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Fiber Optic/Cone Penetrometer System for Subsurface Heavy Metals Detection

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**Fiber Optic / Cone Penetrometer System for
Subsurface Heavy Metals Detection**

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Introduction

Contamination of the soil by heavy metals, such as lead (Pb), chromium (Cr), copper (Cu), zinc (Zn) and cadmium (Cd), is an area of great concern for government and industry. The characterization, monitoring and remediation of these soils is extremely expensive and time consuming due to the magnitude of the effort and the utilization of laboratory chemical analysis techniques. The present laboratory methods of evaluating environmental samples offer high sensitivity and the ability to evaluate multiple chemicals, but the time and cost associated with such methods often limit their effectiveness. Table 1 shows a summary of the metals problem in National Priority (Superfund) Sites. Forty-one per cent of the sites report metals problems, with Pb and Cr being most often cited.

Table 1. Summary of metals contamination in Super Fund sites for (a) different industries and (b) the number of sites reporting specific metal contamination¹

(a)			(b)	
# of Sites	Industry	Metals most often reported	Metal	# of sites
154	landfill/chemical waste dump	As Pb Cr Cd Ba Zn Mn Ni	Pb	133
43	metal finishing/plating/elect.	Cr Pb Ni Zn Cu Cd Fe As	Cr	118
35	chemical/pharmaceutical	Pb Cr Cd Hg As Cu	As	77
28	mining/ore proc./smelting	Pb As Cr Cd Cu Zn Fe Ag	Cd	65
21	federal (DOD, DOE)	Pb Cd Cr Ni Zn Hg As	Cu	49
19	battery recycle	Pb Cd Ni Cu Zn	Zn	40
18	wood treating	Cr Cu As	Hg	32
16	oil and solvent recycle	Pb Zn Cr As	Ni	24
13	nuclear processing/equip.	Ra Th U	Ba	10
3	paint	Pb Cr Cd Hg	Ag	10
29	other	As Pb Hg Cr		

Objectives

The objective of this project is to develop an integrated fiber optic sensor/cone penetrometer system to analyze the heavy metals content of the subsurface. This site characterization tool will use an optical fiber sensor to perform in-situ chemical analysis. The primary objectives for this project are:

- establish that the fiber optic technique can be used to detect heavy metals to the required concentration levels.
- design a fiber optic probe for integration with the penetrometer system for the analysis of heavy metals in soil samples
- design, fabricate, and test an integrated fiber/penetrometer system
- fabricate a rugged, field deployable laser source and detection hardware system
- demonstrate the prototype in field deployments

Approach

Laser-induced breakdown spectroscopy (LIBS) has been recognized as a technique which is very amenable to field applications. Recent advances in critical hardware components, primarily compact lasers, detectors and spectrometers, has made the LIBS technique even more attractive for industrial and environmental analysis, especially soils.^{2,3}

A basic LIBS system is shown in Figure 1. The configuration typically consists of a laser source to produce the plasma, a method of delivering the laser beam to the sample (i.e. optical fibers, free space optics), emission collection optics, a spectrometer to spectrally resolve the emission spectrum, an array detector for simultaneous measurements of emission intensities over a range of wavelengths, a trigger to coordinate the laser pulse and the temporal measurement window of the detector, and a computer to conduct equipment control, data acquisition, and data analysis.

An emission spectrum is obtained by focusing the high power laser on the sample surface. The surface will absorb the laser pulse, heat rapidly, reduce to elemental form, and become electronically excited. When the input pulse is removed, the excited electrons drop to lower energy levels with the emission of characteristic photons. The light emission from the sample will consist of continuum radiation due to Bremsstrahlung effects, single, neutral and multiple ionized atoms, and the emission from the various components will occur at different times after the spark has been initiated. Elemental analysis is conducted by

