A FIBER OPTIC/CONE PENETROMETER SYSTEM FOR SUBSURFACE HEAVY METAL DETECTION

FINAL REPORT

WRITTEN BY:

STEVEN SAGGESE, PH.D.

SUBMITTED:

AUGUST 30, 1999

DOE AWARD # DE-AR21-95MC32089--01

SUBMITTING ORGANIZATION:

SCIENCE & ENGINEERING ASSOCIATES, INC.
6100 UPTOWN BOULEVARD, NE
ALBUQUERQUE, NM 87110

CONTRIBUTING ORGANIZATIONS:

APPLIED RESEARCH ASSOCIATES, INC.
RR 1 Box 120A
SOUTH ROYALTON, VT 05068

ENERGY & ENVIRONMENTAL RESEARCH CENTER
UNIVERSITY OF NORTH DAKOTA
P.O. Box 9018
GRAND FORKS, ND 58202

LOS ALAMOS NATIONAL LABORATORY
CHEMICAL SCIENCE AND TECHNOLOGY DIVISION
LOS ALAMOS, NM 87545

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of the authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ABSTRACT

Science and Engineering Associates (SEA) developed a prototype subsurface soil characterization tool for the evaluation of heavy metals. The system, based on Laser-Induced Breakdown Spectroscopy (LIBS), is deployed using a cone penetrometer. The LIBS system consists of a laser source to produce the plasma, a novel hollow waveguide method of delivering the laser source to the subsurface, a small penetrometer probe for focusing the laser light to create a spark and return the light emission for analysis, a spectrometer to spectrally resolve the emission spectrum, an array detector for simultaneous measurements of emission intensities over a range of wavelengths and a computer to conduct equipment control, data acquisition, and data analysis. Under this two phase effort, the system was designed, fabricated and tested, culminating in a successful field demonstration at the DOE Sandia Chemical Waste Landfill for the evaluation of chromium contamination. During this CPT/LIBS test, six penetrations were conducted and the data obtained with the system was used to generate graphs depicting the concentration of chromium as a function of depth to approximately 15 feet, with a range of concentrations from background (≈ 30 ppm) to about 1200 ppm. In addition, prototype LIBS instruments, developed by DOE LANL personnel, were successfully field deployed by SEA at a Formerly Utilized Remedial Action Plan (FUSRAP) site for the detection of beryllium. This 6 week field effort generated a high density surface contour plot of the beryllium concentration over a 40 acre site. Utilizing both van-mounted and backpack systems, SEA evaluated 1664 samples at the site. This was the first full scale field deployment of the portable LIBS instruments and the beryllium concentration data was used successfully for real-time decision-making during the site characterization and for the development of additional plans for subsurface analysis.

ACKNOWLEDGMENTS

This effort was funded under the Industry Program through the Federal Energy Technology Center (FETC) under contract # DE-AR21-95MC32089. SEA would like to thank the technical contacts at FETC, Karen Cohen and Karl-Heinz Frohne, for their support. SEA would also like to thank the subcontractor organizations on the design, fabrication and deployment of the LIBS/CPT system. This support was provided by Applied Research Associates (ARA) and Los Alamos National Labs (LANL), specifically Wes Bratton, Wayne Russel, Bryon Fisk, and Shaun Ricker of ARA and David Cremers and Monty Ferris at LANL. SEA is also grateful to the Energy & Environmental Research Center (EERC) which operated under a DOE Cooperative Agreement, specifically Ames Grisanti and Charlene Crocker. SEA would also like to thank personnel at the Hanford Site for their assistance in obtaining site access approval, specifically John April of Bechtel, Chuck Hedel of CH2MHILL and Larry Bagaasen of Battelle and similarly at the Sandia Site for providing on-site support during the field test, specifically Jim Phelan and Kim Ford. Finally, the PI would like to thank the SEA personnel involved in this effort, specifically Tom Kendrick and Nora Tocci, for their hard work.

EXECUTIVE SUMMARY

This research and development effort (DOE contract #DE-AR21-95MC32089) conducted by Science and Engineering Associates (SEA) and subcontractors Applied Research Associates (ARA) and Los Alamos National Laboratory (LANL), was focused on the development of sensors for the characterization of heavy metal contamination in soils, both surface and subsurface. This is a well established problem associated with a wide variety of commercial and government sites, including those managed by the DOE, DOD and Superfund program. Numerous types of heavy metals have been reported, with chromium and lead being reported most often.

There were two major efforts under this program. The primary effort was to develop a laser-induced breakdown spectroscopy (LIBS) system integrated with a cone penetrometer test (CPT) system for the subsurface mapping of heavy metal contamination in the vadose zone. Using the CPT for environmental site characterization represents a relatively recent application of the technology, and the DOE uses CPT because it can be more cost-effective than drilling, reduces secondary waste generation, may reduce risk exposure to contaminants, and it is an excellent platform for making continuous subsurface measurements. The goal was to develop a functional system and deploy it at a DOE site with heavy metal contamination. The secondary portion of this effort was to deploy two prototype LIBS field units to evaluate the top surface beryllium concentration at a Formerly Utilized Site Remedial Action Plan (FUSRAP) site in Luckey, Ohio. The goal was to integrate the LIBS sensors into the ongoing site characterization and provide real-time and near real-time data to support the daily and future characterization/remediation activities. A detailed discussion of the LIBS/CPT development is provided in the main body of this Draft Final Report, whereas information on the FUSRAP effort is provided in the form of an Interim Report in Appendix A.

As will be discussed in this draft final report, a LIBS system can be used to perform quantitative elemental analysis on numerous types of samples, especially soils. In the LIBS technique, an optical emission spectrum is obtained by focusing the high power laser on the soil 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 photon. Elemental analysis is conducted by observation of the wavelength, intensity, and temporal characteristics of the emission lines.

A prototype LIBS/CPT was developed and it consists of a Neodymium:Yttrium Aluminum Garnet (Nd:YAG) laser source to produce the plasma, a novel hollow waveguide method of delivering the laser source to the subsurface, a small penetrometer probe for focusing the laser light to create a spark and return the light emission for analysis, a spectrometer to spectrally resolve the emission spectrum, an array detector for simultaneous measurements of emission intensities over a range of wavelengths and a computer to conduct equipment control, data acquisition, and data analysis. In addition to the hardware development, new data analysis techniques that will improve on the quantitative performance of the LIBS system and provide the field operators with more real-time information on the quality of the data for better decision-making in the field.

The LIBS/CPT system was designed, fabricated and tested, culminating in a successful field demonstration at the DOE Sandia Chemical Waste Landfill for the evaluation of chromium contamination. During this test, the data obtained with the system was used to generate graphs depicting the concentration of chromium as a function of depth, with a range of concentrations from background (≈ 30 ppm) to about 1200 ppm. In addition, two prototype LIBS systems were successfully field deployed by SEA at a FUSRAP site for the detection of beryllium. This 6 week field effort generated a high density surface contour plot of the beryllium concentration over a 40 acre site ranging from no contamination to over 5000 ppm. This was the first full scale field deployment of the portable LIBS instruments and the LIBS data was used successfully for real-time decision-making during the site characterization and for the development of additional plans for subsurface analysis.

Authors Note: In parallel with the SEA effort described above, the Energy & Environmental Research Center (EERC) at the University of North Dakota, conducted a support effort. Under the scope of their program, funded under a DOE Cooperative Agreement, the EERC supported this effort by obtaining soil samples for testing from

contaminated sites in Montana, developing detailed procedures for the fabrication of multi-element calibration soils, evaluated standard laboratory methods for metals analysis, performed an evaluation of the performance of contract labs for metals analysis, and most importantly, led the development of new LIBS spectral data analysis techniques. The details of the EERC effort exceed the scope of this report, but can be obtained by reviewing the EERC DOE summary reports for their Cooperative Research and Development Agreement effort.

TABLE OF CONTENTS

Disclaimer	i
Abstract	ii
Acknowledgments	iii
Executive Summary	iv
Table of Contents	vii
 1.0 Introduction	 1
1.1 Extent of Heavy Metal Contamination.....	1
1.1.1 National Extent/Needs.....	1
1.1.2 Department of Energy Needs	3
1.2 Statement of Work (SOW).....	8
1.3 Project Team	10
1.4 Technology Description	11
1.4.1 General Background on LIBS	11
1.4.2 LIBS for Soils Analysis.....	12
1.4.2 Cone Penetrometer Test (CPT)	14
1.5 Other ongoing efforts in LIBS/CPT development	16
2.0 Results & Discussion	22
2.1 Hardware Design & Description	22
2.1.1 LIBS System Hardware.....	22
2.1.2 Laser Delivery	33
2.1.3 Probe Development	56
2.2 DOE Field Test.....	81
2.2.1 Hanford Site	81
2.2.2 Sandia Site Description	81
2.2.3 Historical Data.....	84
2.2.4 LIBS/Penetrometer Procedures	86
2.2.5 Sandia Site Test.....	91
2.2.6 Sandia Site Test – Location of Penetrations.....	93
2.2.7 Sandia Site Test – LIBS Data.....	93
2.2.8 LIBS Spectra for each penetration	94
2.2.9 Sandia Site Test – Calibration Procedure.....	101
2.2.10 Sandia Site Test Performance	104
2.2.11 Cost Data.....	105
2.3 LIBS Data Analysis.....	106
2.3.1 Standard LIBS data analysis	106
2.3.2 Multivariate LIBS Data Analysis.....	109
2.3.3 Comparison of Standard vs. Multivariate with LIBS /CPT Data.....	119
3.0 Conclusions	124
4.0 References	127
Appendix A Luckey, Ohio FUSRAP Interim Report	A
Appendix B LIBS/CPT Workplan for the Hanford Site.....	B
Appendix C Innovative Technology Summary Report (ITSR).....	C
Appendix D LIBS Commercial Product Information – SPARK I.D.....	D

1.0 Introduction

1.1 Extent of Heavy Metal Contamination

1.1.1 National Extent/Needs: This research and development effort was focused on the development of sensors for the characterization of heavy metal contamination in soils, both surface and subsurface. This is a well established problem associated with a wide variety of commercial and government sites. Table 1¹ shows a summary of the metals problem in National Priority (Superfund) Sites, with Table 1a illustrating the wide variety of industries that have this problem, along with the metals most often reported. Overall, forty-one per cent of the sites report metals problems, and Table 1b shows that Lead (Pb) and Chromium (Cr) are the most often cited for this group of sites.

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

(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
5	Pesticide	As	Ag	10
5	vehicle and drum cleaning	As		
3	Paint	Pb Cr Cd Hg		
29	Other	As Pb Hg Cr		

The regulatory limits for heavy metals in soils are presently under consideration and there is a fair amount of debate on what the levels should be and how they should be calculated. The EPA has developed a Draft Soil Screening Guidance which will be used under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). These limits, if fully adopted, would act as a tool to facilitate the prompt identification of contaminated areas that require further remedial actions. If the level of a certain metal falls below its soil screening level (SSL), then further action under CERCLA would not be required. Under state and local regulations, however, the site may need to be remediated, but this EPA document is a first step towards a national standard which can be used. This standard also enables us to benchmark the performance of a field deployable system. At a minimum, the system must be able to detect below the SSL and probably much lower due to more stringent site specific regulations. Table 2 supplies the SSL's for 13 inorganics and the two levels provided represent the limits depending upon whether the contaminant will be ingested or inhaled.

Table 2: Soil Screening Levels (SSL's) from the EPA Soil Screening Guidance

Chemical	Ingestion (ppm)	Inhalation (ppm)
Antimony	31	
Arsenic	0.4	380
Barium	5 500	300 000
Beryllium	0.1	690
Cadmium	39	920
Chromium	390	140
Lead	400	--
Mercury	23	7
Nickel	1 600	6 900
Selenium	390	--
Silver	390	--
Vanadium	550	--
Zinc	23 000	--

A comprehensive study was conducted by the U.S. Army Corp. of Engineers on the heavy metal contamination at numerous military installations. Table 3 provides results on some of the different sites.² The Army report concluded that many installations have soil contamination problems, and that Cr, Pb, and Cd were the metal contaminants most frequently found at military installations, often well over the SSL's. Another conclusion was that there was not adequate remediation and characterization technologies to address the cleanup of heavy metals at the time of publication (March 1994).

Table 3: Range of metals concentration in soils for six Army sites
(total metals, ppm)

Site	Cr	Pb	Hg	Cd	Ba	As	Ag
Letterkenny, PA	14-777	8.6- 4940	--	5.2-308	35-2300	5.7-12.8	--
TCAAP, MN	7-146	3-3000	0.1 - 2	1.5-31.3	6-3800	--	--
Anniston, AL	1.2- 3000	1.16- 956	0 - 23	0.05-453	0.49-343	2	5.58
Riverbank, CA	11- 1109	15-138	--	--	--	8-70	--
Louisiana, LA	9-441	8-89	--	--	--	--	--
Tooele, UT	30	--	--	--	--	8-100	--

1.1.2 Department of Energy Needs

The Department of Energy (DOE) has also conducted a number of studies that document the needs of the individual sites. These Site Technology Needs are disseminated to communicate the deficiencies of the present technologies for conducting environmental remediation and characterization, among other needs. For example, Table 4 shows several sites that have identified the need for technologies that can detect heavy metals in soils.

Table 4: Sites that have identified a need for the characterization of heavy metals in soils.

