

Portable LIBS instrumentation can identify trace levels of environmental pollutants

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The integration of miniature fiber optic spectrometers with small high peak power laser transmitters has led to the development of a low-cost portable analytical instrument capable of real-time qualitative analysis. LIBS (Laser Induced Breakdown Spectroscopy) systems are now assembled with commercial off the shelf 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 1064 nm Nd:YAG laser is focused on a target material with virtually no sample preparation. The pulse power, which is several MegaWatts, generates a plasma with an elemental line spectrum characteristic for the sample. This spectrum is then collected and analyzed for the elements present. The LIBS measurement and data analysis occurs within less than a second using any notebook computer.

1 Experimental Setup

In this article we present environmental analysis performed in field conditions with a low-cost portable LIBS system to determine the presence of hazardous and other elements in various samples. The LIBS system 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 the power of one battery. A schematic in **figure 1** showing the simplic-

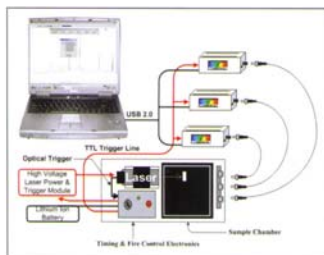


Figure 1: LIBS instrument schematic: via an electronics module, the laser triggers multiple fiber optical spectrometers for a synchronized multi-channel measurement of the laser induced plasma generated within the sample chamber

ity of the instrument, a photograph can be seen in **figure 2**. The entire setup fits into a briefcase that measures 18 x 33 x 46 cm³ and weighs less than 14.5 kg.

The instrument utilized a compact, low-cost, permanently aligned MK-367 Nd:YAG laser from Kigre, Inc., with a passive Q switch and 6 MW peak power per 4 ns pulse (25 mJ) at 1 Hz pulse repetition rate. The beam diameter was 3 mm with a beam divergence of 1 milliradian full angle. Polarization was greater than 99.7%. The LIBS system utilized for this study [1] consisted of two standard resolution EPP2000 LSR spectrometers, each fitted with a 2048 element non intensified CCD detector. The dual channel systems spectral bandwidth was 200-600 nm, and the optical resolution per pixel was 0.19 nm. Each spectrometer was configured with a 14 μ m 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 its versatility, for it can be configured with up to seven high-resolution spectrometers, to give a spectral bandwidth of 200-925 nm with a spectral resolution of 0.1 nm. The only disadvantage to seven 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.

2 Spectral acquisition and identification

Fiber optics were utilized to image the emission line spectra of the plasma onto spectrometer entrance slits. Three optical paths were available and each path was capable of feeding the full optical emission to one individual spectrometer, respectively. In this example, only two spectrometers were utilized, and each spectrometer (i.e. each channel) captured its spectral range simultaneously, post trigger. **Figure 3** shows the spectral emissions from three different standard samples using the dual channel configuration.

Channel 1 covered 200-400 nm and channel 2 covered 400-600 nm. While all of the sample spectra were taken with this dual channel configuration, in most cases, we will here only present data from 200-400 nm because this simplifies the technical discussion and this region possesses more spectral features compared to the visible region of the spectrum.

The SpectraWiz software used provides

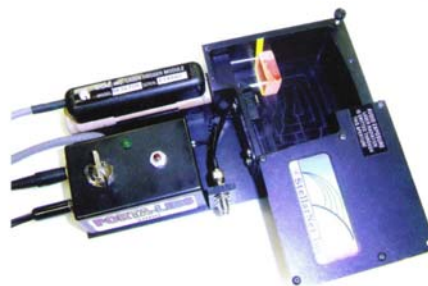


Figure 2: PORTA-LIBS 2000 system photo: sampling chamber, laser, and timing circuit

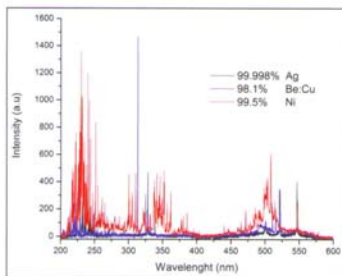


Figure 3: Standard elements: LIBS single shot spectra in dual channel configuration (200-400 nm and 400-600 nm)

simple elemental identification by means of its database search and report features. Several standards were measured and verified using the "Spectral-ID" application including Pb (lead), Be (Beryllium), As (Arsenic), Zn (Zinc), Cd (Cadmium), and Ag (Silver).

3 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 measurement data against ICP standards (Institute of Catalysis and Petrochemistry, which provides XPS (X-ray Photoelectron Spectroscopy) data as well as reported LIBS emission lines found in various technical publications [2,3,4,5,6], that Nickel's emission spectra was very reproducible. An important aspect of the instrument is its ability to reliably identify the same material (i.e. standard), each time the material is loaded into the sample chamber. The results depicted in **figure 4** are showing it clearly: The peak-to-peak variance for twelve spectra across the spectral

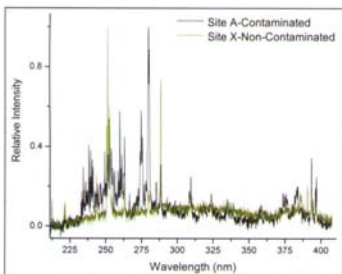
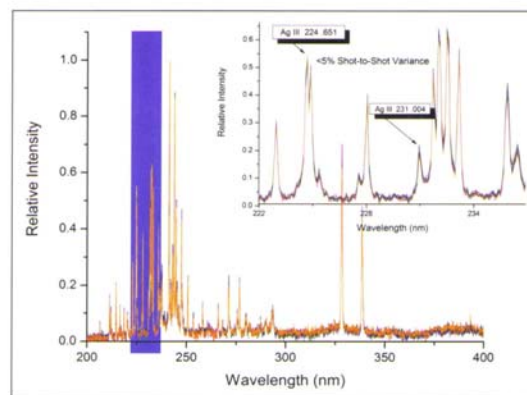