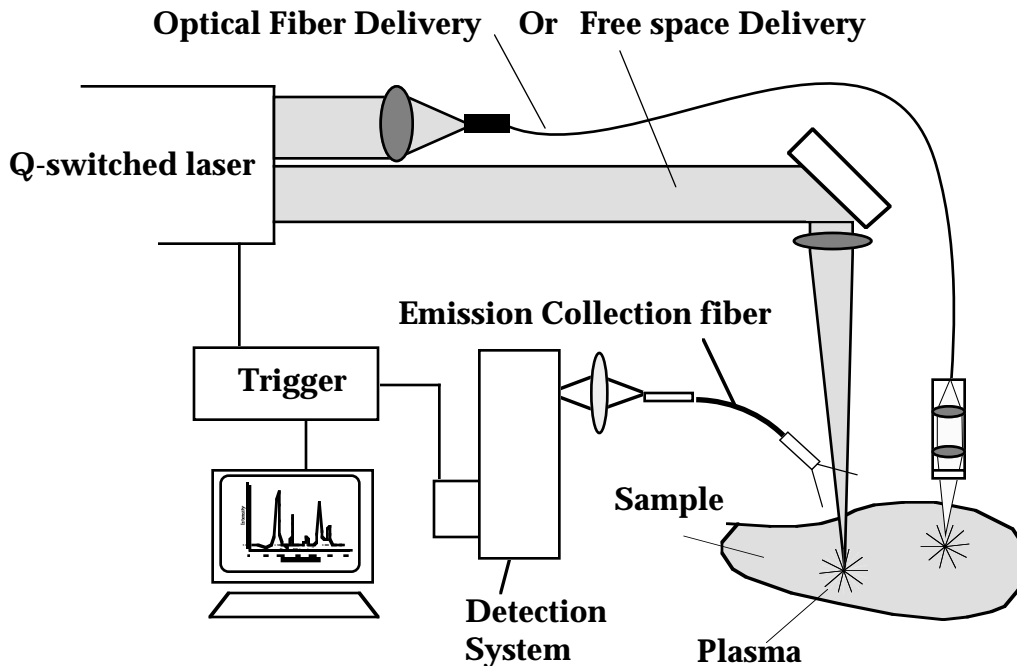


Figure 1. A typical laser induced breakdown spectroscopic (LIBS) system with either free space delivery or fiber optic delivery of the laser pulse.

observation of the wavelength, intensity, and temporal characteristics of the emission lines.

The subsurface analysis for this effort will be conducted by the use of a cone penetrometer truck to deploy the optical fiber portion of the LIBS system shown in Figure 1. The laser pulse will be delivered to the soil and the emission will be received via an optical fiber probe situated within a cone penetrometer rod. Subsurface mapping will occur by pushing the rod vertically in the subsurface and by moving the penetration truck horizontally along the surface. A key portion of this effort will be to develop a probe small enough to fit within the penetrometer (i.d. <math><1.25''</math>) that can deliver a high quality Q-switched laser pulse to produce an adequate plasma.

Project Description

This program included an initial Phase I feasibility evaluation and an optional prototype development. The initial Phase I effort was successfully completed with the demonstration of quantitative analysis of Cr and Pb in various types of soils via an optical fiber probe. The Optional Phase of this project includes the design and fabrication of a field deployable system that integrates the optical source and detection equipment, optical fiber probes, and cone penetrometer. In addition, the Option phase includes a field demonstration of the system at a Superfund/government site TBD. The Optional Prototype Development effort was

started in mid-May 1996 and is scheduled for 18 months. To date, the design of the overall LIBS system has been completed, components that are commercially available have been procured and specialty items are presently being fabricated and evaluated.

Results

For the Phase I feasibility evaluation, the LIBS system consisted of a Spectra Physics Nd:YAG laser with variable pulse energies up to 300 mJ operating at 10 Hz, a 1/2 meter Spex spectrometer with a Princeton Instruments (PI) 1024 element photodiode array, a PI pulse generator to control the gating of the detector, and an IBM compatible PC operating the PI detector array controller and data acquisition software. The set-up also had the optics required to deliver the laser energy to the soil sample via free space optics or optical fibers. The spectrometer was equipped with a dedicated optical fiber input to receive the emission spectra. The arrangement was identical to that shown in Figure 1.

Standard Soil Samples There were two types of soil samples used for this effort. The first type was purchased from the National Institute of Standards & Technology (NIST). NIST has a series of soils that have been certified by EPA methods for a number of heavy metals. Standards #2709 San Joaquin soil, #2710 Montana Soil I, #2711 Montana Soil II, #2704 Buffalo River Sediment, and #1646a Estuarine Sediment were used. These soils were used as supplied by NIST.

The second type of soil was fabricated by mixing standard EPA heavy metal solutions with native Los Alamos National Lab (LANL) soils. The soil was processed by mixing 10 grams soil (with a particle size < #25 sieve) with different amounts of a standard solution containing known concentrations of heavy metals. The solvents were then dried off in an oven. Typical heavy metal concentrations for these samples ranged from several ppm to 1000 ppm.

For LIBS analysis, the soils are pressed into small sampling containers at a press weight of 20 tons, the compacted soils are very uniform and are representative of the compacted soil that will be encountered in this application.

Typical LIBS data analysis The most common method for utilizing LIBS for quantitative analysis is to calibrate the spectral intensities of the LIBS spectra using standard samples with known concentrations of the element of interest. It is often advantageous to use the ratio of several peaks from the sample, one from the element of interest and another from a prominent component in the sample. Using the ratio of peaks helps alleviate any inconsistencies from changes in the sampling conditions. For example, laser energy density variations may cause the sampling volume to vary slightly from laser shot to laser shot, thus the absolute intensity of a specific peak may not be constant for a given concentration of contaminant. The ratio of two peaks, however, will not be as sensitive to these slight variations in sampling volume because the intensities of the emissions from the two materials

will both behave similarly. Figure 2(a) depicts a typical LIBS spectrum for a 1000 ppm Pb-spiked soil sample. This spectrum is an accumulation of 100 sparks on the sample and each spark was obtained from a fresh portion of the sample. Figure 2(b) shows the reduction in the Pb peak as the concentration of Pb is decreased.