Site	Identifier	Description
Hanford ³	SS15	Improved, In-situ characterization to determine the extent of soil contamination of one or more of the following heavy metals: Hexavalent Chromium, Mercury, Lead.
Hanford ⁴	SS13	Improved real-time field screening during excavation of one or more of the following heavy metals: Hexavalent Chromium, Mercury, Lead.
INEEL ⁵	ID-6.1.02	Real-time field Instrumentation for characterization for radioactive and metal contaminated soils
Pantex ⁶		In-field characterization technology for chromium contaminated soils. Characterization technology for chromium contaminated construction media
Savannah River Site ⁷		There is a need for in-situ, direct push technologies to provide real time analysis of VOCs, metals, and radionuclides.

The Hanford Site, in particular, has reported very specific functional requirements⁸:

“The cost effective technology needs to provide real-time, in-situ measurement of heavy metals with field deployable instruments. Data must be easily downloaded into computer systems for analysis and retrieval. Detection limits down to required remediation levels would be preferable but higher detection level instruments that could be deployed economically at depth are also of interest. The following remediation goals can be found in the Remedial Design Report/Remedial Action Workplan, for the 100 Area (DOE/RL-96-17): Cr(VI), 2.2 mg/kg; Hg, 24 mg/kg; and Pb, 250 mg/kg. Analysis down to 200 + feet would be useful in some areas, but deployments to depths of greater than 15 feet is required. If possible, the techniques should

support the eventual elimination of the requirements for sample collection and analysis.”

This needs statement clearly indicates that a cone penetrometer system that can detect heavy metals in the subsurface would be beneficial. In addition, the cleanup effort has both near term immediate needs and long term needs, and the site can afford to integrate new, innovative technologies that may not be field proven to a great extent. This is shown by the continuation of the above comment:

“Consideration of a new technology is ongoing. Mature technologies would support near term actions. Technology must be available to support completion of remedial actions in the 100 Area by 2006...The 100 area has over 3.9 million cubic yards of soil and debris in 340 contaminated soil sites and 50 buried waste sites that will require remediation...A specific near-term need for in situ chromium detection exists in the 100-H and 100-K Areas. Chromium is known to have reached groundwater and resulting in concentrations that require remedial measures but the vadose zone source of this contamination has not been positively identified. Identification and treatment of this contaminant source is an important part of meeting and maintaining groundwater cleanup objectives. Lead and mercury are other potential contaminants of concern.”

The benefits of conducting in-situ analysis are time and money. It currently takes about 4-6 weeks to obtain the results of samples obtained via current baseline technologies - mainly conventional drilling and laboratory analysis – and an additional two weeks for data analysis. This lag time does not allow for real-time decisions during remediation and may contribute to increased costs. For example, when unexpected results occur when using conventional techniques, additional field work may be necessary to confirm the data. In general, real-time, non-invasive field analysis

techniques could save as much as 40%-60% of the sampling costs. At the Savannah River Site, for example, this translates to \$11M to \$30M over 25 years.⁹

The DOE supported a study to determine the overall needs of the DOE for field deployable chemical sensors, including a market study on the potential for new technologies overall. Similar to the heavy metal data presented in Table 1, Table 5 shows the overall number of sites needing remediation.¹⁰ With a total in excess of 585,000 sites, the market potential for field instrumentation has been estimated at \$1.9B over the next 10 years.¹¹ This, of course, includes a wide variety of instrumentation for conducted numerous types of analysis. Table 6a shows the top needs based upon the type and form of the pollutant and Table 6b on the general class. It is seen that the instrumentation for organics will dominate the market, but those for metals will be in high demand. These values represent the percentage of the overall market potential.

Table 5: Number of sites requiring remediation

Site Category	Number of Sites Requiring Remediation
National Priority List (NPL) Sites 9/30/92	1235
RCRA Regulated Hazardous Waste Sites	1500 to 3500
Underground Storage Tank (UST) Sites	360,000
DOD Sites	7313
DOE Sites	About 4000
Civilian Federal Agency Sites	925
State Hazardous Waste Sites	69,808
Private Party Sites	Large but unknown, 1991 remediation market estimated as \$1B, implying 140,000 sites based on hazardous waste site expenditures
Total	>585,000

Table 6a: Site Needs Ranked by Percent Market Potential

13%	Detecting individual organics in air
12%	Detecting individual organics in soil
7%	Detecting individual organics in water/liquids
6.1%	<i>Detecting individual RCRA metals in soil</i>
5.7%	Detecting individual organics in soil
4.9%	<i>Detecting individual RCRA metals in water</i>
4.8%	<i>Detecting individual RCRA metals in water in-situ</i>
4.8%	<i>Detecting individual RCRA metals in soils in-situ</i>
4.0%	Detecting individual organics in water in-situ
3.2%	<i>Detecting individual RCRA metals in air</i>
3.2%	<i>Detecting individual RCRA metals in sludge</i>
43 Needs <3%	

Table 6b: Overall Pollutant Classes Ranked by Percent of Total Market Potential

55%	Organics
30%	<i>Metals</i>
10%	Inorganics and other Pollutants
5%	Radioactive Metals

In general, these figures show that there is a need for field instrumentation for the evaluation of metals in soils - although not the largest - it is substantial. In addition to the data above, the market survey also emphasized that the users required that the instrumentation be simple to use, rugged, and cost effective. If the instruments were not reliable, then it would not be used in the field.

1.2 Statement of Work (SOW)

The primary objective of the effort was to develop a laser induced breakdown spectroscopy system integrated with a cone penetrometer system for the subsurface mapping of heavy metal contamination in the vadose zone. The Base Program of this effort investigated the requirements of such a sensor and showed the feasibility of evaluating heavy metal contaminated soils via an optical fiber probe. The Base Phase consisted of the following Tasks:

- Task 1: Requirements Analysis for the Sensor System
- Task 2: Probe/Cone Penetrometer Evaluation
- Task 3: Fiber optic Probe Fabrication and Laboratory Evaluation
- Task 4: Draft Final Report

In Tasks 1-4, the objective was to evaluate the use of optical fibers to deliver the laser to a remote, small probe, and evaluate its utility and potential for integration with a cone penetrometer. This was successfully conducted and the Optional Phase of the program was initiated. The Optional Phase of the project developed a field deployable prototype system and consisted of the following seven tasks:

- Task 5: Information Required for the National Environmental Policy Act (NEPA) and Project planning
- Task 6: Design of prototype field deployable optical fiber sensor system
- Task 7: System Fabrication and Evaluation
- Task 8: Laboratory Evaluation and Optimization of LIBS system
- Task 9: Field Testing
- Task 10: Government Facility Demonstration
- Task 11: Final Report

Task 5 included the information required to satisfy the National Environmental Policy Act (NEPA) for the laboratory testing and field work and this task also included

the development of a program management and costing plans. Building on the results of the Base program, the Task 6 effort designed the prototype field deployable system. As will be discussed, the overall system consists of a number of subsystems, including: 1) the LIBS hardware, 2) a laser delivery system, 3) an optical probe, 4) a computer control, data acquisition, data analysis system, and 5) the penetrometer housing.

For Task 7, the designs developed in Task 6 were fabricated and functionally tested. For Task 8, the subsystems and overall system was integrated to evaluate contaminated soils. For Task 9, the system was field tested several times to develop the deployment procedures, and to evaluate the survivability and performance of the system. The field testing commenced during the design phase of the subsystems and continued through to the full prototype development. For Task 10, the prototype system was field tested at the Sandia National Laboratory Chemical Waste Landfill (CWL) Site.

For Task 11, the final report discusses the initial evaluation using optical fibers, the rationale of the new laser delivery method employed in the final system, a detailed description of the system design process, a discussion on the performance of system during field trials, and the results on the development of new data analysis techniques for LIBS.

In addition to the penetrometer system development, SEA was tasked to deploy and evaluate several types of LIBS instruments developed by Los Alamos National Lab (LANL) personnel, at a Formerly Utilized Site Remedial Action Plan (FUSRAP) location. The SOW for this portion of the effort also had two Phases, A & B, with only Phase A being exercised by the Corp of Engineers/FUSRAP office. The Phase A SOW was as follows:

- Task A1: Information required for the National Environmental Policy Act (NEPA)
- Task A2: Provide inputs and comments to FUSRAP Health & Safety Plan for the Luckey, Ohio FUSRAP Site
- Task A3: Provide inputs and comments to FUSRAP Sampling and Analysis Plan for the Luckey, Ohio Site
- Task A4: Provide further development to the standard operating procedures for the LIBS instruments and perform a 6 week evaluation at the FUSRAP site.

- Task A5: Comply with all Health and Safety requirements for site.
- Task A6: Principle Investigator attend project initiation meeting and project closeout, if required.

Again, all of these Tasks were successfully completed and an Interim Report was written on this portion of the effort to satisfy the project closeout for Task A6. A copy of the Interim Report which discusses the results and findings of the FUSRAP portion of the effort as been included in Appendix A of this Draft Final Report.

1.3 Project Team

The team for this effort was lead by Science & Engineering Associates (SEA) in Albuquerque, NM. SEA personnel have a strong background in the use of optical waveguides for high power laser energy, optical fiber sensor applications, the test and evaluation of optical fiber systems for adverse environments, and the application of LIBS for environmental monitoring. Inputs on the cone penetrometer designs and field evaluations were provided by Applied Research Associates (ARA), South Royalton, VT. ARA personnel have successfully developed numerous advanced cone penetrometer systems for the chemical and physical evaluation of the subsurface, including the integration of fiber optic sensors. Technical assistance on the design of the rugged, field deployable system and LIBS facilities were supplied under a Users Facility Agreement (UFA-97-001-A001) by Los Alamos National Laboratory (LANL). The LANL personnel are recognized experts on the development of LIBS systems for a wide variety of applications. In addition, the Energy & Environmental Research Center (EERC) at the University of North Dakota (funded though a DOE Cooperative Agreement, UND Fund 4619) provided invaluable assistance on the development of standard soil samples, the laboratory analysis of field samples, and on the development of new LIBS spectral data analysis techniques.

1.4 Technology Description

1.4.1 General Background on LIBS: Laser-induced breakdown spectroscopy (LIBS) systems are just now being developed for the field due to recent advances in critical hardware components, primarily compact lasers, detectors and spectrometers. At the present time, there are various types of LIBS instruments being developed for field applications, such as hand-held devices and van or truck mounted systems for both surface and subsurface analysis.

Regardless of the deployment technique, all LIBS systems contain the same basic components. As shown in Figure 1, a LIBS system consists of a laser source to produce the plasma, a method of delivering and focussing the laser beam onto the sample, 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.

Figure 1: A typical laser induced breakdown spectroscopic (LIBS) system

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

1.4.2 LIBS for Soils Analysis: When evaluating soils, the spectrograph is tuned to the wavelength(s) where the element of interest has an emission. Figure 2(a) through 2(c) show LIBS spectra determined for a NIST sample from a Montana Superfund Site with high heavy metals contamination. Figure 2(a) shows the spectral region for Pb, Figure 2(b) for Cr, and Figure 2(c) for Cu, Zn, and Ag.

**Figure 2(a): LIBS spectrum of a NIST Superfund soil in the Pb spectral range
(y-axis values are arbitrary)**

Figure 2(b): LIBS spectrum of a NIST Superfund soil in the Cr spectral range

Figure 2(c): LIBS spectrum of a NIST soil in the Cu/Zn/Ag spectral range

Each spectra contains information on other elements. For example, Figure 2a, shows that the spectral window from 402 nm to 410 nm 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.

1.4.3 Cone Penetrometer Test (CPT): The CPT was originally developed in the Netherlands in about 1934 for geotechnical site investigations. Simply stated, the CPT uses a large mass (e.g. the truck) to push a metal probe into the subsurface. The modern CPT probe contains the primary geotechnical sensors for tip stress, sleeve friction, pore pressure along with options of an inclinometer to measure the tilt of the probe, resistivity, soil moisture, soil pH, and redox potential. Major components of the modern cone penetrometer system are the instrumented probe, the instrumentation conditioning and recording system, the hydraulic push system, and the vehicle on which the system is mounted. The common configuration provides the reaction mass for a hydraulic push force of about 20 or 30 tons.

Due to the high cost of drilling at contaminated sites, both the DOD and DOE have initiated aggressive programs to develop chemical sensors and sampling methods for the minimally intrusive CPT.¹² Using the cone penetrometer for environmental site characterization represents a relatively recent application of the technology. Significant advantages of the CPT include: eliminating drilling wastes and the need for treatment and disposal of drill spoils as hazardous material; providing continuous data on the subsurface stratigraphy in real time; identifying thin layers of significantly different hydraulic conductivity; minimizing the potential for crew exposure to the potentially hazardous material; reducing the possibility of cross-contamination (by pressure grouting the hole as the probe is withdrawn); and speed, when compared to conventional drilling and sampling. CPT is an excellent platform for making continuous measurements of contaminant information with depth, is useful for pushing monitoring sensors into the subsurface, for installing monitoring wells and points, and for taking gas, water, or soil samples for environmental testing.

The CPT truck used in this effort is shown in Figure 3 with the inside configured as shown in Figure 4.

Figure 3: ARA CPT truck used in this effort

Figure 4: The inside configuration of the CPT truck

1.5 Other ongoing efforts in LIBS/CPT development

The Army Corp of Engineers conducted two separate programs on the development of LIBS heavy metal sensors integrated with the DoD cone penetrometer system called the Site Characterization and Analysis Penetrometer System, or SCAPS.¹³ One of the efforts was conducted by Naval Research and Development (NRaD), in San Diego, and the other by the U.S. Army Engineer Waterways Experiment Station (USAEWES) in Mississippi. Each organization took a different approach on the integration of the LIBS system with the cone penetrometer, and as will be discussed later, SEA opted for a third integration approach. All three of the designs have advantages and disadvantages.

