instrument configuration.

The purpose of this research was to demonstrate the viability of a new low-cost portable LIBS system for the qualitative detection of heavy metal contaminants in the environment.

Figure 2. The LIBS system. The entire platform, including the laser, sample compartment, and trigger module measures 5 cm x 21 cm x 10 cm. Not shown is the battery pack or the laptop computer.

The LIBS system described in this work was comprised of a high peak power laser, a spectrometer, a sampling chamber, and an optical trigger module, all of which can be run via battery power. A schematic showing the simplicity of the instrument can be seen in Figure 1 and a photograph of the sampling chamber, the laser, and the timing circuit is shown in Figure 2.

The entire setup fits into a Pelican briefcase that measures 18 cm x 33 cm x 46 cm and weighs less than 14.5 kg. A schematic of the system and a photograph are shown in Figure 2.

The instrument utilized a compact, low-cost, permanently aligned MK-367 6-Megawatt, 4 ns per pulse, 25 mJ Nd:YAG laser with a 1 Hz pulse repetition rate and a passive Q switch (Figure 3).

The beam diameter was 3 mm with a beam divergence of 90% less than milliradian full angle (i.e. 50% less than 0.8 mr) and the polarization was greater than 99.7%.

This laser head and mounting chassis was designed for a light weight commercial Air-Dropped Lidar Ceilometer that had to survive being dropped from an aircraft without a parachute. The assembly has been tested and shown to withstand an impact of 1000 G with a lifetime in excess 300,000 shots.

The LIBS system utilized for this study consisted of a two (2) standard resolution EPP2000 LSR spectrometers from StellarNet Inc, both of which were fitted with 2048 element non intensified charge-coupled device (CCD) detectors.

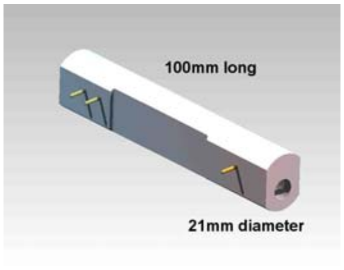


Figure 3. LIBS MK-367 laser head. A trigger module, not shown, attaches to the laser via the three gold posts shown in the image. An image of the entire assembly can be seen in Figure 2.

The dual channel systems spectral bandwidth was 200-600 nm, and the optical dispersion per pixel was 0.19 nm. Each spectrometer was configured with a 14 um slit which resulted in a spectral resolution very near the dispersion limit of the optical bench at 0.2 nm.

One of the benefits of the system utilized is it's versatility, for it can be configured with up to seven (7), high-resolution spectrometers, to give a spectral bandwidth of 200-975 nm with a spectral resolution of 0.1 nm (1-Angstrom). The only down-side to (7) channels is that the size of the system increases. Fortunately however, for most field applications, the analyte of interest is known and thus the system can be scaled back to a single high-resolution or standard resolution spectrometer for that particular measurement. The ability to add and remove channels as needed is a key feature for this system.

Shown in Figure 12 is a photograph of the portable LIBS system in the field.

A. SAMPLE PREPARATION

One of the benefits of LIBS is the fact that very little sample pretreatment is needed in order to measure a sample. In this work, most of the elemental standards were purchased from Johnson Matthey, Alfa Aesar ® in solid metal form. Sample preparation simply involved cutting standards into ¼" x ¼" pieces and placing the samples in the sample chamber via double sided tape. The double-sided tape was placed on the back face of the sample to ensure that the sample did not move during the measurement. The front-sides of the samples were subsequently positioned in the LIBS system sample compartment at a pre-aligned and marked position coinciding with focal point of the laser output pulse.

With respect to the environmental samples discussed below, the contaminated mud samples were prepared for analysis by taking samples and placing them in specially designed liquid sampling cells. These cells were simply micro-wells on quartz substrates. After loading the wells, the quartz substrates were then placed in the LIBS sample compartment, just as the solid samples were, onto the sampling pedestal.

B. HARDWARE SETUP

THE LASER

The passively Q-switched laser pump voltage was set between the single and double pulse thresholds (~673 Volts = 4.5 Joules) for stable single pulse operation. Single pulse operation provided a nominal 25mJ over a 4ns pulse-width, which provided approximately 6 mW of energy for plasma formation. This setting was found to be sufficient for all standards and samples that were evaluated.