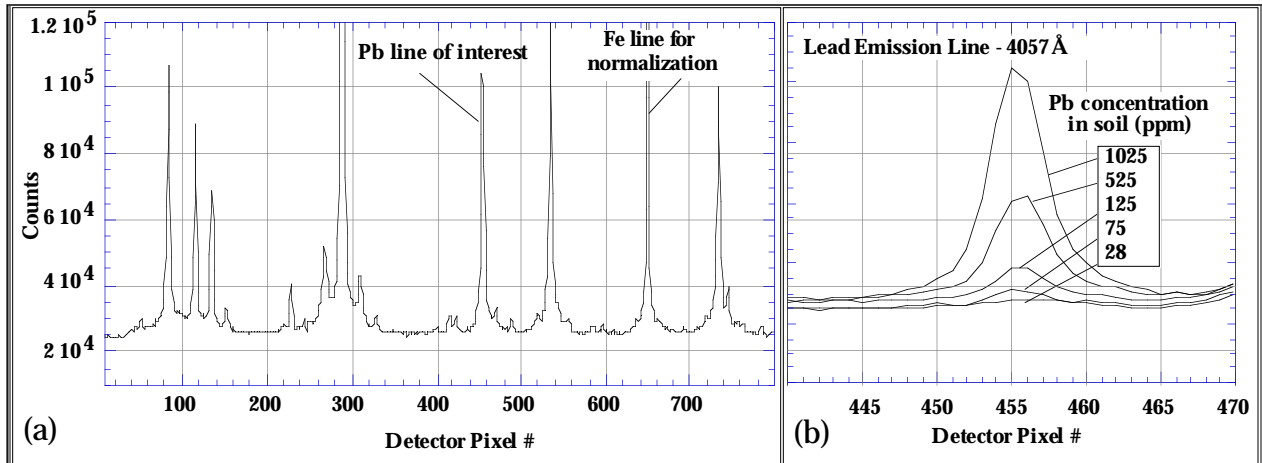


Figure 2. (a) A typical LIBS spectrum for a 1000 ppm Pb-spiked soil sample. (b) The intensity of the Pb peak is reduced as the Pb is decreased.

Calibration curves for conducting quantitative analysis are constructed by plotting the ratio of the analyte of interest peak and the standard element vs. the concentration of the heavy metal in the soil. For the calibration curves, each data point is the average of 10 individual spectrum, therefore a total of 1000 sparks were used for each data point. Figure 3 shows the calibration curve for the Pb-spiked sample used using the Fe line as an internal standard.

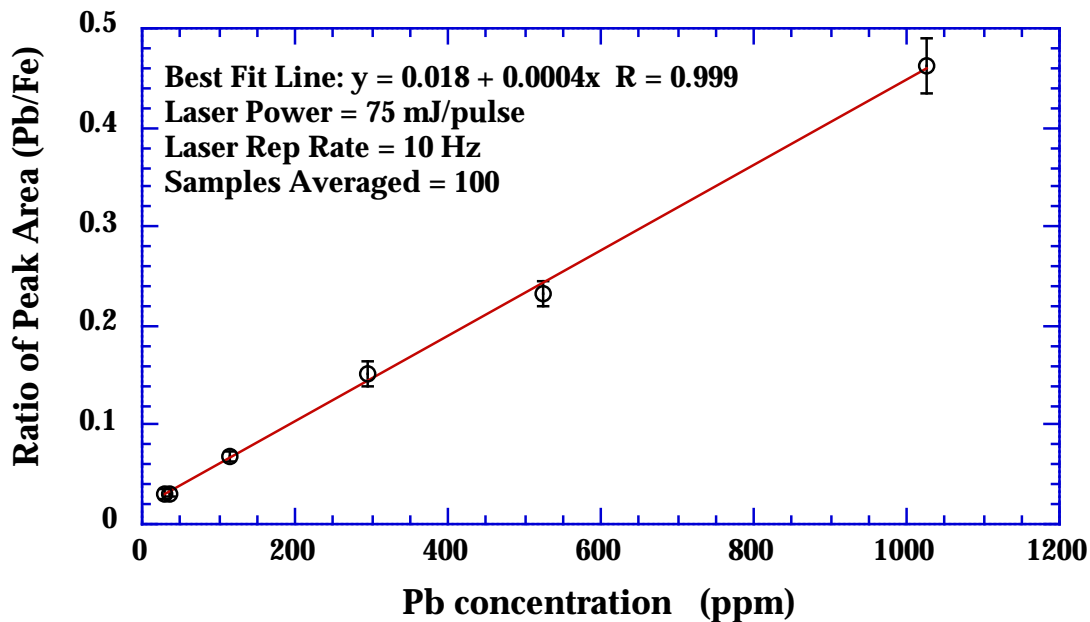


Figure 3. Calibration curve for Pb in soil using free space delivery of the laser

The minimum detectable limit (MDL) for LIBS on a specific set of standard soils, is determined from the calibration curve. The MDL is calculated by: $(3s) / S$ where s is the standard deviation of the lowest concentration data point and S is the slope of the calibration curve at the low concentration range. For the data shown in Figure 3, the minimum detectable limit was 20 ppm. The MDL is used here to compare testing under similar conditions, and is not the ultimate detection limit for the technique. MDL's will depend on the soils being analyzed, the element being evaluated and the experimental conditions.