The sensor developed by NRaD is configured with the laser and spectrometer in the SCAPS truck utilizing a fiber optics system to deliver the laser to the probe head. Figure 5 shows the design of their probe (Note: this is a schematic to convey the concept and may not be to scale). The probe uses an optical fiber to deliver about 25-30mJ laser pulses at 10 Hz. The output of the optical fiber is collimated by the first lens, redirected 90 degrees by the prism, and focused through a window to the soil by the second lens. One of the issues with any of the LIBS/cone penetrometer designs is the ability to focus the laser beam onto the soil surface. In this design, the external surface of the window is flush with the exterior of the penetrometer rod, thus the location of the soil surface is precisely known. After the soil has been sparked, the emitted light travels back through the optical system, back up the optical fiber where it is collected and delivered to a spectrometer for analysis.

There are several advantages to this design. The collinear launch/detection system works very well and the alignment of the detection system onto the spark is inherent in the design. The other advantage is the small size of the probe since you only need a single optical fiber for both laser delivery and reception and all of the associated optics can be relatively small. There are several key disadvantages, however. The first is that the laser power handling capability of the optical fiber is a limiting factor, this is why these researchers only deliver about 30 mJ of laser power. (This property was also encountered during this effort and will be discussed in detail in the following section).

Figure 5: Schematic of the NRAD LIBS/Penetrometer Design

Another disadvantage is the close proximity of the soil to the window. Since the soil is pushed against the window, the window will be damaged by the laser spark during analysis. The energy density at this interface, which is high enough to spark the soil, will cause the window to pit and crack. Thus, as the analysis is progressing, the transmission and mechanical integrity of the window is being compromised. Both the laser light and the emission signal will be scattered and the overall quality of the LIBS signal will be reduced. To solve this problem, the researchers at NRAD designed the probe so that the laser could be launched through different locations of the window. The optics can be moved around the window so that the damaged portion can be avoided, as shown at the bottom of Figure 5. This was accomplished mechanically by using two stepper motors, situated above and below the optical portion of the probe, to traverse the laser around the window. After sampling through one portion of the window, the optics can be moved to another, pristine location of the window. One of the unknowns in this procedure is the extent of the damage during sampling, since laser damage on optics is somewhat unpredictable. Does the window become damaged to the point where it doesn't transmit

the laser after 10 pulses or 300 pulses? This could vary from sample to sample and the soil spectra will be intermingled with the emission spectra of the window material.

The design appears to be fairly complex, but absolutely necessary if optical fibers are used to deliver the laser. The reasons for this will be elaborated in the next section, but a short description will be provided here to describe the reason for the complexity of the NRAD probe. For this probe, the optical fiber used was 600 microns in diameter, which is probably the smallest fiber that could be used when using a high power laser in the field. In order to achieve the energy density required to spark the soil, very fast (i.e. short focal length) optics are required to obtain a small spot size. In general, the optics image the distal end of the optical fiber onto the soil. Since only 30 mJ of laser power is being delivered by the optical fibers, the optics must demagnify (e.g. reduce) the 600 micron image of the optical fiber onto the soil surface. For this probe, the image of the optical fiber was reduced by a factor of three to attain a spot size of about 200 microns on the soil surface. The small spot size creates the proper energy density to spark the soil, but the corresponding working range is very small. The power density will only be high enough to create a spark over about ½ millimeter outside the window. This means that in order to utilize this optical deliver system to spark the soil, the location of the soil must be 1) very close to the optics and 2) be within ½ mm of the focal point of the final optic. It is apparent that the only way to guarantee the position of the soil was to have it pressed against the window. Thus, the probe was designed accordingly. As will be discussed in the next section, SEA followed the same design path as NRAD with the optical fibers, but opted for a different solution.

The USAEWES configuration, on the other hand, houses a small laser into the cone penetrometer. Figure 6 shows the configuration for this probe (Again, this figure shows the general layout and may not be to scale). In this design, a specially designed laser is placed into the penetrometer rod, with an optical system that enlarges the beam diameter, redirects the beam 90 degrees and focuses the light onto the soil surface through a protective window. Unlike the previous design, there is a space between the window and the soil created by the removal of a sacrificial sleeve. On penetration, the sleeve covers the optical system. Upon retraction, the frictional forces will remove the sleeve and it will remain at the bottom of the hole. This creates the space between the

final window and the soil. A key to this design, in comparison to the previous, is that the laser power density on the final window will be relatively low, such that it will not be damaged. After the spark has occurred, the emitted light is detected by a separate optical fiber bundle and delivered to a spectrometer up in the truck.

Figure 6: The USAEWES LIBS/penetrometer design with the laser located within the penetrometer rods.

Again, there are advantages and disadvantages to this design. By far, the most important advantage is the excellent beam quality that is attained by using the output of the laser directly. Once the laser is sent into an optical fiber, the beam quality is severely

degraded and it becomes much more difficult to focus. In addition, there are numerous precautions which must be taken when launching a high power laser beam into optical fibers. This design bypasses those difficulties by placing the laser close to the location of the spark. The excellent beam quality also means that the working range will also be very good. Unlike the previous design which had a working range of about $\frac{1}{2}$ mm, this probe should easily exceed that by at least an order of magnitude, if not more, thus slight movement in the location of the soil surface can be tolerated.

Placement of the laser in the penetrometer also creates a couple of disadvantages. The most important one, especially when a commercial product or service is being considered for the technology, is the cost and ruggedness of the probe head. The laser used in this design was specially fabricated by Kigre laser¹⁴ with maximum energy/pulse = 80 mJ and a repetition rate 1/3 Hz. A standard 30 mJ laser fabricated by the same company sells for about \$9,000, so it is safe to assume that the laser used in this design is more expensive. Based on our experiences with fabricating probes and penetrometer housings, a \$15,000 pricetag for each probe would probably be a conservative low estimate. It is not uncommon to damage or bend the tip of a penetrometer, especially in rocky subsurfaces, and be forced to leave portions of the rod string in the hole. Even if this never occurs, it would be good commercial practice to have at least 1 or 2 additional probes on hand in case of damage during use. With this design, the probe cost becomes a major concern.

Another disadvantage of placing the laser into the penetrometer rod is the limitations on the types and sources of lasers. Due to space requirements, the type of laser used can only be pulsed once every three seconds. This limits the speed at which data can be attained. When using a laser that is used within the truck, the number of vendors and types of lasers that can be used increases and the size or ruggedness of the laser is not a concern. In the previous design, for example, the laser could be operated at 10Hz or more, thus data could be collected much faster.

Both of these design and deployment efforts were being conducted prior to and concurrently with the present effort by SEA, thus we often encountered the same problems and issues. As will be discussed, SEA set out to design a system that would be amenable to long term commercial deployments, thus when faced with many of the

problems discussed above, we took a different course to solve them. Which design is “best” cannot be readily answered, but may be evident after all have been utilized repeatedly in the field.

2.0 Results & Discussion

2.1 Hardware Design & Description

As previously stated, the LIBS/cone penetrometer system consists three subsystems: a) LIBS hardware, b) Laser delivery system, and c) the LIBS/penetrometer probe. Each of these subsystems will be described below, with an emphasis on the development of the laser delivery system and penetrometer probe.

2.1.1 LIBS System Hardware: The LIBS hardware consists of the following components:

1. Rugged cases for transporting the hardware to the job site and for protection within penetrometer truck.
2. A Continuum Surelite I Nd:YAG Q-switched laser with a maximum energy of 450 mJ/pulse, with a 4-6 ns pulsewidth. This laser was also capable of producing double pulses of lower total energy and extended pulse lengths.
3. An Acton Research 0.75 meter spectrometer, with three accessible gratings of 1200 grooves/mm, 2400 grooves/mm and 3600 grooves/mm. The system is completely computer controlled via software supplied by the gated intensified detection system listed below.
4. A Princeton Instruments time-gated, intensified photodiode array with 1024 elements.
5. A Dolch field rugged computer system to operate the detection system and acquire data.

Rugged Cases: In order to minimize the potential for damage during transport and use, all of the primary components were housed within molded plastic cases manufactured by Hardigg, Inc. For the laser and spectrometer, shock mounted supports were specifically designed and implemented for each. For the electronic components (laser power supply and detector electronics) the Hardigg units were purchased with standard shock-mounted 19 inch racks. Over the course of the project, the units were

shipped across country numerous times without incident, so the designs were very acceptable. The type of container that was used for the laser and spectrometer is shown in Figure 7. These containers were all constructed with a thick molded plastic, with covers that fastened with multiple latches that could be locked. Each unit also had pressure releases for air travel and were all well marked for proper handling.

Figure 7: Laser Container for shipping and use within penetrometer truck

Laser Requirements: Since the initial concept was to use optical fibers for the laser delivery into the penetrometer, the primary concern for the selection of the laser was to insure that the system could deliver enough laser light through an optical fiber to create a spark on soil. During the Base Phase of the program, we launched approximately 80 mJ into the optical fiber during testing, so this would be a minimum requirement for the laser used in the penetrometer. Some additional features that we required for selection of the laser were: 1) Remote computer control via RS232, 2) Self-contained cooling, 3) Rugged construction, 4) Variable repetition rates up to 10 Hz, 5) Energy of up to 200 mJ/pulse, minimum, with a pulsewidth <15ns.

The parameter that separates the commercially available lasers is the laser energy per pulse. The commercially available lasers are grouped in lasers equal to or less than 50 mJ/pulse, then there are a number of units at about 100mJ/pulse, then they jump to over 400 mJ/pulse. These different categories are determined by the designs being

implemented at this time. Since the optical fiber delivery system was not yet developed, a laser was chosen for the higher end of the energy scale to account for any losses associated with coupling the laser to the fiber. It was also postulated that we might use several fibers to deliver the laser into the penetrometer.

Laser Selection: A Continuum Surelite I was selected because it satisfied the requirements indicated above. The characteristics of the laser is provided in Table 7.

Table 7: Characteristics of the Continuum Surelite I

Parameter	Value
Wavelength	1.064 nm
Max Energy/pulse	450 mJ
Pulsewidth	5-7ns
Divergence	0.6 mrad
Beam diameter	6mm
Electrical Power	10A
Optical Head Size	30 x 7 x 6 in. (LxWxH)
Power supply	25 x 11 x 21 in. (LxWxH)
Weight of Head	52 lbs
Weight of Power supply	96 lbs
Temperature range	60-85deg F
Umbilical Length	12.5 ft

Another reason for selection of this specific laser was that it also had a variable pulse option (VPO). The VPO on the Surelite laser enables the user to “stretch out” the laser pulse. Instead of having a 5 ns pulsewidth, for example, the VPO could be used to generate a 10 ns pulse. This is advantageous because, in general, optics will have a higher laser damage threshold as the pulsewidth is increased. In addition to the pulsewidth extension, the VPO also enables the user to double pulse the laser very quickly – on the order of <1 microsecond. Double pulsing the laser has shown to produce interesting LIBS results. This too, will be discussed in the laser delivery section.

Laser Packaging: The laser head and the laser power supply are individually contained within rugged transportable cases. Figure 8 shows a top view of the laser head container and Figure 8 shows the power supply. As shown in Figure 8, the laser was

placed off-center to allow room for an optical bench at the front end of the laser and other components along the side. The laser and optical bench were both mounted onto a single plate, reinforced with angle iron, so that laser and bench would stay well aligned. In addition, the plate was shock mounted to the side walls of the container to allow for slight movements in the vertical direction during shipping and a thick foam rubber pad was placed under the laser and plate. The shock mounts inhibited horizontal movement so that the laser would not strike the side walls during shipping. To facilitate easy set-up in the field, the laser power connector was modified and mounted to the wall of the container. As shown in Figure 8, an electronics box, that could be covered during shipping, was used to feed-through the primary power and signal wires. The coolant lines were also modified so that the laser could be disconnected from the power supply box and stored within the container during shipping.

Figure 8: Top view of Laser within rugged case.

The laser power supply, shown in Figure 9, was supported by a 19 inch shock-mounted rack within the rugged enclosure. All of the pertinent controls for our application were located on the front panel. The extra room within this case was used to store a variety of items during transport.

Figure 9: Front view of laser power supply

Spectrometer Requirements: For conducting LIBS analysis, the requirements for the spectrometer will vary greatly, depending upon the application. For single element applications, where the end use is well defined, a low end spectrometer may be applicable. Under this effort, for example, the work done at the FUSRAP site for the detection of beryllium was a well defined, portable application, thus a low end spectrometer that had the performance necessary was applied. For the cone penetrometer system, on the other hand, the applications could vary greatly, with any number of elements being characterized, thus a more versatile spectrometer was necessary. The following characteristics were required for this LIBS system: 1) Angstrom to sub-Angstrom wavelength resolution, 2) readily integrated to a computer system (RS-232 compatible), 3) Turret-style gratings for simplified alteration of central wavelength and range, 4) all functions software controllable, and 5) easily integrated with the array detector selected. These five requirements were developed to insure that we were not in a situation where an element of interest could not be detected due to overlapping peaks from other elements, and to facilitate the easy integration into a computer operated field deployable system.