It should be noted that it is possible to configure the system for stable double pulse or "pulse-train" operation by setting the laser pump voltage above the double pulse pump threshold value (~724 Volts = 5.2 Joules). A value of approximately 800 Volts suffices.

This configuration provides two 23mj, 4nm pulses separated in time by 25us. The first focused pulse initiates plasma formation and the second pulse injects additional energy into the plasma plume. It has been reported that this technique increases the total plasma energy, the size of the plasma ablation field and the emission line spectra signal-to-noise (S/N) ratio[10,11,12,13,14,15].

THE TRIGGER MODULE

The LIBS system also includes an integrated trigger module that allows for a variable time delay between the laser firing and the triggering of the spectrometer capture. This is accomplished through the use of a high-speed photo-trigger. Specifically, a single element InGaAs photodiode with a 5 ns rise/fall response time was utilized to sense the leading edge of the laser pulse and start the system event clock. The system possessed a user selectable variable [10 position] delay circuit that could be utilized to maximize the S/N of the instrument.

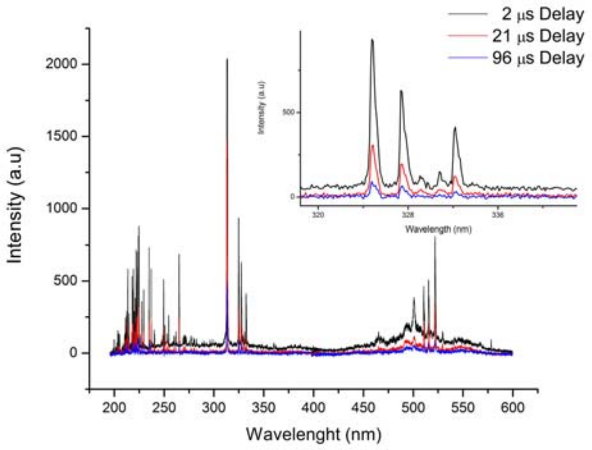


Figure 4. The instrument provided for a variable delay via a high-speed photo trigger and a user selectable (10) position variable delay circuit. It was determined that a 21 µs delay between the laser firing and the spectra being captured was optimal for the majority of samples measured. At 21 µs, the recombination and the Bremsstrahlung effects had subsided and the elemental emission line peak amplitudes were still sufficient for elemental indexing.

For all sample reported in this body of work, a 21 µs delay was utilized, as discussed in Figure 4.

SPECTRAL ACQUISITION

Fiber optics was utilized to image the plasma and allow each spectrometer to capture the emission line spectra. Three optical paths were available and each path was capable of feeding the optical emission to three (3) individual spectrometers. In this work, two (2) spectrometers were utilized and each spectrometer (i.e. channel) captured its spectral range simultaneously, post trigger. Figure 5 shows the spectral emissions from three different standards using the dual channel configuration. Channel (1) covered 200-400 nm and channel (2) covered 400-600 nm.

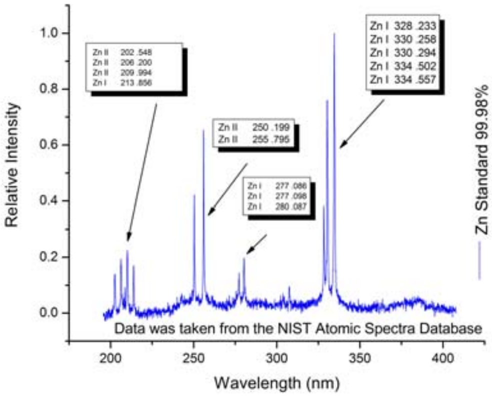


Figure 6. Shown above is a representative spectra of a 99.98% pure zinc [Zn] standard. All of the elemental emission lines that are shown were identified using the NIST Atomic Spectra Database as Zn lines.