Figure 5: Contaminated & non-contaminated lake mud spectra (details see text and Figures 6-8)

Figure 4: 12 LIBS single shot spectra of Ag standard 99.998%, taken at different locations. The insert (top right) zooms into the region marked blue in the main spectrum



region examined was less than 5%. This is extremely important due to the fact that many samples must be repositioned between subsequent laser shots since 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. Thus the importance for accurate single shots results.

4 Sample measurement

Presented in **figure 5** is LIBS data of samples taken from a contaminated lake bottom. 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 the LIBS spectra, peaks for elemental iron are found in the non-contaminated sample which is not present in the contaminated samples. Since the soil (both contaminated and non-contaminated) originated from

the same location, it was expected to possess similar iron content.

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

Figure 6 shows that all three contaminated samples possess ionized iron which is absent in the non-contaminated samples. Is there a pollutant 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 sulfite, which could be a secondary indicator of water contamination due to the fact that sulfur derivatives are a byproduct of wood treatment and manufacture of paper pulp using the chemical sulfite process.

5 Results and discussion

The same mud samples were sent to an independent lab for analysis using an XRF instrument (**table 1**). The XRF machine cost over \$250,000 and required 3000 watts of power, was very large (750 kg

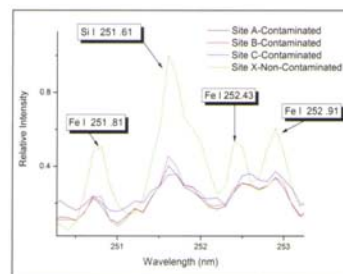
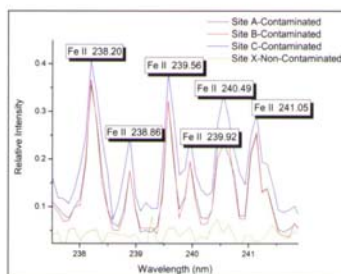


Figure 6: Contaminated mud spectra with ionized iron. Slightly above 250 nm (spectral diagram on right hand side), the non-contaminated sample shows the presence of elemental iron while the contaminated samples do not

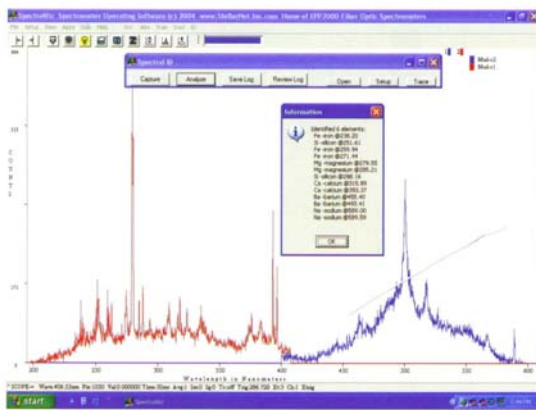


Figure 7: SpectraWiz software Spectral-ID report with two channels combined: 200-400 nm (red) and 400-600 nm (blue)

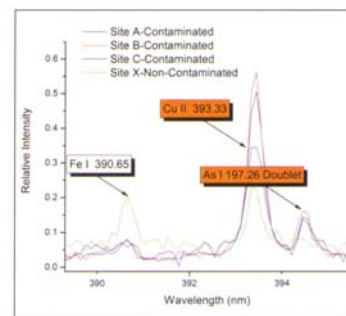


Figure 8: Detail from contaminated mud spectra with Cu and As. Note that the peak at 394.52 nm is a doublet resulting from a second diffraction order of As at 197.26 nm (which is below the 200-400 nm channel)

- not portable), and required sample preparation (dried for 72 hours and ground to a 400 µm mesh).

Figure 7 is a screen shot from the SpectraWiz Spectral-ID software showing the elemental detection report for the contaminated samples. It lists several Iron II peaks, Si, Ca, Na and also includes Mg and Ba not reported by the XRF.

Upon visual examination of the LIBS spectra (**figure 8**), two peaks are identified in the contaminated samples that are indicative of wood treatment processing, specifically, copper (Cu) and arsenic (As). The copper levels are 2 to 3 times higher than found in the non-contaminated sample and the relative amplitude of the arsenic peaks are quite low. Arsenic was also not detected by the XRF analysis.

6 Conclusion and outlook

From the data presented, we have shown that a low-cost portable LIBS system 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 specific software tools, some of which are currently under development by the authors.

References:

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Chemical Substances Found		Relative Concentration [%]
Quartz	SiO ₂	19.7
Labradorite	(NaCa)(AlSi ₃)O ₈	64.7
Zinc-Hydroxide	Zn(OH) ₂	6.6
Pyrite	FeS ₂	0.6
Magnetite	Fe ₃ O ₄	4.2
Cronstedite	Fe ₃ (FeSi)O ₄	4.3
		100

Table 1: Semi-quantitative XRF results (X-Ray Fluorescence Spectroscopy) from contaminated mud samples, with ±3% accuracy. The non-contaminated samples did not contain Pyrite or Cronstedite