The first requirement stated above was the most important consideration. The attainable resolution of a spectrometer is primarily dependent upon its focal length. For example, Table 8 shows the resolution for a series of focal length spectrometers with a 1200 groove/mm grating and 10 microns wide slits.¹⁵

Table 8: Typical Resolutions for Spectrometers as a function of focal length

Focal Length	Resolution	Wavelength coverage with 1 inch detector
150 mm	0.4 nm	107 nm
300 mm	0.1 nm	61nm
500 mm	0.05nm	39nm
750 mm	0.023 nm	26nm

As shown by Table 8, if Angstrom to sub-Angstrom resolution is required, then a spectrometer with a focal length of at least 500 mm would be required. In order to attain this high of a resolution, however, the light input slit width must be 10 microns. The resolution will scale directly with slit width, thus a twofold increase in the slit width will correspond to a twofold increase in the resolution value. During the design phase, it was unknown what the performance of the light collection system would be and whether the spectrometer could be used with a 10 micron slit. If the overall spark emission signal was not very high, then the slit widths would have to be increased to allow more light into the spectrometer. Thus, in practice, the actual resolution will increase from that shown in Table 8. Based on this argument, it was decided to utilize a 0.75 meter focal length spectrometer to account for the possibility that the actual slit width would be on the order of the diameter of the optical fibers planned for this application (100 to 200 microns). There were several different suppliers for this category of spectrometers with similar performance characteristics at the time this system was being assembled, therefore, the deciding factor hinged upon the ease of integration of the spectrometer with the detector.

Spectrometer Selection For this effort an Acton Research spectrometer was selected and it's characteristics are provided in Table 9.

Table 9: Characteristics of Acton Research (ARC) Spectrometer

Parameter	Value
Focal Length	0.75 meter
Gratings (all mounted on triple indexable turret)	1200g/mm 2400g/mm 3600 grooves/mm
Wavelength accuracy	$\pm 0.1\text{nm}$
Resolution	0.023 nm (with 10 μm slits)
Dimensions	30 in x 10.6 in x 7.25 in (l x w x h)
Weight	70 lbs

In addition to having the applicable resolution and optical properties, the ARC unit was beneficial because the software supplied by the detector manufacturer could operate all of the spectrometer set-up functions, thus eliminating the need for two separate software programs.

Detector Requirements: The LIBS signal intensity will vary after the laser has sparked. At the early stage of the spark, over approximately the first 2-10 microseconds (depending the sample type) the emitted light is very high due continuum radiation. This background due to the continuum radiation will essentially “mask” the elemental emission. After the continuum radiation has subsided, the emissions due to specific elements are distinguishable. One method of removing the continuum emission component is to use a detection system that is time-gated, such that it will only detect over a brief timeframe after the continuum signal has subsided. In addition, the detector needed to be capable of simultaneous multi-channel analysis so that a range of wavelengths can be detected for each spark. There are not many commercially available detectors with these characteristics and performance of the units available were fairly

similar, with cost playing a major part in the selection of the Princeton Instruments unit. The characteristics of the photodiode array detector are provided in Table 10.

Table 10: Characteristics of photodiode array detector from Princeton Instruments

Parameter	Value
Detection Elements	1024
Intensifier	Fiber optic plate, 24mm wide
Gating Range	> 5ns
Dimensions	9.9 in x 4.3 in x 4.8 in (l x w x h)
Weight	6.5 lbs

Spectrometer & Detector Packaging: As shown in Figure 10, the spectrometer, intensified detector and spectrometer controller were housed within a single container, and Figure 11 shows the detector electronics in a case with rack mounting.

The optical fiber delivering the emission signal accessed the spectrometer through a port on the side of the case. During transport the fibers were removed and the port sealed with a heavy duty screw cap. The optical fibers were specially designed for this particular application. The spark emission, as will be described in the probe development section, was delivered to the spectrometer with two optical fibers. The signal from each emission collection fiber was coupled into a 7-fiber bundle with a circular cross section to match the single input fiber. Figure 12 shows that the optical fibers from the two input legs were alternately merged into a single linear array of fibers to match the rectangular input slit of the spectrometer.

Since the spectrometer is susceptible to temperature fluctuations, the container was equipped with a heating element and cooling fan controlled by thermistors set near room temperature. Also included in this container was a mercury (Hg) optical source for wavelength calibration of the spectrometer, and all of the power and electronic wires were fed through the side of the container via a junction box.

Figure 10: Top view of spectrometer in the rugged field container

Figure 11: The detector electronics and pulse delay generator

Figure 12: The fiber configuration for the spectrometer input

- 1) LIBS hardware integration: The individual components of the LIBS system are arranged as shown in Figure 13, below. A description of the procedure for use will be provided in a later section.

Figure 13: LIBS hardware configuration

System Arrangement in Penetrometer Truck: Figure 14 shows the general layout and dimensions of the cone penetrometer truck used for this effort. The primary issue was to place the laser and power supply close enough to the penetrometer head clamp so that the laser could be properly delivered, without getting in the way of the operators. As shown in Figure 14, the laser was placed onto an auxiliary rod storage compartment, just in front of the head clamp and behind the cab of the truck. The power supply for the laser was placed directly to the left of the head clamp, leaving enough room for the rack for the rods for deployment. The spectrometer, detector electronics, computers, and the LIBS operators were situated in the back of the truck. The electronic wires and optical fibers were run along the ceiling of the truck. Figure 15 shows a picture of the loaded truck during a field deployment. The operator is setting up the laser delivery system.

Figure 14: Figure showing the layout of the LIBS hardware inside the penetrometer truck.

Figure 15: Picture taken from back door of penetrometer truck with the LIBS hardware in place.

2.1.2 Laser Delivery

As stated previously, the original intention was to use optical fibers to deliver the laser energy into the penetrometer. A large portion of the developmental effort was focused on attempting to make this concept a reality. As the following section highlights, the conditions of the present cone penetrometer field application and the properties of an optical fiber deliver system were ultimately determined to be incompatible. The following sections describes the reasoning for this determination, discuss some of variations considered including optical fibers, and concludes with a description of the novel hollow waveguide system utilized.

2.1.2.1 Laser Power Requirements for LIBS Analysis: In order to conduct LIBS measurements, the system must adequately delivery high peak power laser energy to the sample. It is not the necessary that the total energy be high - typically reported in mJ's - it is the power density, often represented in units of GW/cm^2 , that is important. This accounts for the laser power per pulse, pulse width, and area on the sample. Other

researchers have reported that a minimum of 0.5 GW/cm^2 is required to attain a spark on soils, and we have seen very similar results. In general, the spark initiation that occurs at about this power level is probably not adequate in all situations, depending upon the quality of the surface. In practice, we have seen that the power density on the sample should generally be in the range of 0.5 GW/cm^2 to 1.5 GW/cm^2 . Anything higher will produce very “hot” sparks that produce very good emission signals. As far as LIBS analysis is concerned, more power is usually better.

These power densities can be attained over a wide range of laser pulse energies, depending upon the pulse width of the laser and the spot size on the sample. For example, Table 11 shows that as little as 0.45mJ (at a pulse width of 6ns) can be used to attain a power density of 1 GW/cm^2 on a sample if the spot diameter is 0.1mm. Of course, as the energy delivered increases, the spot size can increase. As Table 11 shows, 106 mJ pulse can have a spot size of 1.5mm to get to the 1 GW/cm^2 density.

Table 11: Laser energy and spot size conditions required to achieve 1 GW/cm^2 on a sample for LIBS analysis using a 6 ns laser pulse

Energy Delivered to sample (mJ)	Spot Size on Sample (mm)	Relative Area
0.45	0.1	0.4%
4.25	0.3	4%
12	0.5	11%
23	0.7	22%
38	0.9	36%
57	1.1	54%
80	1.3	75%
106	1.5	100%

If the optical system is very good and small spot sizes can be achieved, this puts less emphasis on the amount of energy that needs to be delivered. On the other hand, the small spot size translates into a smaller amount of sample evaluated. As Table 11 shows, even though the peak power density is identical, reducing the spot size from 1.5 mm to 0.3 mm will reduce the sampling area by a factor of 9. A bigger spot size will integrate a larger amount of material and reduce the effects from inhomogeneous samples. A good example of an inhomogeneous sample is shown in Figure 16. The pressed soil sample on

the left is from the DOE Hanford facility and the sample on the right is a well prepared (e.g. sieved and mixed) Montana soil sample obtained by the EERC at a contaminated site. It is clear that these samples are very different and that the Hanford soil is inhomogeneous. If all of the samples we might encounter in the field are of the Montana type, then it probably doesn't matter what the sampling volume is. It is clear that for the Hanford soil, we could easily spark and evaluate a discrete particle that is not representative of the sample as a whole. In general, the goal for this effort was to have as large a spot size as possible without dipping below the 0.5 GW/cm². The way to accomplish this is to deliver as much energy as possible via the laser delivery system.

Figure 16: An example of an inhomogenous and a homogenous soil sample

2.1.2.2 Critical aspects of the optical fiber laser delivery system for LIBS analysis: The components of a fiber optic laser delivery system are shown in Figure 17 and there are a number of factors, corresponding to the different locations labeled (a) through (e), which should be discussed. The laser beam delivery system areas of concern are: a) the laser beam characteristics, b) the input launch configuration, c) laser waveguide, d) focussing optics and e) the laser/sample interactions.

Figure 17: The components of an optical fiber laser deliver system LIBS

- (a) Laser beam - The laser beam must be transmitted well by all of the optics and it must not damage any of the optical materials along the beam path. Nd:YAG laser light at 1.06 μm is well transmitted by the silica and silicate glasses typically used for the optics in this application and optical grade materials with damage thresholds in the 3 –5 GW/cm^2 range can be readily attained.
- (b) Input launch configuration – Proper design of the launch optics will help minimize the potential of damaging the optical fiber waveguide by several different mechanisms. One mechanism is bulk damage due to internal focusing of the laser light within the fiber. As shown in Figure 17, this can be alleviated by using a lens that focuses the light in front of the fiber at location so that the light is diverging as it enters the input face. Focusing the laser at the surface or into the fiber, will cause a localized high peak power density within the fiber core that can cause bulk damage.

There is a problem with this configuration, however. The laser just prior to the optical fiber, will be very tightly focused by the launch lens. The energy density at this point is often high enough to cause air breakdown, especially if the user is trying to maximize the power delivered into the fiber. This air breakdown, or spark, will consume the laser energy and very little light will get into the optical fiber. The effect can be minimized by enclosing the launch assembly and keeping the air dust free, since the dust often initiates the spark.

Another concern with the launch optics is proper horizontal and vertical (x,y) alignment of the laser such that the laser beam is centered onto the core of the optical fiber waveguide, and proper z-axis alignment, such that the spot is the correct size to

get into the core diameter and does not exceed the laser damage threshold. If any of these conditions are not met, then the laser light will either damage the input surface or it will cause heating of the jacketing material, eventually causing damage to the optical fiber.

All of these mechanisms can be prevented by having tight control over the laser power, the cleanliness of the environment and the fiber positioning.

- (a) Optical fiber waveguide - Optical fiber laser delivery is very attractive for the penetrometer application because of its small size, flexibility, ruggedness, and transparency to the Nd:YAG laser wavelength at $1.06\ \mu\text{m}$. A basic optical fiber is shown in Figure 18. The optical fiber consists of a light guiding core and a light retaining cladding which surrounds the core. Light is guided down the optical fiber by total internal reflection because the index of refraction of the core material is higher than the index of refraction of the cladding. A light ray launched at an angle below θ_{max} will be transmitted by the fiber. The numerical aperture (NA) of an optical fiber is a measure of its light gathering ability, and it is defined as the $\sin \theta_{\text{max}}$. Typical commercial optical fibers that use a glass core and a glass cladding have a $\text{NA} = 0.22$, which corresponds to a θ_{max} of $\approx 13^\circ$.

Figure 18: Basic optical fiber structure

The most prevalent mechanism for fiber failure is caused by surface damage by the laser. The $5\ \text{GW}/\text{cm}^2$ power density limitation often stated as the power handling capacity of an optical fiber is erroneous because it is based on bulk silica glass in a pristine environment. Since the optical fiber is typically not in a well controlled environment, the peak power transmitting ability is much less. In practice, we have seen that the optical fiber damage threshold under normal handling of an optical fiber in a

controlled environment is in the 1-2 GW/cm² range. This lower level is primarily due to imperfections of the surface, either from the fiber polishing process or due to environmental contamination during use.

The peak power that can be transmitted by the optical as a function of optical fiber diameter is shown in Figure 19(a) and 19(b) for different laser power. It is seen in Figure 19(a) that at very large fiber diameters, the pulse energy can get up to 200 mJ for a 1500 μ m optical fiber. The power levels implemented for the NRaD LIBS/penetrometer probe are supported by the data shown for the smaller fiber diameters in Figure 19(b). In that program, a 600 micron fiber was used to deliver about 25 – 30 mJ of laser energy. This corresponds to a power density of about 1 to 1.5 GW/cm² on the fiber input face. A key to the design of any laser delivery system for high peak power lasers is the determination of acceptable risk. How close to the power handling limit should the optical fiber be driven? The present application will require that the system be deployed in the field under conditions that are far different from the laboratory. In addition, if this technology is to be accepted for general use, it must have a low probability of equipment downtime to address fiber failures. The goal must be to minimize the risk of damage; therefore, a 1-1.5 GW/cm² power density on the fiber input would be an acceptable risk.

Figure 19(a): The pulse energy which can be delivered via an optical fiber as a function of fiber diameter up to 1500 microns for a series of launch power densities.

Figure 19(b): The pulse energy which can be delivered via an optical fiber as a function of fiber diameter up to 600 microns for a series of launch power densities.

An important physical parameter of the optical fiber for the present application is diameter. The diameter of the fiber effects the cost, the amount of light that can be launched into the optical fiber, the bending radius, and the launch tolerances. Table 12 gives the average cost of an optical fiber for various core sizes. The cost is generally associated with the volume of glass that it takes to produce it, and it is seen that the large sizes can get expensive. As shown previously in Figure 14, the optical fiber must pass from the laser, through all of the rods, then to the penetrometer, thus the length of fiber required is at least twice the depth of penetration. For a minimal deployment of 10 meters into the subsurface, the optical fiber can get quite expensive for the larger core sizes.