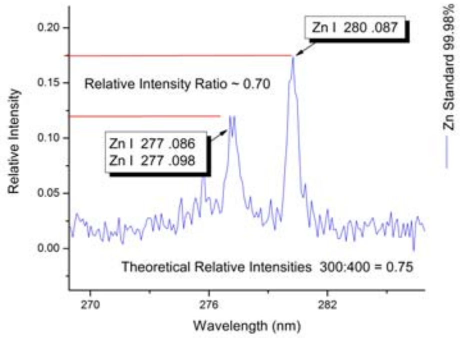


Figure 7. This graphic illustrates the performance that was achieved with the low-cost ($20,000) LIBS system that was utilized for this study. Two features are important: 1)the doublet at 277 nm is partially resolved which is surprising due to the fact that the instruments dispersion limit was 0.19 nm., and 2) the relative amplitude of the two peaks shown is very close to the theoretical value for the relative intensities (0.75).

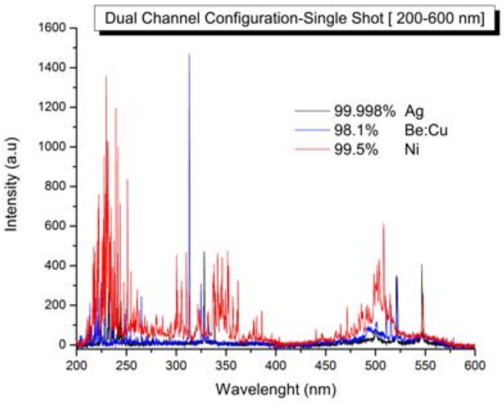


Figure 5. Representative spectra from Silver, Copper-Beryllium, and Nickel Standards.

While all of the sample spectra were taken with this dual channel configuration, in most cases, only data from 200-400 nm has been presented because: 1) this simplifies the technical discussion and 2) this region possesses more spectral features compared to the visible region of the spectrum.

3. RESULTS AND DISCUSSION

SPECTRAL RESOLUTION

In order to show the viability of the technology for elemental emission, Figure 6 and Figure 7 were taken of high purity zinc [99.98%]. Two important features, which allude to the quality of the data gathered with the low-cost LIBS system, are documented in the captions for Figure 6 and Figure 7. The first important feature, from Figure 6, is the presence of all the expected elemental emission lines, per the NIST Atomic Spectra Database. The second feature, and perhaps the most important aspect of the data, is shown in Figure 7. In this figure, both the spectral resolution of the device and the relative intensity of the peaks can be seen to be extraordinary.

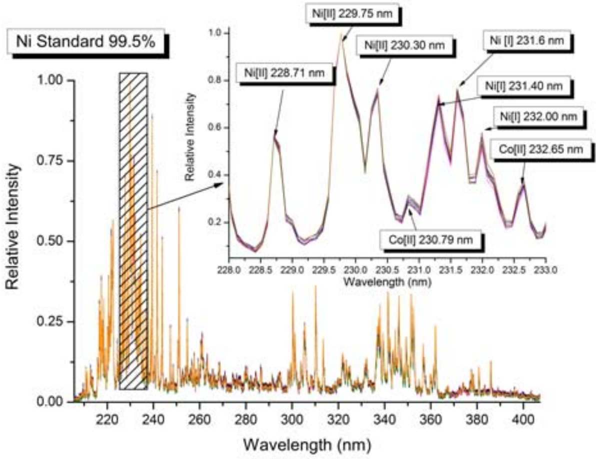


Figure 8. Shown above is the spectral signature of a 99.5% nickel standard. The data appears noisy at first glance, but upon zooming in on some spectral features, it is found that the data is representative of the sample and the repeatability of the measurement is extremely high.

The relative amplitudes per the NIST database are 300:400 or better yet, peak one is 75% that of peak two. The correlation in the data is very high, for peak one is ~70% the height of peak two. In addition, notice the ability of the instrument to partially resolve the doublet at 277 nm. This is very impressive due to the fact that the diffraction limit of the optical spectrograph is 0.19 nm. The next phase of this research will reexamine many of these standards using the high-resolution version of the LIBS system.