Multi-element analysis One of the advantages of the LIBS technique is the ability to evaluate the samples for a number of elements simultaneously. Figure 4(a) through 4(c) show spectra determined for a NIST sample from a Montana Superfund Site with high heavy metals contamination. Using a LIBS system with a free space delivery of the laser, Figure 4(a) shows the spectral region for Pb, Figure 4(b) for Cr, and Figure 4(c) for Cu, Zn, and Ag. The spectral window from 402 nm to 410 nm, for example, contains peaks for Mn, Fe, and Sr in addition to Pb. These peaks can be used to evaluate the concentrations of those elements or they can be used to help evaluate the Pb peak. The NIST traceable concentration values are indicated on each spectra.

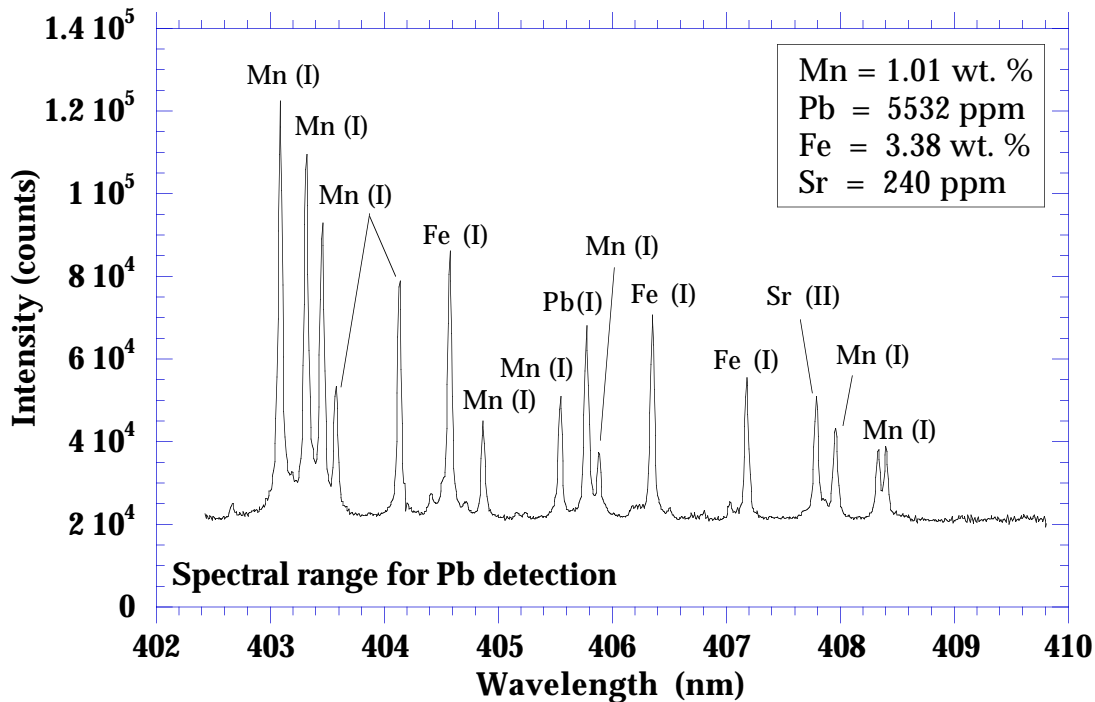


Figure 4(a). LIBS spectrum of a NIST Superfund soil in the Pb spectral range

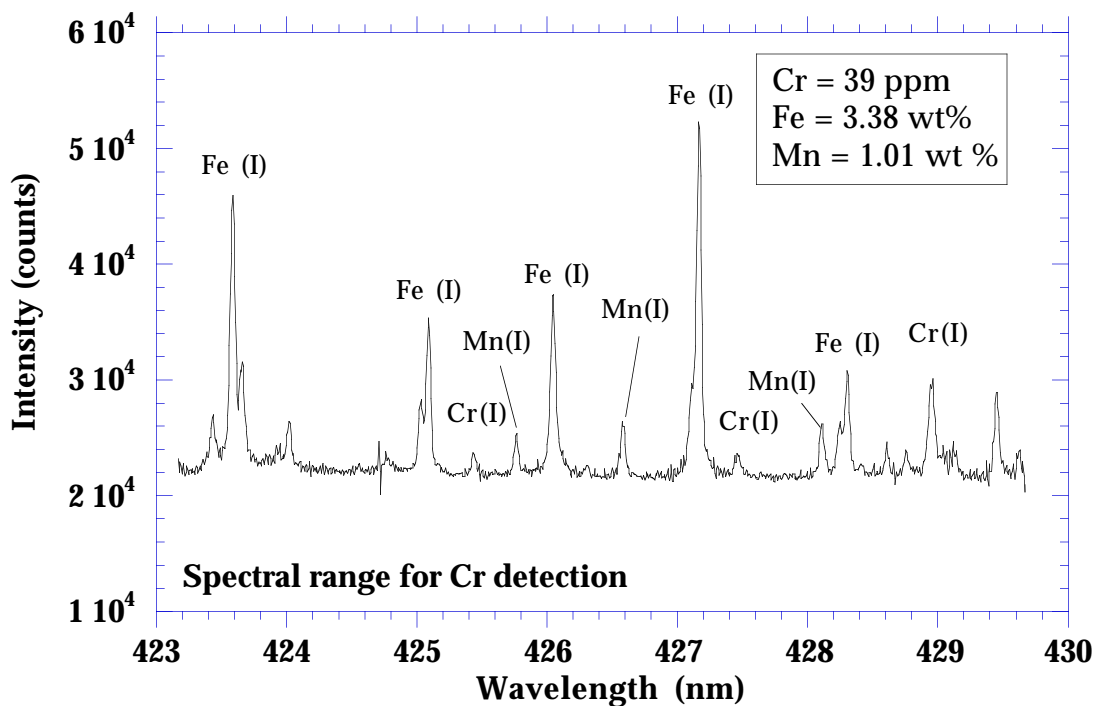


Figure 4(b). LIBS spectrum of a NIST Superfund soil in the Cr spectral range

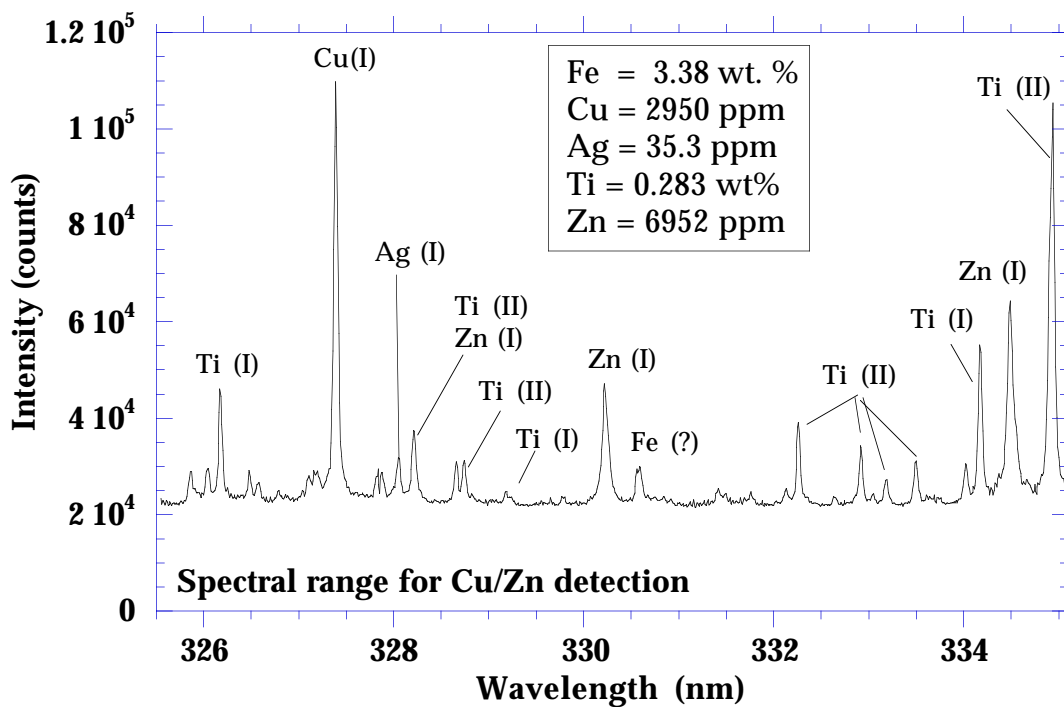


Figure 4(c). LIBS spectrum of a NIST Superfund soil in the Cu/Zn spectral range

Effect of Sample Matrix When evaluating the heavy metal concentration at a single contaminated site, it may be valid to assume that the matrix of the soil will be relatively constant within a small geographic area. The LIBS results for Pb-spiked soil that would model this situation were shown in Figure 3. The Pb peak was altered as the Pb-concentration was reduced, and the calibration curve was very linear. In reality, however, the soil will not always have the same composition with a simple alteration of a single elements concentration. To investigate the more realistic scenario, NIST standard samples, shown in Figure 4a-c, from different portions of the country were used to formulate a calibration curve.

Using these standard samples, the calibration curve shown in Figure 5 was constructed for Pb. It is seen that the calibration is not linear over the range tested, but it can be fitted nicely with a 2nd order relation. Using these data, the minimum detectable limit for the NIST analysis was 50 ppm. The different soil matrices did have a slight effect on the performance of the LIBS system, but the performance was still very good. These results show that the present methods of data analysis (i.e. ratio of two peaks) may require the use of multiple calibration curves depending upon the soil matrix.