Table 12: Typical costs of optical fiber as a function of core size

Fiber Core Size (μm)	Cost/meter	Cost for 20 meters
1500	\$250	\$5000
1000	\$75	\$1500
600	\$25	\$500
400	\$11	\$220

The size of the optical fiber also effects the radius that the fiber can be bent during use. Table 12 shows the bend radius for several optical fibers with varying diameters. This is a very important for the present application because the optical fiber will be handled roughly and will be bent during the deployment process.

Table 13: The short and long term recommended bending radius for optical fibers of various core sizes.¹⁶

Core Diameter (μm)	200± 5	400±8	600±10	1000±8
Recommended Short Term (cm)	3.3	6.6	9.9	16.6
Recommended Long Term (cm)	5	10	15	18

As an example, Figure 20 shows a typically penetrometer deployment. (In this example, standard electronic cabling is being deployed, but the process is identical.) In Frame 1, it can be seen that the fiber string will be pre-thread through the rod on the rack located on the left side of the picture behind the operator. To deploy, the operator lifts the top rod and removes the slack in the cable by pulling it through the rod, as shown. In Frame 2, the operator is lifting the rod over the head clamp and inserting it into the lower rod already in the clamp. In Frame 3, note that the cable exits the top of the rod and is bent down towards the floor.

Remove rod from rack
& remove slack

Lift rod over head clamp

Insert into lower rod

Twist to assemble

Tighten with pipe wrench

Upon removal, headclamp
reaches to roof

Figure 20: The cone penetrometer deployment process

In Frame 4 the operator screws the rods together and then uses a pipe wrench, as shown in Frame 5, to tighten the joint. The head clamp is then raised to the top of the new rod and the assembly is pushed into the ground. Frame 6 shows that when the head clamp is raised to the highest point in the stroke, the top of the clamp is nearly touching the roof of the truck. There is a hole, with a door, cut into the roof to allow space for the cables to exit the top rod and wrap around back into the truck. As it turns out, this is the critical spot that limits the bend radius of the optical fiber. During the use of the LIBS system, the fiber will have to make this bend so that we

can keep a continuous path from the laser to the probe tip. Based on the values in Table 13 and the deployment procedure depicted in Figure 20, a 600 μm core diameter fiber has the desired flexibility.

- (d) Focusing optics - Referring back to Figure 17, the next critical component for the laser delivery system is the focusing optics which need to collect the output of the optical fiber and refocus it down onto the sample with the appropriate energy density. In addition to the lenses, there may be a window inserted to protect the focusing optics. In general, there is a wide selection of lenses which can be used to refocus the light without difficulty at the desired location. The critical portions of this system are the size of the optics (limited by the available space in the penetrometer), and the energy density of the laser on the lenses and window. In the example shown in Figure 17, the window is the most critical because it sits at a point in the optical path where the power density will be high and it is in contact with the dusty environment.
- (e) Laser/sample interactions - The lens-to-sample distance is an important consideration. In general, the laser should be focussed *into* the soil to achieve the best LIBS signal because there is a tendency for air breakdown to occur when the soil is at or farther away than the focus. The air breakdown consumes the laser light, preventing it from interacting with the soil. As an example, Figure 21 shows the change in peak height of an iron emission peak as a function of laser-to-soil distance for a 75 mm focal length lens. The best LIBS signal is obtained prior to lens focal length. The graphics along the top of the figure show that when the sample is too close, the spot size does not achieve the power density required to create a spark, and when too far, the air sparks.

Figure 21: The effect of Lens-to-sample distance on LIBS signal

In the present application, we can design the system to place the focal point of the laser beam at the required position. The uncertainty in the problem is the location of the soil relative to our probe. Will the soil always be in the same spot? In order to understand the problem better, we conducted an experiment where a camera was used to video the wall of the soil as a penetrometer rod was being retracted. Figure 22 shows the camera assembly and several stills from the video. The system was a B&W CCD camera with an LED light source for illumination. The unit was housed into a sacrificial tip penetrometer rod. Upon retraction, the tip was frictionally removed, exposing the camera to the soil. In general, the video showed that even though the penetrometer rod is being forced into the subsurface and compacting the soil out of the way during penetration, there are soil types that will show a lot of porosity. The picture on the bottom, right shows a nearly ideal surface for conducting LIBS analysis. The penetrometer rod compacted the soil and it was at a consistent distance from the camera. The top, right picture, on the other hand, is an

example of when the soil is not compacted and there is a fair amount of porosity. There were portions of the video where loose soil was seen to drop past the camera and portions that showed large empty areas. Naturally, we cannot expect this sensor, or any other, to have 100% coverage, but the need for a laser focusing system with a large working range was very apparent. A conclusion from this experiment was that the focusing system should be able to spark the soil over a range of about ½ inch.

Figure 22: The downhole camera and pictures of the subsurface soil

2.1.2.3 Fiber Optic Delivery System Development: The previous general discussion highlighted some of the design trade-offs that we considered during the fiber optic delivery system development. It was apparent that based on the cost and bend radius constraints, that we should use an optical fiber of 600 μm in diameter. The downside of using that size fiber is shown clearly by Figures 19, by the sharp decrease in the amount of energy that can be transmitted relative to the larger core sizes. During the Base Phase of this effort, for example, a 1500 micron optical fiber cable was effectively utilized to transmit about 80 mJ of laser energy to a probe for LIBS analysis. According

to Figure 19(a), this laser level was very conservative for the launch end, with a power density of less than 1 GW/cm². For the present work, if we were to use a 600 μ m optical fiber and bring the launch energy density to a still conservative 1 GW/cm², then we could input about 15-20 mJ/pulse with the 6ns pulse width of the Surelite. Accordingly, if we want to delivery a 1 GW/cm² power density onto the soil, then the spot size achieved must also be 600 microns.

Figure 23 shows the beam diameter as a function of distance for three different lens combinations arranged as shown in the Figure. Each combination uses a ½ inch diameter, 50 mm focal length lens to collimate the output of a 600 μ m optical fiber, with the second lens varying from focal lengths of 9mm, 25mm and 50mm. The data points represent the radius of the laser beam (e.g. the position on the beam intensity profile that was 1/e² of the maximum).

Figure 23: Beam profile of the focused output from a 600 micron fiber with different lens configurations

As Figure 23 shows, the achievable spot size decreases as the focal length of the second lens is decreased. Figure 24 shows the power density as a function of distance after the second optic for these different configurations using a 1GW/cm² input and a 5GW/cm² input. It is seen that the maximum energy densities for the 50 mm and 25 mm lenses barely achieve the 0.5 GW/cm² power density required when 1 GW/cm² is launched into the fiber, and only at the focal point. The 9 mm lens does achieve excellent energy density, but it all occurs over a range of less than 1 mm. These results show that when using an acceptable power density at the fiber optic input (1GW/cm²) it is difficult to achieve the required power density on the sample for LIBS. In addition, when using the 1GW/cm² launch, the working range is on the order of several millimeters. In order to achieve an acceptable working range, as shown by the 50 mm focal length data in Figure 24, the input power density to the optical fiber must be increased.

Figure 24: Achievable power density as a function of distance from the second lens in the configuration shown in Figure 23

2.1.2.4 Alternative Fiber Optic Delivery: The analysis above showed that for the present application, the original concept of using a single optical fiber to create the LIBS spark would not be effective. At this point in the development process, we looked into several other alternatives utilizing optical fibers so that we could still exploit their advantages. The following options were pursued:

- 1) Improved coupling into the optical fiber,
- 2) Increase the number of fibers delivering the power, and
- 3) Double pulse the laser

Improved coupling into the optical fiber: The goal of this alternative was to improve the coupling into the optical fiber in regards to energy density. If the energy density coupling into the optical fiber could be improved to 2-3 GW/cm², for example, the energy density on the soil would be more usable. One of the keys to this would be to enclose the input to the optical fiber in a vacuum chamber so that the laser would not spark at the focal point prior to the input face of the fiber. The other key would be to use a type of optical fiber that has a tapered input. A tapered optical fiber has an enlarged input face so that the energy density on the front surface can be decreased. For example, the front face can be enlarged to 1000 microns and then taper down to 600 microns for the remainder of the fiber. The laser can then be launched into the optical fiber at a low energy density with a spot size of 900 microns, then the fiber can taper down to the 600 microns required for the rest of the system.

The conclusion of this evaluation was that the complexity added to the input configuration by using a vacuum chamber was not warranted for a field system. In addition, the tapered optical fibers are very expensive, and based on previous work, the commercial availability of quality tapers is questionable.

Increase the number of fibers delivering the laser: The goal of this alternative was to split the input beam into beamlets that could be launched into a number of small optical fibers. These small optical fiber are then bundled and used to deliver the energy to the

probe. Within the probe, the bundle of small optical fibers are coupled to a larger optical fiber that mixes all the beamlets together. The output of this larger fiber is then used to spark the soil. This methodology has been used by others for laser delivery in other types of applications. The thought for this effort was to bundle 3-4 fibers delivering the 10-20 mJ to get more power into the probe. In effect, this would be the equivalent of using a 1500 micron fiber, split into 3 or 4 thinner fibers that have the ability to bend throughout the penetrometer system.

The conclusion from this evaluation was that, again, the launch complexity would increase to a level that was not desired for a field system. The optics required to produce the beamlets do exist, but the alignment of multiple fibers would be difficult to accomplish. The use of multiple fibers will also increase the cost of the delivery system to unacceptable levels, depending upon the number of fibers used.

Double pulse the laser: Using a double pulsed laser beam for the fiber optic delivery system was the most promising of the fiber optic alternatives looked into. Over the course of this effort, we had the opportunity to be involved with a study on using two laser pulses for LIBS, in cooperation with the LANL researchers working on this effort. The results of this study are reported in literature¹⁷, so the primary conclusions as it relates to this project will be discussed here.

The principle of the double pulse technique is very simple. The LIBS hardware configuration is identical to that shown in Figure 1, except there are two lasers that provide collinear laser beams. The LIBS analysis is conducted by pulsing the first laser, then after a delay of approximately 1 to 10 microseconds, pulsing the second laser. The dynamics of the laser/soil interaction are such that the spark is initiated by the first pulse, material is ejected into a plume, and the second pulse sparks the plume and underlying material a second time. The results of the LANL study showed that when two laser pulses with energies of 50 mJ were used, for example, the LIBS signal obtained was as good as, or better than, the LIBS signal obtained with a single 100mJ pulse. The resultant detection limit was the same or slightly reduced.

The results of these tests were very encouraging for using the double pulse laser for optical fiber delivery in the cone penetrometer. The speed of light within an optical

fiber is approximately 1 foot per nanosecond. Therefore, if we are using a pulse separation of 1 microsecond, the first pulse will travel 1000 feet down an optical fiber, if it is that long, just as the second pulse is entering the fiber. The amount of laser energy incident upon the fiber input face, therefore, is reduced by a factor of 2, and the LIBS signal is not reduced. For the LANL study, they used two separate lasers to generate the two pulse, but that would not be economically feasible for the cone penetrometer system. As stated in the hardware section, the Surelite laser purchased for this effort has the capability of double pulsing.

At this point in the development process we looked at the double pulse characteristics of the Continuum laser to understand if it could be applied to the present application. Figure 25(a) shows the basic premise of generating a laser pulse with a flashlamp pumped laser. The process is as follows: 1) a pump lamp is initiated and the temporal profile of the lamp output, shown by the dashed line in Figure 25(a), peaks at about 180 microseconds and extends out to several hundred microseconds, 2) after a predetermined delay to allow for the buildup of stimulated emission within the laser cavity, a signal is delivered to the Q-switch (i.e. a light gate or valve) to allow the laser light to dump out of the cavity and be emitted. The power output of the laser can be altered by changing the delay of the Q switch to a lower flashlamp power, as shown in Figure 25(b), or the intensity of the flashlamp can be reduced or increased to change the power of the laser pulse, as shown in Figure 25(c). In normal operation, the flashlamp voltage is kept constant and the Q-switch delay is varied to alter the pulse energy.

Laser emission at optimum delay and maximum lamp voltage

Laser emission at long delay

Laser emission at reduced lamp voltage

Figure 25: The timing of the laser to generate laser pulses and the methods for changing the energy in the laser pulse

In order to double pulse the laser, the Q-switch is opened twice, thus the laser energy is allowed to dump out twice. The timing is shown in Figure 26 and an unfortunate characteristic of this mode is evident. As the graphic indicates, the pulse energy, represented by the peak height, and the pulse width, represented by the broadness of each of the pulses, are not equivalent for the two. Characterization of the laser showed that the pulse characteristics would vary considerably depending upon the timing parameters.

Figure 26: The timing characteristics for double pulsing the laser

The goal for the present fiber optic application was to deliver a minimum of 50 mJ to the sample in two 25 mJ pulses, thus the fiber would only be exposed to a peak of 25 mJ since they would traverse down the fiber sequentially. Figure 27 shows the output power of the double pulsed laser as a function of Q-switch delay. This data shows that at the lower powers required for fiber delivery, the laser does not double pulse, due to insufficient overlap with the flashlamp window. In order to get in a region of double pulsing and have the laser pulses with nearly identical pulse energies (to match the experimental arrangement used in the LANL study) we would have to operate at a Q-switch delay of about 150 microseconds. At 150 microseconds delay, the pulse energies are similar, but the overall power of each is above the fiber optic limit at about 125mJ.