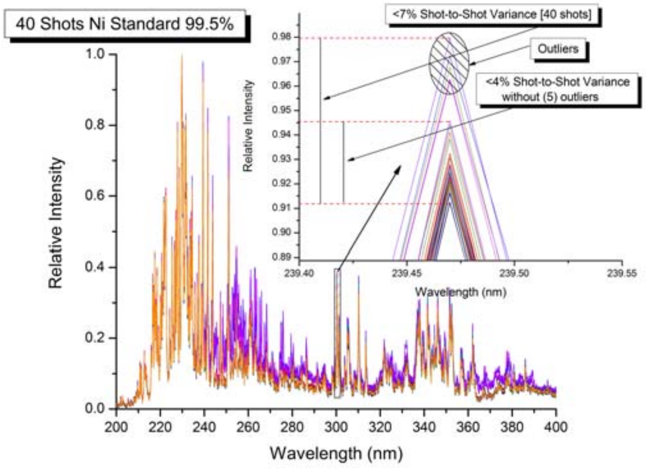


Figure 9. Shown are 40 single shot spectra overlaid. Upon zooming in on a specific spectral peak, it is found that the maximum shot-to-shot variance was approximately 7%. More important however is the fact that if the (5) spectral outliers are removed from the data, the shot-to-shot variance is under 4%.

REPEATABILITY

Numerous studies were performed to evaluate the stability of the LIBS system. The first standard analyzed was Nickel (Ni). It was found, upon comparing our LIBS data against ICP standards as well as reported LIBS emission lines found in various technical publications[16,17,18,19,20], that nickel's emission spectra was very reproducible (Figure 8). In addition, as evidenced in Figure 9, it was found that the stability of the system with respect to shot-to-shot variance was extremely high (<7%). This data represents 40 single shot spectra overlaid to determine shot-to-shot variance. It was found that the data possessed five (5) spectral outliers, however, even with the outliers the maximum shot variation for the spectral range examined, was under 7%. Upon removeal of the spectral outliers, the shot-to-shot variance became 4%.

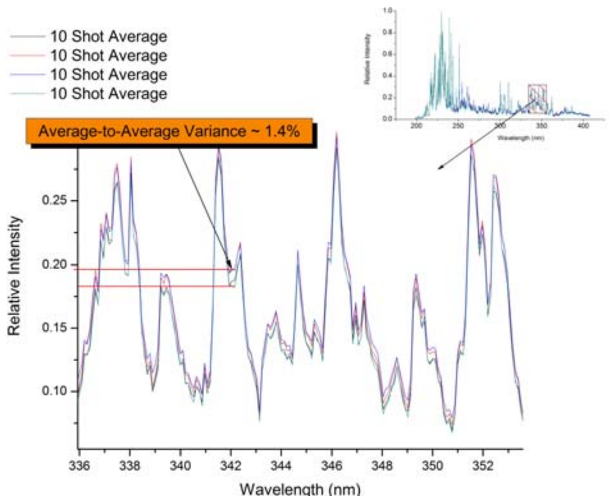


Figure 10. . The average shot-to-shot variance shown in Figure 9 was, wort-case, 7%. In an attempt to improve upon this uncertainty, the same data was analyzed as four (4) sets of ten (10) averages. In doing this, it was found that the maximum variance in the spectral region that was analyzed was only 1.4%. This is a significant improvement in the uncertainty. The inset graphic in the upper right-hand corner is the full spectral signature.

The stability of the system with respect to averaging multiple shots was also examined. The same data shown in Figure 9 was reanalyzed to yield four (4) averaged spectra, where each spectra was an average of ten (10) shots.

Even with the outliers present, the variance in the data dropped to 1.4%.

Another important aspect of the instrument is its ability to reliably characterize the same material (i.e. standard), each time the material is loaded into the sample chamber.

The results depicted in Figure 11 are outstanding. The peak-to-peak variance for twelve (12) spectra across the spectral region examined was less than 5%. This is extremely important due to the fact that many samples must be translated between subsequent shots since laser ablation rates for some materials are very high. In fact, it turns out that silver has a high ablation rate and if the sample is not translated, the shot-to-shot variance can exceed 20%. This is due to the fact that pitting of the material with each subsequent shot, significantly affects the spectral signature.