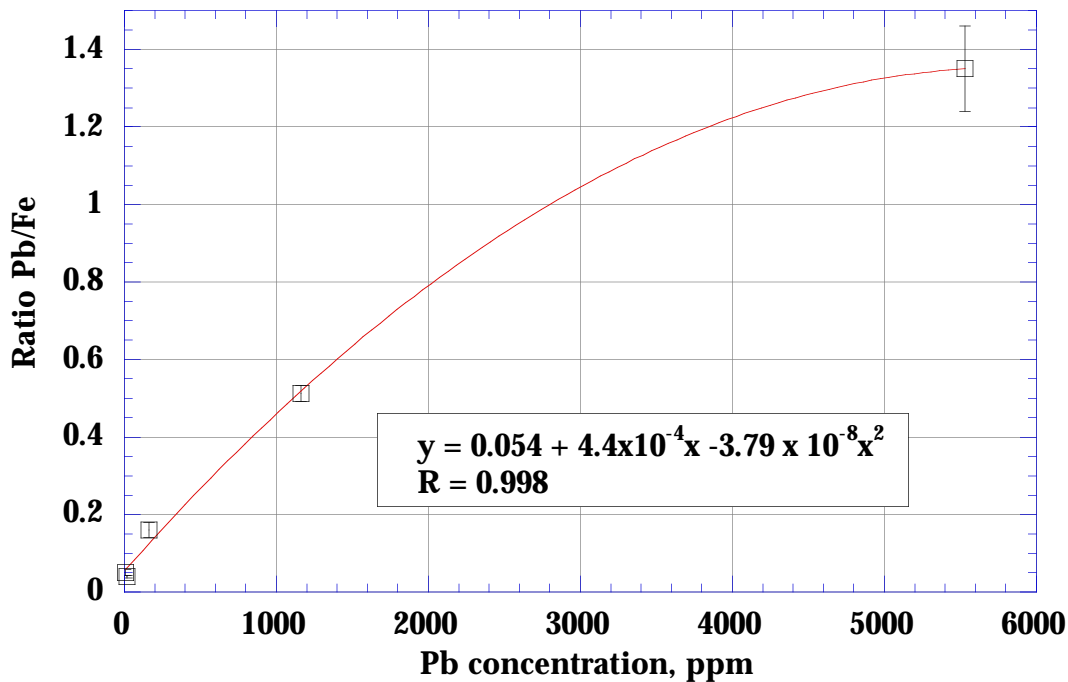


Figure 5. Calibration curve for the NIST standards for Pb using 150 mJ/pulses.

Effect of emission wavelength and laser energy level For the analysis of soils with Pb- contamination, the selection of the emission wavelength was relatively simple since the Pb peak at 405.78 nm is rather intense. For Cr, on the other hand, there are three peaks available. We looked at the changes of each with concentration

to determine which would be best for quantitative analysis. Figure 6 shows the emission spectra for a 1000 ppm Cr-contaminated sample, with the three Cr lines labeled.

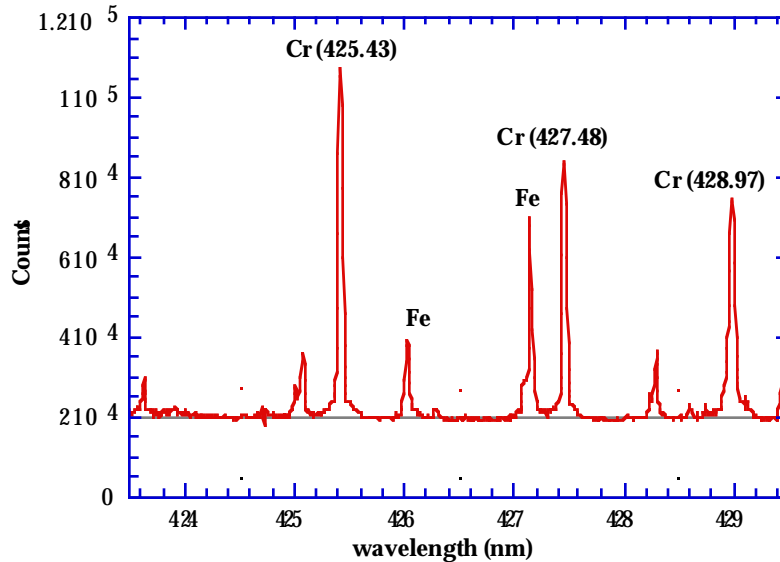


Figure 6. The emission spectra of a 1000 ppm Cr-contaminated soil sample

Using the spiked samples with varying Cr concentrations, calibration curves were constructed for a variety of wavelengths and laser powers. Figure 7 depicts the calibration curves for each of the Cr peaks calculated using an Fe reference peak for 150 mJ pulses. Since the minimum detectable Cr concentration will be dependent upon the slope of this plot, the highest slope should offer the highest sensitivity.