Figure 27: The pulse energy of each pulse as a function of Q-switch delay

As a result of this, we did begin to design an attenuator for the laser so that we could operate in this region to attain the double pulse, but tune down the power to an acceptable level for the fibers. In general, this is yet another complexity to the laser hardware that would not be preferred for a field unit and this was a contributing factor to the investigation of hollow waveguides. Once the hollow waveguide approach was exhibiting promising results, as described in the next section, the double pulse laser concept was dropped for this effort. It is, however, an excellent approach that can be exploited when optical fibers need to be brought into remote, small, or hazardous locations.

2.1.2.5 Hollow Waveguide Laser Delivery: Hollow waveguides offer a number of advantages over optical fibers and several disadvantages. Figure 28 shows that the hollow waveguide are highly reflective and they do not have an input or an output surface that limits the power density of the launch. In addition, since the copper tube is rather large, anywhere from a diameter of $\frac{1}{4}$ to 1 inch, no optics are required to launch into the waveguide. Since the beam stays large and is never focused within the tube, the air core will not break down either. As a result, the power handling ability of the hollow

waveguide far exceeds the laser we have for this application. Thus, the hollow waveguide offers the ability to launch as much power as desired.

Figure 28: The advantages of a hollow waveguide for high power laser delivery

In addition to the advantages listed above, the waveguide is durable, inexpensive, and can be purchased at the local hardware store. The disadvantages are that the waveguide is susceptible to bending losses and, in comparison to a glass optical waveguide, the losses at the wall can be relatively high. A 97% reflectivity at grazing incidence is very good, but the losses add up if the waveguide is very thin and/or long. The bending and reflectivity losses are shown by the data provided in Figure 29.

Figure 29: Throughput of copper waveguide as a function of length for different alignment qualities and waveguide internal diameters.

Figure 29 shows that when the throughput was tested as a function of length, the straightness was critical. For the two tests using the 9/16 inch i.d. tubes, we used great care in aligning the tubes optimally using very sturdy alignment tubes (solid circles) and less optimally with short couplers (open circles) that allowed the tubes to flex slightly at the joints. It is clear that the optimal alignment allows us to transmit a relatively constant laser power down a length of copper tubes that will be used in the penetrometer system. In addition, in comparison to our work with the optical fibers and the systems described in the Introduction that were developed by the Army, this delivery system can transmit far more power than any other system. In the case of the optical fibers, the copper tubes can transmit an order of magnitude more laser power. A key advantage that this offers to the field deployable system is that we can attain “laser in the penetrometer” levels of power without having to fabricate an expensive, small format laser. If anything should

occur to the probe tip and it becomes unretrievable, we stand to lose inexpensive copper water tubes. The lower data set in Figure 29 shows the effect that the wall reflectivity has on the laser attenuation. The lower two curves were obtained under the same conditions except that the tube i.d. was changed from 9/16" to 7/16" for the lower data. The decreased i.d. increased the attenuation due to two factors: 1) the smaller i.d. will result in more interaction between the laser and the wall, resulting in higher losses, and 2) the smaller tubes were more likely to be bent slightly when purchased, also resulting in more wall interaction and higher attenuation.

In order to transfer the laser beam from the laser head container to the penetrometer entry point, an articulated arm was required, as shown in Figure 30. The articulated arm consists of three long sections, each attached with mirrored knuckles, allowing for unlimited motion in all direction. In order to launch the laser into the articulated arm, the optical plate within the laser container was configured as shown in Figure 31. In alignment mode, a removable front surface mirror on a gimbal mount was used to launch a green diode laser along the high power laser path to assist in alignment. In spark mode, the mirror for alignment was removed and the IR beam allowed to pass through to a high power thin film dielectric mirror that redirected the Nd:YAG laser to the articulating arm.

Figure 30: The articulated arm being used to delivery the laser to the rodstring

Figure 31: A top view of the optics to launch into the laser articulated arm

2.1.3 Probe Development

2.1.3.1 Background on the LIBS/Penetrometer Probe: The probe development effort was slow to start due to the uncertainty in the laser delivery method. Once the decision was made to use copper tubes instead of optical fibers for the laser delivery, the probe development was free to continue with a known set of parameters. There were four separate probes developed, with each subsequent probe designed to improve the deficiencies of the prior probe. One of the primary lessons learned from this effort was that the quality of the probe design could not be adequately evaluated in the laboratory. In general, almost everything worked in the lab and the full field deployments with the cone penetrometer truck were the only true test of the designs. As a result, the development of the probes was closely related to the experiences we had in the field and new probes were designed after every field test.

As described previously, the general concept for obtaining LIBS data of the subsurface with a penetrometer is as follows: the penetrometer rod, with the integrated LIBS hardware, is pushed to refusal or to the maximum required depth for analysis; upon retraction a sacrificial sleeve is removed and the LIBS probe is exposed to the soil; the LIBS system is activated and the soil is sparked continuously as the rods are retracted; the light emission is collected and analyzed with the LIBS detection system. In this fashion, the LIBS system can provide a nearly continuous concentration profile. For the purposes of this discussion, the LIBS/penetrometer probe system consists of the following:

- Copper tubing and associated hardware for coupling the tubes together
- Optics and associated hardware for focusing the laser light onto the soil
- Optical fiber system for collecting the spark emission
- Air delivery system for dust control
- Penetrometer housing

Figure 32 depicts the integration of all of these components and some of the areas of concern are:

- (1) A basic constraint of the entire system is that all of the components must fit within the penetrometer rod. The standard 1.75 inch (44.5mm) o.d. CPT rod has an i.d. of 1 inch (25.4 mm), thus the copper tube, optical fibers, air hose, and any electrical wiring must easily pass through the rods – especially during the assembly procedure. As shown in Figure 20, the rods are screwed together, then tightened down with a pipe wrench. During this process it is critical that the components do not become tangled.

- (2) As stated previously, the copper tube is very susceptible to bending, so during use and during the assembly procedure, the copper tube cannot be flexed.
- (3) Since the rods are placed one at a time onto the string and pushed into the ground, the laser delivery tubes must also be assembled one at a time. The hardware used to connect the copper tubes must: a) provide a simple means to assemble and disassemble the tubes in the field (with gloves), b) must enable the laser to pass without appreciable loss, c) must keep the copper tubes straight, and d) must not add too much diameter to the copper tubes since space is already at a premium.
- (4) Within the LIBS housing, the laser enters the optics system. The optics system must: a) redirect the laser 90 degrees towards the soil, b) focus the laser at the correct distance with a wide working range to account for variations in soil locations, and c) minimize the laser power density on all optics so that laser damage does not occur. As will be discussed below, item (c) was of critical importance for all of the redesigns. Damage to the final optic, whether it be a simple window or a lens, either caused the system to fail or was the end result of some other failure. Maintenance of the optics, therefore, took on a great amount of importance in the context of system downtime.
- (5) The collection fiber optics must have the field of view required to collect the spark emission. It is

Figure 32: Basic LIBS/CPT elements

important that the collection fibers can be easily aligned prior to insertion into the ground and once aligned, they are able to account for variations in soil and/or spark location.

- (6) Due to the close proximity of the optics to the soil and spark, the probe contains an air system to keep the spark debris and dust from collecting onto the exposed optics. The quantity of air and flow rate was a continuous debate during the development and was a primary factor on several of the redesigns.

2.1.3.2 Probe Housing: The two designs evaluated for the penetrometer housing are shown in Figure 33; the sacrificial tip and sacrificial sleeve concepts. The sacrificial tip concept was unfavorable because it would require that the probe be fully exposed to the environment during analysis, thus making it susceptible to damage and also making it difficult to adequately water and dust seal the LIBS probe. This probe housing was built, tested and was eventually used for the downhole camera test.

Figure 33: Sacrificial sleeve and Sacrificial tip concepts

The penetrometer housing posed some physical limitations onto the design of the LIBS probe. Figure 34 shows the diagram of penetrometer housing along with a picture of the unit with the sacrificial sleeve in place. The general configuration and dimensions of the penetrometer housing were based on prior experience of ARA in deploying optical sensors through a side window. As Figure 34 shows, the upper portion, which connects to the 1 inch i.d rods, had an i.d of 1.25 inches. The lower portion, where the LIBS probe would be positioned, had an i.d of just over 1 inch. The increased i.d of 1.25 inches at the top was required to allow for the various optical fiber and air tube connections and the

reduced i.d. at the probe tip was required to allow room for the sacrificial sleeve and to allow for enough wall thickness to insure probe integrity during the high stress push. The sleeve had an outer diameter of 2 inches, which is slightly larger than the 1.9 inch outer diameter of the housing. This larger diameter created a “lip” that would help remove the sleeve on retraction.

Figure 34: The probe housing

2.1.3.3 Probe #1 Design: A drawing of the first probe design is shown in Figure 35. The hardware consisted of 14.5mm i.d. copper tubing for laser delivery, a waveguide support at the end of the string to align the copper tubes with the focussing lens, a lens holder, a turning mirror support and a window support that was attached to the penetrometer housing. Figure 36 shows a picture of the actual probe hardware and the primary components are shown. The general concept of this design was that the penetrometer housing would support the internal LIBS components and the laser would be focussed through the window attached to the penetrometer. The system was assembled by placing each of the components into the housing individually, starting at the bottom. When all of the components were stacked on top of one another, several

washers and a rubber seal were placed on top and the system was fastened down with a large threaded washer.

Figure 35: A drawing of the design of LIBS Probe #1

Figure 36: A picture of the LIBS Probe #1 components

The copper tubes were connected together as shown in Figure 37. Each of the tubes had a sleeve attached onto one end that acted as a female receptacle. The male end of all the tubes could then be inserted as the penetrometer rods were added. Since the string was being assembled vertically into the penetrometer rod string, it was not necessary to provide any locking mechanism – gravity held the copper tubes together. These connectors were advantageous because they held the copper tube fairly straight, were easy to connect and disconnect, and did not add a lot of diameter to the assembly.

Figure 37: Copper tube with small connector

At the bottom of the copper tubes, within the penetrometer housing, a single focussing lens was used to spark the soil. Figure 38 shows a schematic of the optical design of this probe. A 40 mm silica lens was used and the lens holder was threaded so that the lens could be moved vertically during set-up to optimize the focal point so that the laser/soil interaction was correct. After transmitting through the lens, the laser was redirected 90 degrees by a dielectric coated high power mirror, then through a silica or sapphire window in the side of the penetrometer housing.

Figure 38: The optical configuration of probe #1

After the removal of the sacrificial sleeve, the soil was about 7mm from the external surface of the window. With the spark being 3-5 mm in length, the material ejected from the spark can readily cause damage to the final optic. In lab tests, it was

determined a flow of air across the outer face of the window would help keep the window free from dust and potential laser damage. As shown in Figure 39, there was a small air tube situated above the window.

Figure 39: Picture of the probe housing for LIBS probe #1

The spark emission was collected by a single 600 micron fiber situated vertically outside the window, next to the air/water tube, as shown in Figure 39. The optical fiber was housed within a steel tube and it had a ball lens on its output to increase the angular light reception cone. As shown in Figure 38, the fiber was positioned so that it would view the entire spark area. The steel tube shown in Figure 39 was long enough to protrude up the penetrometer housing and into the first rod where a standard optical fiber cable was connected with an SMA connector. This fiber was then sent up to the spectrometer.

2.1.3.4 Probe # 1 Evaluation This probe was taken to the ARA facility in Vermont for testing. The goal of this first field trip was to determine how to deploy the LIBS hardware onto the truck and evaluate the probe design. The deployment issues were completed and many issues were raised with the probe design. In general, no downhole data was obtained due to a variety of issues. The following results and conclusions arose from this first field effort:

- *Probe Assembly:* The probe assembly procedure was very difficult with the number of components that had to be inserted into the housing and locked in place.
- *Component Alignment:* Since there were so many individual components, the alignment between each was very critical. For example, a slight horizontal movement of the lens holder relative to the mirror holder would cause the laser to be directed off center on the window. If the laser does not go through the center of the window, then the spark will not be positioned at a location where the emission collection fiber is viewing.
- *Laser Damage on Window:* Since the soil was so close to the window, the power density of the laser on the window was causing a lot of damage.
- *Inconsistent laser delivery:* During the course of the evaluations, it appeared that the laser power getting to the probe was very inconsistent.
- *Air Flow:* The air flow across the window was inadequate. The size of the tube and its location were not adequately protecting the window surface.
- *Spark Emission Collection:* The optical fiber was not adequately picking up the spark light. This appeared to be primarily due to inability to “point” the fiber easily in the proper location.

2.1.3.5 Probe #2 Design: A drawing of the second probe and housing is shown in Figure 40. Again, the hardware consisted of 14.5 mm i.d. copper tubing for laser delivery, an integrated tube and focussing lens holder at the end of the tube, a 45 degree mirror holder and a window/lens holder that was attached to the penetrometer housing. The lower portion of Figure 40 shows that the probe piece count was reduced by integrating the front lens with the copper tube. Figure 41 shows a picture of the actual probe hardware and the primary components are shown. The system was assembled by placing the mirror holder into the housing and then inserting the copper tube/lens/fiber optic integrated assembly on top. When these were stacked, several washers and a rubber seal were placed on top and the system was fastened down with a large threaded washer.

Figure 40: Drawing of Probe #2 copper tube with integrated lens

Figure 41: Picture of Probe #2 hardware

This new design improved the assembly procedure by reducing the number of primary components to two. As shown in Figure 40, the integration of the copper tube and focussing lens into one housing guaranteed that their alignment was satisfactory. In addition, the mirror alignment was improved by incorporating a channel into the mirror holder and using an alignment pin on the penetrometer housing, thus the height and

rotation of the mirror was fixed relative to the window/lens of the housing, as shown in Figure 41.