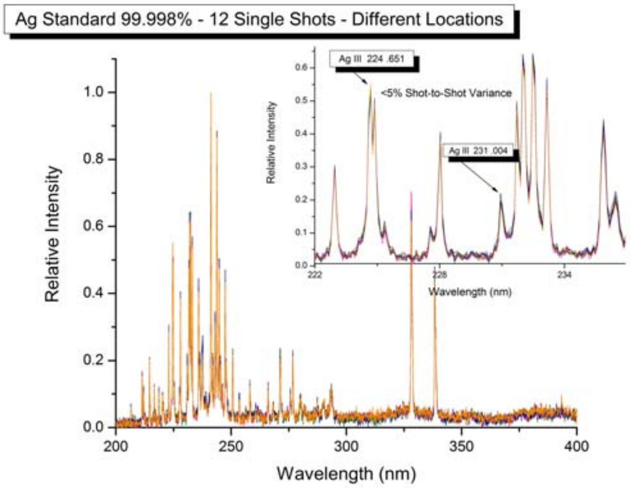


Figure 11. A key aspect for any instrument is its ability to reproducibly characterize a material over and over again, each time that material is loaded into the instrument. This graphic shows the 12 spectral signatures of silver. Before each shot, the sample was translated under the laser head to simulate reloading the standard into the sample chamber.

FIELD WORK

Figure 12 shows the LIBS system being utilized in the field to characterize oyster beds in Hilton Head, South Carolina.

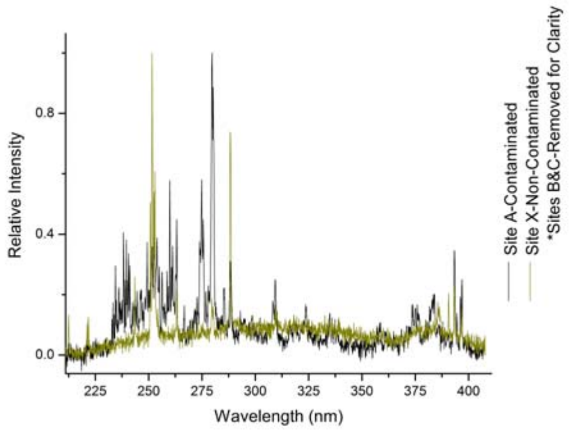


Figure 13. Shown above is data from a contaminated watershed near a wood treatment facility in the Pacific Northwest. The difference between the contaminated and non-contaminated sample is clear to see.

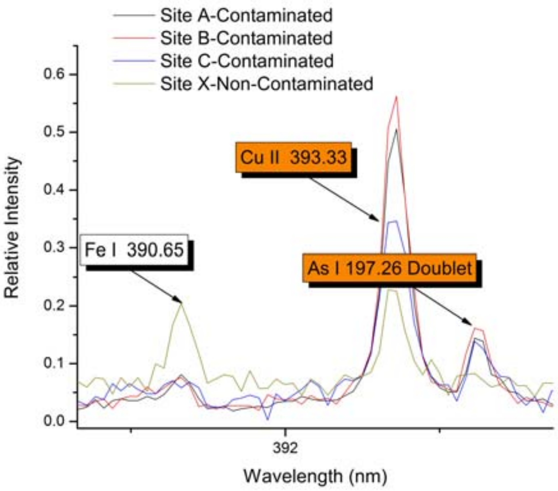


Figure 14. Upon close examination of the spectra, small peaks for copper and arsenic are found. Unfortunately, copper was also found in the non-contaminated reference and the relative amplitudes of the arsenic peak in the contaminated samples was quite low.

Figure 12. Shown in the photograph is the LIBS system being used to analyze oyster beads in Hilton Head, South Carolina.

Presented in Figure 13 is LIBS data taken from a contaminated watershed in the Pacific Northwest. The site was near a wood treatment facility and it is clear to see from the data that the contaminated and non-contaminated samples look very different spectrally.

Upon close examination of Figure 14, two (2) peaks are identified that are indicative of wood treatment facility contaminants, specifically, copper and arsenic. Unfortunately, copper is also found in the non-contaminated reference and the relative amplitude of the arsenic peak was quite low.

However, upon closer examination of the spectra in Figure 14, a peak for elemental iron is found in the non-contaminated sample which is not present in the contaminated samples. Since the soil originated from the same local, it was expected to possesses similar iron content.

A detailed study of the spectral features of all three contaminated sample reveled an interesting difference between the contaminated and non-contaminated samples.

Figure 16 again shows the presence of elemental iron in the non-contaminated sample, however, it is relatively absent from the contaminated samples.