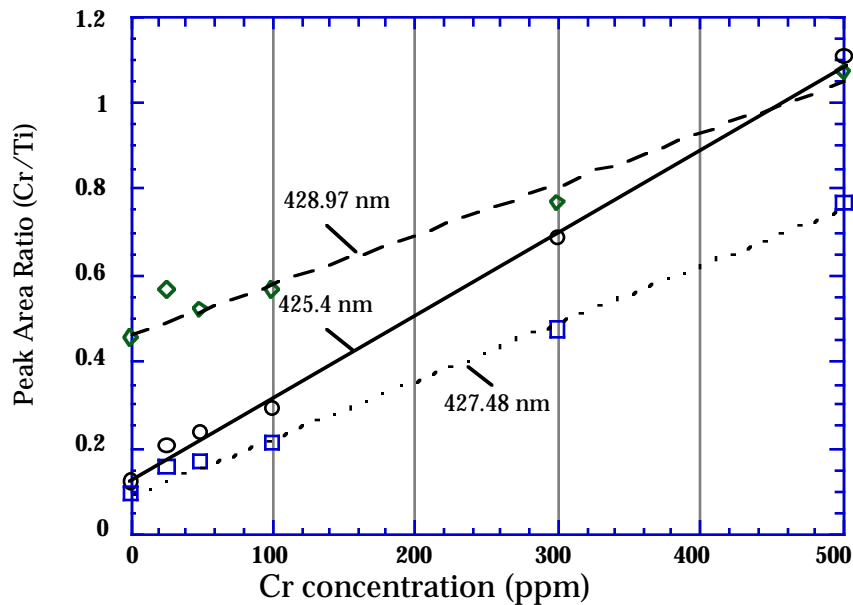


Figure 7. Calibration curve for different Cr spectral emissions

From this plot it is seen that the 425.43 nm emission line of Cr has the highest slope, followed by the 427.48 nm line. Table 2 summarizes the analysis of each individual line with additional data on different laser power levels. These data show that analysis using the 425.43 nm and 427.48 nm lines produce essentially the same minimum detection limits of 50-60 ppm for the spiked soils samples, and the 428.97 nm line could not be used for low concentration analysis. The EPA Soil Screening Level (SSL) for Cr is 390 ppm for ingestion and 140 ppm for inhalation, which is easily detectable by a LIBS system, and the Pb SSL = 400 ppm. ⁴

Table 2 Minimum Detectable Limits for Cr in spiked soils

Wavelength (nm)	Detection Limit (ppm)
425.43	50-60
427.48	50-60
428.97	350-400

Soils analysis using a fiber optic probe One of the concerns of a fiber optic LIBS sensor is that the fiber will fail under the high peak power Q-switched laser. The amount of power which can be transmitted by an optical fiber is ultimately limited by the surface laser damage threshold of the glass. The damage threshold for a silica glass surface using the type of laser required for LIBS is $\approx 5\text{GW}/\text{cm}^2$. ⁵ At this damage threshold level, a 10ns laser focused to a 1000 μm spot on a glass surface will fail at $\approx 400\text{ mJ}/\text{pulse}$. The surface of the glass will fail before the bulk due to light scattering by surface roughness, dust or stresses caused by surface treatment.

For optical fibers, however, our experience is that the damage threshold of an optical fiber waveguide in a rugged connector is about $1.5\text{ GW}/\text{cm}^2$ for consistent, damage free operation. For real applications we would like to keep the pulse energy below this maximum, thus a 1000 μm fiber should be used around $\approx 80\text{ mJ}$.

In general, we have seen that the overall intensity of the LIBS spectral peaks are lower for the fiber obtained spectra in comparison to the peaks obtained using free space delivery. Figure 8 shows a comparison of the spectra obtained on a NIST sample in the Cr spectral region using a 1500 μm optical fiber delivering approximately 55 mJ pulses to the sample in comparison to free space delivery. As shown in Figure 1, the optical fiber probe consisted of two identical 1/2 inch, 50 mm focal length lenses to collimate the laser out of the fiber and refocus onto the soil. It is seen that all of the peaks detected with the free space delivery are detected with the probe, but the overall peaks are not as intense. Part of the difference in the intensity between the two curves is due to the fact that the free space delivery curve was obtained using 75 mJ pulses, but the bulk of the difference is due to the fact that the spot size on the soil from the optical fiber probe is larger than that produced by the free space optics. Thus, the energy density, and therefore, the spark intensity is lower for the fiber case.

The overall intensity of the spectra is not the deciding factor on performance, however, since the area of the emission peak of interest is referenced to that of another element (i.e. Fe, Ti) for quantitative analysis. Figure 9 shows a comparison of calibration curves for lead in soil determined using free space optics and the optical fiber probe at very similar laser power levels. The slope of the curves are nearly identical, and when the minimum detectable limits are calculated, the free space system had a 50 ppm minimum detectable limit and the fiber had a 50-60 ppm limit. This performance is very good for the fiber, since it is still well below the EPA SSL.