In the first probe, it was believed that the inconsistencies with the laser delivery may have been due to the small connectors being used. The short connectors do allow the tubes to flex slightly at the joint, so for this probe the copper tube connectors were changed to a longer steel tube which improved the rigidity of the string with a nominal increase in diameter. The o.d. of the previous connectors were 17.8 mm and the diameter of the new connectors were 19 mm, thus making the fit of all the components in the 25 mm rod a little tighter.

The focusing system was altered to use two lenses to focus the laser light onto the soil. By splitting the focussing power into two lenses, the focal length could be kept constant with a decrease in energy density on the second lens. We investigated a variety of different lens combinations to minimize energy density and optimize the location of the spark with the constraint that the optics had to fit within the housing. Figures 42 shows some of the results of the two lens analysis. For Probe #1, a 40mm focal length lens was used with a window. The configuration parameters for Probe #1 are represented by location 1 in the graph. For that probe, the first lens and the window were 30mm apart, which places the focal point at 10 mm in front of the window. (Note: This placed the focal point 3mm into the soil for an optimized spark). With this configuration, the power density on the window was at 0.68 GW/cm², which is too high for a field environment. The 50 mm FL/ 30 mm FL lens combination, configured to spark at the same 10 mm distance as shown by position 2 in Figure 42, had a reduced power density on the second to a level of 0.32 GW/cm². Other lens combinations were looked at which produce lower power densities on the first lens, but the spark location could not be attained.

Figure 42: Data analysis of the laser power density on the second lens or window

The single optical fiber located outside the housing in Probe #1 was replaced by two “side viewing” fibers situated behind the second lens. Figure 43 shows that these special fibers have a bevel polished on their end so that the light will reflect at a 90 degree angle to the normal axis, nearly co-axial with the laser delivery. In this situation, the exact location of the spark is not as critical as for probe #1, as shown in Figure 43. The use of two fibers in the probe allowed us to align them in a slightly overlapping configuration so that reception could be optimized.

Top view of fibers in probe

Side viewing optical fiber

Copper Tube in Tube Support with optical fibers

Optical fiber in SS tubes

Fiber in probe connected to long fibers with SMA fittings

Figure 43: The beveled optical fibers used to view the emission

Figure 43 shows that these fibers were also packaged in steel tubes and again we used an SMA bulkhead to fasten these fibers to the probe and to the optical fibers transmitting the light up to the spectrometer. The tip of the fiber could be placed at the correct height and aimed in the proper location by threading them into the tube support with that SMA bulkhead. Another feature of this design was that the optical fibers were protected from the environment by the second lens.

As shown in Figure 44, the tube for supplying airflow on the outside of the window was increased in size and positioned directly over the window. This configuration allowed us to produce a laminar flow over the window using a fairly high stream of air traversing across the lens to sweep away any material thrown towards it by the spark. (i.e. 1/8 diameter tube at 60 psi) In the lab we observed the spark to actually flatten near the window due to the laminar air flow that we were using - thus the lens is well protected.

Figure 44: An external view of Probe #2 showing the better air nozzle and the optical fibers behind the lens.

2.1.3.6 Probe #2 Evaluation: The second field evaluation occurred in the Albuquerque area. At this point in the effort, we were planning on deploying the unit at the DOE Hanford facility. It was felt that the soil conditions in Albuquerque were more representative of the Hanford soils than what we would encounter in Vermont. As during the first field test, this effort did not produce a lot of subsurface data, but it highlighted a number of deficiencies in the system design and application.

Unlike the first field deployment, it was relatively easy to assemble the probe into the penetrometer housing, and the LIBS system was operating properly. It became standard practice to deploy the rod to the soil surface, manually place a soil sample in front of the probe, activate the LIBS system, and obtain LIBS data prior to pushing into the ground to insure that the system was operating properly. After the initial check of

the LIBS system at the surface, the sacrificial sleeve would be employed and the probe pushed into the ground. For this field work, we pushed to depths ranging from near surface to about 6 meters.

During this testing, no spark emission characteristic of the soil was obtained when the penetrometer was deep in the ground. We would continue moving the penetrometer up the hole, in the hopes that at some point we would obtain a decent signal. Typically, we would not obtain a signal and there was a better than average chance that the window was dusty and damaged. Over the course of this field test, we tried to diagnose why we were not obtaining a LIBS signal. Was a spark being formed? Were we sparking, but not receiving the emission signal with the optical fiber? Was the laser always damaging the window? The unfortunate reality is that the probe is literally in a black hole and no information is available to diagnose the problem.

In the process of trying to determine what might be wrong, we proceeded to disassemble the probe. Upon trying to remove the last rod from the penetrometer housing, the internal components – the copper tube with the new larger connector, the two reception optical fibers and a plastic air tube - were essentially wedged in place within the rod. The items all fit within the rod internal diameter, but the process of spinning the rods on/off caused the various cables to tangle and get stuck. In order to extricate the last rod from the penetrometer housing, the threads on both had to be stripped. This highlighted the necessity to keep the various items transferring through the rods to as small a diameter as possible, and that the new connector tubes were simply too large. After the probe was fixed on the second day of the field test, we returned to using the smaller connectors on the copper tubes and changed some of the other connections so that more room was available in the probe housing. As for the tube alignment, it was decided to use the original connectors, as shown in Figure 37, and take extra care in keeping the copper tubes pushed to one side within the rods to minimize bending losses.

Over the course of our field testing, we performed multiple evaluations of the probe at the surface using a handheld soil sample and we could effectively spark and receive the emission signal, thus we knew that the LIBS hardware was operating correctly and consistently. We also could verify that a spark was being formed in the hole by re-inserting the probe, without the sacrificial sleeve, into a previous hole. Near

the surface, a spark on the sidewall could be seen and heard. Once the probe was in several feet, the sound of the spark was effectively muffled, thus we could not verify if it was occurring. At best, we would see very small LIBS peaks in the spectral areas where we should see them.

After a series of pushes without much success, we postulated that fouling of the probe and dusting deep in the hole might be our problem. One clue to the problem was that during shallow penetrations, a flow of dust was seen shooting out the top of the hole. In the deeper penetrations, however, it appeared that the air did not have as simple an escape route during our analysis. Thus, the air we were using to keep the window clean was, in fact, creating more of a dust problem. The air was forcing dust to completely fill the space where our analysis was taking place, and probably causing the absorption of both the laser light and any emission possibly created. All of this additional dust would eventually contribute to laser damage of the outer lens. This reasoning explained why the probe worked at the surface but not downhole. By the time the sleeve was removed and data collection started, we had kicked up enough dirt to create these problems. A summary of the results and conclusions from this second field effort are:

- *Probe Assembly:* The probe assembly procedure was better, but there were still space issues which needed to be improved.
- *Laser Damage of Optics:* Damage to the second lens was prevalent due to the dusting environment. This could be improved by reducing the airflow and/or reducing the energy density even further on the lens.
- *Laser delivery:* The tube alignment was improved by the longer connection tubes, but the space required for them was unavailable. For the near surface testing where we could evaluate the laser throughput, we were getting adequate laser power, thus it was not a concern at this time.
- *Air Flow:* The air flow appeared to be too high and the creation of dust was believed to be causing the system to be inoperable.
- *Spark Emission Collection:* The new fiber coupling scheme worked much better than the Probe #1 arrangement. The only issue that arose was

that it was often labor intensive to align the fibers due to how they attached to the probe.

2.1.3.7 Probe #3 Design: A drawing of the third probe and housing is shown in Figure 45. The hardware still utilized the 14.5 mm i.d. copper tubing for laser delivery, but the entire probe assembly was now integrated into one unit. As shown in Figure 46, a single piece of hardware was used to hold the copper tube, first lens, high power mirror, optical fiber, air hose and second lens. One of the underlying difficulties with the first two probes was the mechanical tolerances between the LIBS probe and the penetrometer housing. For the initial probes, it was critical that all of the internal pieces lined up correctly with the final lens that was mounted to the penetrometer housing. This single unit design, on the other hand, removed that requirement by housing all of the optics in the LIBS probe. The penetrometer housing, therefore, only needed an access hole and the high LIBS hardware/ probe housing alignment tolerance was eliminated. Figure 46 shows several different views of the actual probe and the redesigned probe housing. For alignment, this approach is ideal since all alignment variables were removed. Another major change from the previous probe was the removal of the screw threads that enabled movement of the first lens up/down. Additional lab testing revealed that this variable was not required and that proper selection of the focal length of the lenses was all that was required. This made the probe simpler and easier to fabricate.

Figure 45: Drawing of Probe #3

Figure 46: Pictures of Probe #3

To further reduce the potential for laser damage, the second lens was moved even closer to the first lens, so that the area of the laser spot on the second lens was again increased. In this case, the probe used an 80 mm FL first lens and 30 mm FL second lens, which is represented by spot 3 in Figure 42. It was possible to use this lens combination because the spark distance was increased by the new placement of the second lens. This inward placement of second lens forced the movement of the collection optical fibers to the outside of the lens, as shown in Figure 46. In addition, there was not enough room to mount the second lens with a threaded ring threading ring as in the previous probes, therefore, we had to glue the lens directly to the probe.

Another positive result of these changes was the lower dependence upon the airflow to keep the lens clean. Thus, the laminar airflow required when the lens was 2-3 mm away from the spark could be reduced to a low flow to minimize any dust settling on the lens and optical fibers.

2.1.3.8 Probe #3 Evaluation: Primarily for scheduling reasons, the LIBS system was deployed again at the ARA facility in Vermont. Once again, the results were very similar to the previous field deployments. The assembly procedure for the probe was vastly improved with the single unit and the procedures for deploying the hardware in the penetrometer were improved. The probe optics were much more durable with very few failures occurring. As before, the unit would work very well when deployed to the top surface and tested with a pressed standard sample.

Unlike the previous field tests, however, the number of uncertainties in the design had been reduced. When the system did not function during the previous tests, there were several layers of problems that could have been the cause. During this field test, however, we were confident that we had solved any issue with the probe optics, airflow, and reception fibers. When the inability to obtain good down hole data occurred on this test, we were able to isolate and identify the copper tubes as the primary cause. The procedural changes we had made to insure that the copper tubes were well aligned were not sufficient. During one down hole test, for example, we were able to obtain down hole LIBS spectra simply by moving the copper waveguides within the penetrometer rods a very small amount. In real time, we could misalign the tubes and cause the system to not function properly.

One of the causes for the copper tube losses was rooted in the assembly procedure. Since the copper waveguide was 19mm in diameter and the optical fibers and air hose were each about 2-3 mm in diameter, there is not much room within the 25.4 mm i.d penetrometer rods. During assembly, it was very difficult to keep the cables from overlapping when the rods were screwed in place. Once any of the cables crossed, the i.d of the rods would be impinged and friction would cause things to get tangled. The penetrometer operator became proficient at minimizing this during rod assembly, but it was often inevitable. Once the optical fibers and/or air hose got wrapped around the copper tube, it would flex. When the next rod and copper tube was assembled, the flexure would occur again, thus creating a corkscrew pattern for the copper waveguides.

2.1.3.9 Probe #4 Design: Since we had a lot of difficulty fitting the copper tubes and the various cables into the standard 1.75 inch rods, we decided to have 2 inch rods

fabricated for the LIBS system. The 2 inch o.d. rods have a 1.25 inch i.d., so there was plenty of room for the copper waveguide, the optical fibers, and the air hose. Figure 47 shows the new penetrometer housing, with all dimensions.

Figure 47: The dimensions of the new probe housing with a diameter of 1.125" allowed for the LIBS probe

The next development was the design and fabrication of copper-lined stainless steel tubes. The key to the laser delivery system is that the copper has a very high reflectivity at grazing angles for the Nd:YAG laser. Since copper is a very soft metal and susceptible to bending, stainless steel tubes were used to provide strength and rigidity. Figure 48 shows the design of the hybrid tube. The copper was press fit into a stainless tube and the ends were machined into male and female receptacles with 2 inches of overlap. This assembly produced a very straight tube along its length and rigidity of the connection was outstanding. This assembly solved any issue we had with flexure of the copper tubes.

Figure 48: The improved copper waveguide with stainless steel housing. On the right is the lowest tube with the first focussing lens.

The last improvement concerning the laser delivery system was the development of rod inserts to align the laser delivery tubes and the cables running up the penetrometer rods. Figure 49 shows the insert and the positions for each of the components are labeled. This unit was inserted at the top of every penetrometer rod to position the copper tubes at the same location within each rod. The slits in the insert kept the cables in position so that they would not get tangled during the rod assembly, especially when the rod was being spun to screw it to the lower, previous rod.

Figure 49: A picture of the rod insert to align the laser waveguides and control the air hose and optical fibers

These three advancements: 1) the increased rod diameter, 2) the copper lined stainless steel tubes and 3) the rod inserts, created an exceptionally straight beam path for the laser. Laboratory tests with this system showed that we could transmit over 85% of the laser input through a 30 foot assembly. As an example, using an input of 350mJ at the input, we were able to deliver approximately 300mJ.

The probe housing design is shown in Figure 50 and it is not much different than the previous design. It is still a single piece construction to support and pre-align all of the optical components. There are several modifications, however, which improve several deficiencies of the previous design. These modifications were possible because the internal diameter of the lower section of the penetrometer housing was increased to 1.25 inches from 1 inch. The new probe housing is shown in Figure 51 and the larger

diameter at the bottom allowed us to: 1) return back to a screw mount for the second lens (so that it could be easily removed if it got damaged), and 2) place the optical fibers behind the second lens so that they are not exposed to the environment., as shown in Figure 52.