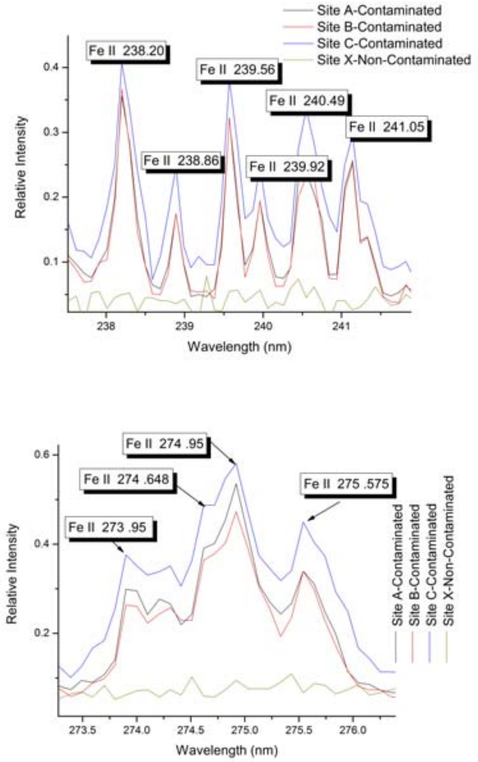


Figure 15. Both graphics above show the presence of ionized iron in all three contaminated samples. In addition, the reference lacks any indication of ionized iron.

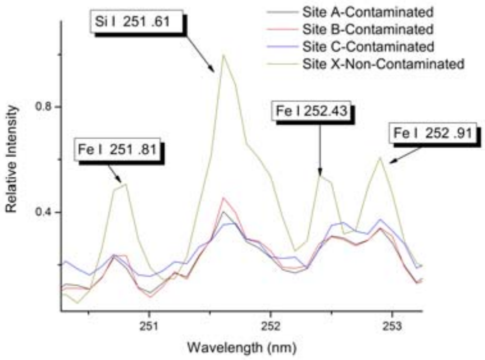
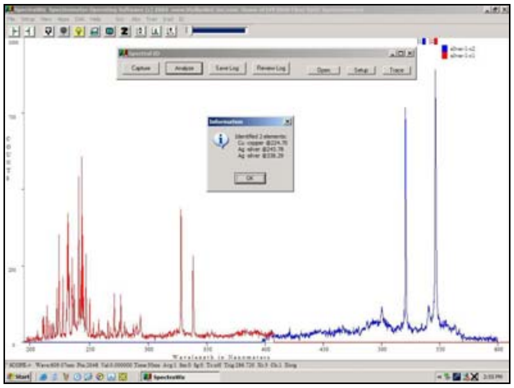


Figure 16. Again, the non-contaminated sample shows the presence of elemental iron while the contaminated samples do not.

An indication as to why the contaminated samples lack elemental iron can be found in Figure 15. All three contaminated samples possess ionized iron. It is suspiciously absent from the non-contaminated samples. Is there a correlation?

While organic decomposition could have oxidized the iron in the contaminated samples, the odor associated with the samples led us to believe that the contaminated samples contain FeS or iron sulphide, which could be a secondary indicator of water contamination due to the fact that sulfer derivatives are a byproduct of wood treatment and manufacture of paper pulp using the chemical sulfite process. Further studies are underway to try to answer the question raised above.

C. SOFTWARE



Identified 2 elements:
Cu copper @224.70
Ag silver @243.78
Ag silver @338.29

Figure 17. ***Computer display of line spectra & element library comparison report.***

We configured a spectral library for 83 different elements into the database of our SpectraWiz® spectrometer operating software package. Search and report algorithms were installed to provide a robust set of analysis tools for application specific projects. The LIBS specific toolkit was named "Spectral ID" and could be started from an icon on the toolbar or from the Applications pull-down menu. During field testing, the software automatically compared and matched unknown line spectra against known spectra found in the library. Matching element data was displayed on a laptop computer screen window and presented in a pop-up window over the emission line spectra of the unknown test sample. Elements with matched line spectra were then listed in order from maximum intensity at the top of the list to minimum intensity at the bottom of the list. This feature provides the user with instant qualitative compositional data with approximate quantitative information for each test fire of the laser. Additional reporting functions allowed data filtering such as base to peak threshold level, optical resolution tolerance, and spectral recognition plurality. The software was also setup to provide simplified spectral capture and post capture spectral analysis with comprehensive graph displays.