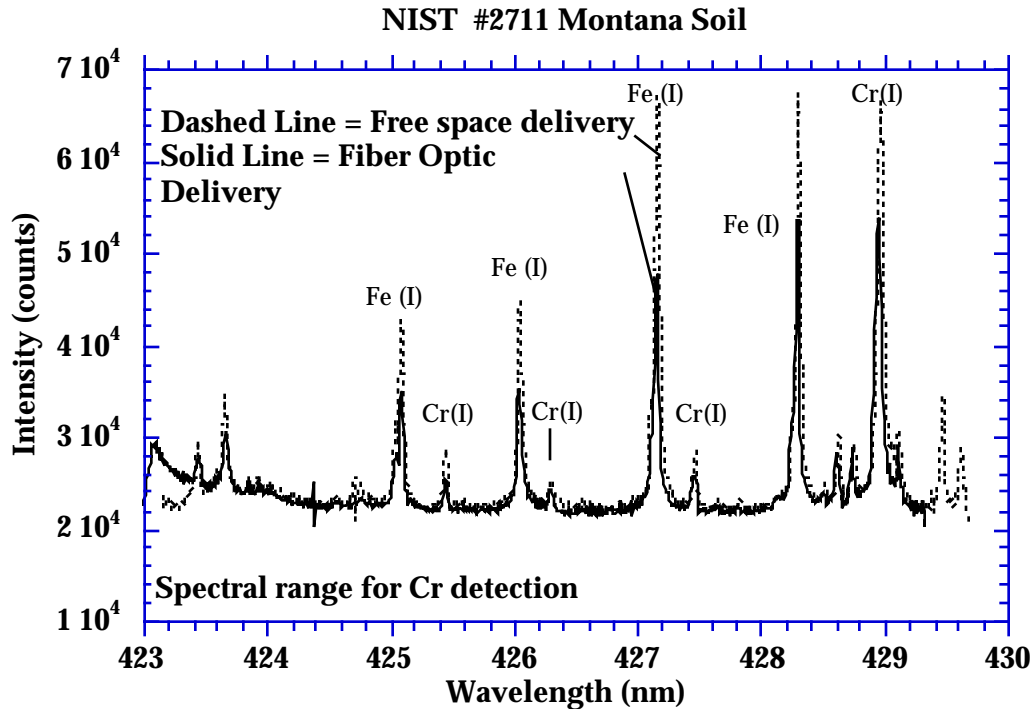


Figure 8. Comparison of the LIBS spectra of NIST #2711 in the Cr spectral region with free space laser delivery and with optical fiber delivery.

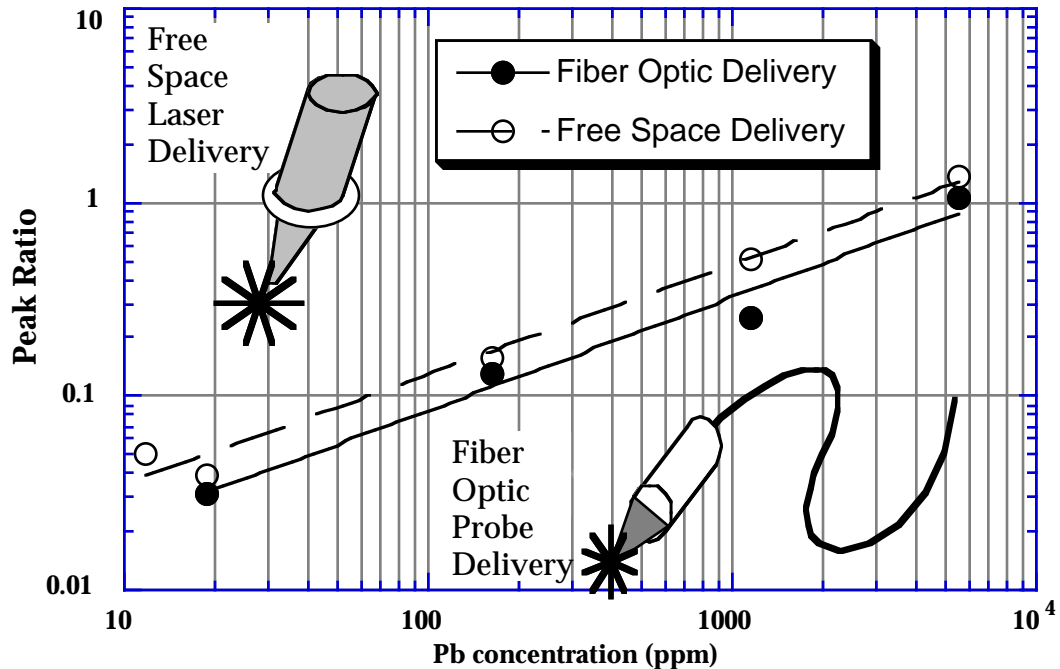


Figure 9. Calibration curve comparison for a fiber optic delivery and a free space delivery of the laser for Pb-analysis

Benefits

The benefits of this system are:

- In-situ evaluation will limit the personnel exposure and public exposure during transportation of samples, and sites will be characterized faster, therefore, remediation can occur sooner.
- The system will provide a more detailed, higher resolution analysis of the site.
- The system will reduce the need for expensive laboratory techniques.
- Since the system is real time, decisions on the remediation can be made faster with more intelligence. The system could be used to monitor the remediation process in-situ, thus enabling this process to be modified for optimum performance.
- The LIBS technique has a broad range of applicability and the addition of optical fibers makes remote applications and industrial applications feasible.

Future Work

The development of this prototype system is on-going. The encouraging results presented above show that a LIBS fiber optic system can be used to quantitatively detect heavy metal soil contamination. At the present time, work is being conducted on the development of a truck mounted system, including the optical fiber probe that will be housed within the penetrometer rod. The prototype system is planned for completion by April 1997, with the field deployments beginning in the Summer.

Acknowledgments

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