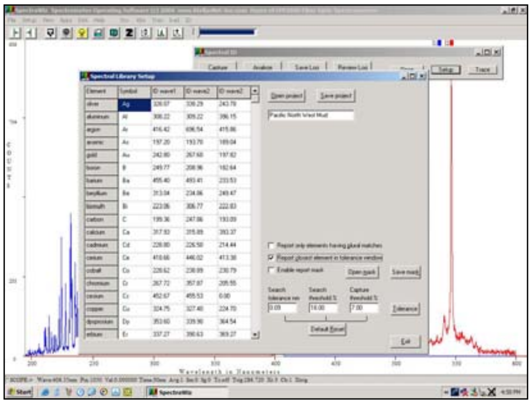


Figure 18. ***Spectral library setup panel showing various reporting and project options.***

For more precise quantitative data calibration projects, sample concentration and line intensity curves can be produced from known standards. In the field, an unknown sample may be mixed with sodium borate and fused into a glass bead. Formation of the bead should negate the host influence of the unknown element and allow for quantitative determination by direct comparison or ratio comparison with the element concentration intensity curves stored in the computer.

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D. PORTABLE EYE-SAFE LIBS SYSTEM

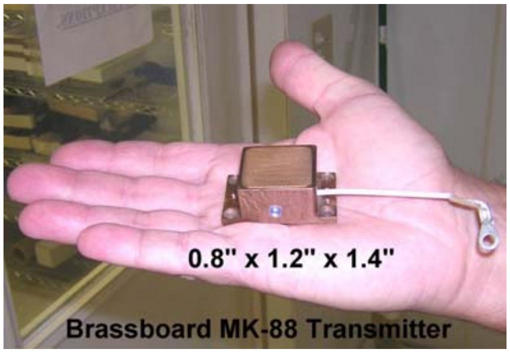

Figure 19. New Diode Pumped Eye-Safe erbium glass 1.54um LIBS laser

High peak power Q-switched lasers operating in the narrow spectral window between 1.5um and 1.6um are approximately 8000 times more "eye-safe" than other laser devices operating in the visible and near infrared[26]. Fore example, a laser operating at 1.54um may emit Q-switched pulses with up to 7.9mj of energy and still be considered a Class I laser (no laser eye protection required). However, a 1.064um Nd:YAG laser that emits energy at the micro-joule level is still considered as a very dangerous Class IV system (eye-protection required). As such, we have been working on the integration of an eye-safe erbium glass laser into a portable LIBS system. Initial trials included air breakdown plasma generation testing of a lamp pumped EMK-50 1.54um laser head (similar to the MK-367 laser head) in a double pulse "pulse train" mode of operation. The EMK-50 laser produced two Q-switched pulses (6mj, 30ns and 15mj, 60ns) with 350us between pulses. Reliable air breakdown plasma was readily produced from the double pulsed (0.5-Megawatt) EMK-50 with a simple optical delivery system. However, the long time period between the two pulses was deemed a problem for efficient LIBS performance. Therefore, we initiated LIBS testing with a newer diode pumped MK-88 erbium glass transmitter that produces 8mj in 7ns (1.1-Megawatts). The MK-88 head is more compact than the MK-367 or EMK-50 and allows for 1-10Hz pulse repetition rate without active cooling (figure11). Further MK-88 LIBS performance test data will be presented in another paper at a future date.

4. CONCLUSION

From the data presented, it is the authors' opinion that the low-cost portable LIBS system discussed throughout the paper is a viable technology for the remote detection of many environmental pollutants. While the instrument was presented as a tool for qualitative measurements, the data given also substantiates the use of this technology as a quantitative device. All that is necessary to move this technology forward with respect to quantitative measurements is the development of application specific standards and some specific software tools, some of which are currently under development by the authors.

The aurthors are with (1) StellarNet, Inc., 14390 Carlson Circle, Tampa, FL 33626, E-mail: wPierce@stellarnet.us and (2) Kigre, Inc., 100 Marshland Road, Hilton Head Island, SC 29926, E-mail: KigreInc@cs.com.

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