Figure 50: The final LIBS probe with optical path indicated

Figure 51: A picture of the final optical probe

Figure 52: The final LIBS probe moved the fibers behind the lens and returned to the threaded mounting for easy repair.

The last modification we made to the probe was to remove the discrepancy between the diameter of the sacrificial sleeve and the penetrometer housing. In all of the previous probes, the sacrificial sleeve was slightly larger than the penetrometer housing. This difference created a “lip” that would help remove the sleeve upon retraction. One of the effects of this, however, was to add an uncertainty to the exact location of the soil. Since the hole generated by the probe during the push phase would be the size of the sleeve, upon retraction the 1.9 inch diameter probe of the original housing could shift within a 2 inch hole. This doesn’t sound like a lot of difference, but it could decrease the efficiency of the spark/soil interaction. For this probe design, it was decided that the frictional forces on the side of the sleeve were more than adequate to remove it upon retraction, and the “lip” was not required. As a result the sleeve was kept at 2 inches, identical to the probe housing. This effectively extinguished the concern about the location of the soil and the optics were designed accordingly.

There was not any significant changes to the optical design of the probe. The new probe dimensions required that the first lens be a 100 mm focal length and the second a

20 mm focal length. This combination will create a worst case power density on the second lens of $< 0.2 \text{ GW/cm}^2$ and it will create an air spark at about 1.5 cm from the outer surface of the second lens. Figure 53 shows that this design produced a very good working range over at least 1.5 cm. Using the peak area shown in the upper spectra shown in Figure 53 as the figure of merit, the LIBS signal on soil with the probe will peak at a lens to soil distance of 1.3 cm – the exact location of the soil in the present design – and 2mm inside the location of the air spark (shown by the star). The example spectra show that even at the extreme ends of the working range at 0.5 and 2.0 cm, the probe can obtain acceptable spectra.

Figure 53: The working range of the final probe with the location of the air spark indicated. (x-axis in mm)

2.1.3.10 Probe #4 Evaluation: This primary evaluation of this probe design was conducted during the DOE Sandia site test which is detailed in the next section. In general, the probe was used very effectively.

2.2 DOE Field Test

2.2.1 Hanford Site

Over the course of this effort, representatives for the DOE Hanford Site were very interested in the use of the cone penetrometer to evaluate both uranium and chromium in the 300 and 100 Areas. A fair amount of work was conducted during this effort to arrange a DOE Field Test of the penetrometer system at Hanford, but the schedule delays with the system development resulted in an inability to coordinate a test in the available time at the Hanford Site. It was mutually determined by SEA and the Hanford personnel that the system operational issues should be worked out prior to deployment at that Site and an open invitation still exists if the opportunity arises.

In preparation for the Hanford effort, soils from the site were spiked with chromium to establish a calibration curve. Soils with a range of chromium concentrations from 76 ppm to 5250 ppm were fabricated and Figure 53 shows an overlay of the LIBS spectra for those samples. The lower set of curves show a close-up of the first chromium peak and it is seen that there is a very good correlation to the concentration data. In addition, a Workplan was developed and approved for the field test up at Hanford and this document is included in Appendix B.

2.2.2 Sandia Site Description

The Sandia National Labs (SNL) is southeast of Albuquerque, New Mexico, in Bernalillo County. The regions climate is semiarid, with an average annual precipitation of approximately 8 inches. Most of the precipitation occurs as thunderstorms during late summer to early autumn; some snow also falls in the winter. The SNL facilities are within the boundaries of Kirtland AFB. Within SNL are five designated Technical areas and Technical Area III (TA-III) contains the Chemical Waste Landfill (CWL).

Figure 53: Calibration data for Hanford soil spiked with chromium. The top is a wide wavelength range and the bottom shows the variation in intensity of the first chromium peak as a function of chromium concentration.

The CWL was created in 1962 to accept waste chemicals generated by SNL facilities. The landfill was designed to segregate incoming wastes by chemical group to minimize any adverse chemical reactions. Individual disposal pits were excavated from the soil for each chemical group, including oxidizers, reducers, acids, metals, and organic material. Typical pits were about 15 feet wide and 45 long by 15 feet deep, although larger trenches were also created. Figure 54 shows the location of the penetrometer test site in relation to the SNL boundaries and Kirtland AFB.

Figure 54: The location of the CWL on the Sandia National Labs Site

2.2.3 Historical Data

The site has a known chromium contamination, among other waste products. Several different studies were done on the site over the past 25 years, with a fairly recent study on the geochemistry of chromium in the soils at the site.¹⁸ This report presented the results of several subsurface evaluations at the CWL for chromium, and it was concluded that the highest concentrations of chromium at the CWL occur at the near subsurface at a depth of approximately 3 meters, and the background concentration for the area is about 20 - 30 ppm.¹⁹ Since the site does have this known chromium contamination problem, it was decided to evaluate chromium with the LIBS/penetrometer system.

Chromium analysis as a function of depth have been conducted within the CWL using standard borehole extraction and laboratory analysis techniques for total chromium. Figure 55 and Figure 56 show data that were taken along the west edge of the CWL site and Figure 57 shows the data from a borehole in the identical location to our testing.

Figure 55: Chromium analysis as a function of depth for a borehole designated UCAP-3 (data points indicated by triangles)

Figure 56: Chromium analysis as a function of depth for a borehole designated A-7.
(data points indicated by triangles)

Figure 57: Chromium analysis as a function of depth for a borehole close to demonstration site. (data points indicated by triangles)

All three of these borehole evaluations show elevated levels of total chromium in the near subsurface with peaks occurring at about the 10 foot range.

2.2.4 LIBS/Penetrometer Procedures

The physical deployment of the LIBS/penetrometer system can be categorized in the following five areas:

- LIBS assembly in the penetrometer truck
- Daily Set-up of LIBS system
- Probe Deployment
- Data Acquisition
- System Teardown

2.2.4.1 LIBS Assembly in truck: For the initial set-up at the start of a job, the following procedure is followed to set-up the LIBS hardware:

- The LIBS components are placed at the proper location on the truck. For the field work, the power for the LIBS instruments can be supplied by a gas powered generator or, as in the case of the Sandia CWL Site, electrical power was available at the site.
- Once the laser is powered, it must be turned on and warmed-up for ½ hour.
- All of the LIBS components must be connected appropriately and checked.
- The articulated arm is attached to the laser and aligned with the green beam. After the ½ hour warm-up time for the laser, the alignment and power throughput can be checked for the Nd:YAG beam.
- The air hose and two emission collection optical fibers used in the probe must be pre-thread through the rods and the rods assembled onto the rod rack.
- *The above process would be conducted on the first day of the deployment and should take approximately 3-4 hours to complete, not including travel time.*

2.2.4.2 Daily Set-up Once the system as been installed, as described above, the following process would occur on a daily basis:

- The laser is powered up and allowed to warm up for ½ hour.
- The probe (which can be assembled prior to deployment) is installed into the probe housing and can be chunked into the head clamp with the first rod for preliminary testing.
- The spectrometer is wavelength calibrated using a standard light source and the detector parameters are set.
- The repetition rate and power level of the laser are set and the laser power through the articulated arm is checked.
- The entire LIBS system can be checked by sending the laser into the probe head while still in the truck and manually holding a standard in front of the probe lens. For the present deployment, a chrome plated washer and a pressed sample of the Sandia soil were used.
- *This process should take about 45 minutes to accomplish.*

2.2.4.3 Probe Deployment Once the system has passed the daily check the following process is conducted to deploy the probe into the subsurface.

- The probe, with the first rod installed, is chunked into the head clamp
- The penetrometer operator takes the next rod, pulls the slack out of the optical fibers and positions the rod over the head clamp.
- Once in place, a second operator removes the lower dust cap on a copper/stainless tube and the tube is inserted into the lower laser delivery tube.
- The optical fibers and air hose are taped to the laser delivery tube.
- The upper rod is lowered and screwed tight to the lower rod.
- The plastic tube guide is inserted at the top of the new rod.
- The rod assembly is pushed one rod length into the ground
- The process is repeated.

- *At the start of the Sandia test, this assembly process (not including the push time) took 3-3.5 minutes/rod to complete. By the end of the effort, the process took about 2 minutes/rod.*

Note: When the rod string reaches the top of the soil surface, the LIBS system can be checked by bringing a standard sample under the truck, activating the LIBS system, and obtaining LIBS data. This will enable a fix to be made prior to penetration. This was done each time during this present deployment, but would probably not occur as the system performance became more established.

2.2.4.4 Probe retraction/Data acquisition: Once the system has been pushed to the depth of analysis, or refusal, the following process is conducted to obtain data.

- The penetrometer is raised at least a foot to remove the sacrificial sleeve.
- The articulated arm is placed on the laser waveguide
- As a system check, one of the emission collection fibers can be removed from the spectrometer and the laser manually fired. If the laser spark occurs, the LIBS operator will see the spark light through the fiber. This is another check that was routinely done during this test, but might not be conducted as the system performance became more established.
- The detection system is initiated and set in stand-by. It is triggered electronically by the laser when the laser is activated.
- The depth of penetration is recorded
- To start the data acquisition process, the penetrometer operator and the LIBS operator simultaneously initiate the rod retraction and the laser pulsing. The laser is initiated via the laser trigger switch. This trigger starts the following process (refer to Figure 58):
 - the laser is activated by the laser power supply at a 10Hz rep rate
 - at each firing of the laser, the laser power supply sends a trigger pulse, via the Laser Trigger Output line, to the detector electronics.

- using the trigger signal as a reference, the detector electronics activate the detector at the appropriate time via the Gate Pulse line. The light collection by the detector is typically delayed several microseconds after the trigger pulse, then it is activated for about 30 microseconds. This scheme will neglect the continuum light generated at the beginning of the spark.

Figure 58: The LIBS system configuration

- The spark is generated and the emitted light is detected by the optical fibers and delivered to the spectrometer.
- The spectrometer separates the light into a range of wavelengths and transfers the light to the array detector.
- The spectroscopic data is sent back from the detector directly to the system control computer via the I/O line.
- This continues until the penetrometer retraction has reached the end of a rod.

- The LIBS operator and the penetrometer operator simultaneously stop the retraction and data collection. To stop the LIBS data acquisition, the laser is deactivated with the trigger switch.
- The spectral data is transferred to the data analysis computer via a network link. This allows for data analysis during subsequent data collection.
- The new depth of penetration is recorded
- The articulated arm is removed from the tube
- the penetrometer rod is unscrewed, removed and placed on the rod rack
- the optical fiber and air hose are untaped from the laser delivery tube
- the copper/stainless steel laser delivery tube is removed
- The articulated arm is replaced and the process repeated
- *The data collection during retraction takes about 1- 2 minutes and the removal of the rod and resetting the detection system would take about 3-4 minutes for a total of 4-6 minutes per rod.*

2.2.4.5 Daily Shutdown: If the operation is to continue the following day, then the system can be shutdown by simply powering down all of the units and covering the laser unit. *This can be accomplished in 15 minutes.*

2.2.4.6 Project Shutdown: To remove the hardware from the truck, all of the components must be disconnected and the containers sealed for transport. In addition, the optical fibers must be removed from the rod assembly. *This process takes about 1 hour to accomplish.*

2.2.4.7 Data Analysis Time Budget: Using this preliminary data presented above, which is based on the Sandia Field Test described below, it would take about 2.5 hours to deploy the system to a depth of 30 feet, obtain data on retraction, and move the truck to a new location. Thus, using the 30 feet/push assumption, the system could obtain data of about 90 linear feet/day. Using a 15 feet/push assumption, which would take about 1.5 hours to collect data and move the truck, then about 105 linear feet/day could be

accomplished. Both of these calculations would be true for 7.5 hours of pushing on days when the system is not being set-up or torn down.

2.2.5 Sandia Site Test: The on-site schedule for the Sandia test allowed for less than three days to mobilize, take data, and demobilize the equipment at the CWL site. The following is a daily summary of the events and the results of the effort.

Day #1 Log

Time	Description
0800	Prepare truck for mobilization to SNL CWL site
1200	Finish securing LIBS equipment in truck for trip to SNL CWL
1300	Meet escort to site at entrance gate
1330	Continue through security
1400	Arrive at push site, begin setting up LIBS hardware
1830	Exit site

Day #2 Log

Time	Description
0815	Arrive at DOE gate
0830	Arrive at push site
0845	Safety Meeting
0900	Fire up laser and assemble probe
1020	Start loading probe into head clamp, Checked LIBS operation at surface, system operational
1140 - 1202	Insert probe into ground, stop at 17.8 feet
1210	Retract, remove sleeve. Upon removal the penetrometer rods became stuck in the rod scraper underneath the truck. The probe needed to be periodically pushed deeper and retracted several times during the process to fix the problem.
1447	The problem with the penetrometer was fixed. LIBS analysis attempted and no signal produced. Assumed that the re-insertion of the unprotected probe up and down the hole fouled the optics.
1500	Removed probe from ground. Replaced outer window on probe due to laser damage. At this time, it was noticed that the compressor being used for the air hose in the probe was injecting moisture into the line and onto the outer lens of the probe. An in-line filter was placed into the air supply line to remove all moisture. Moisture probably caused lens damage.
1600	Threaded rods for a second push
1647	Thunderstorms in area. Break for day.

Day #3 Log

Time	Description
0715	Arrive at DOE Gate
0730	Arrive at push site
0750	Safety Meeting
0815	Probe assembled and loaded into head clamp. Pushed to top soil surface, LIBS system operational
0830	Calibrate spectrometer
0835 - 0840	Push probe to 4.75 feet – Penetration #1
0842 - 0854	Activate LIBS system, retract and obtain LIBS data for about 2 rods
0907	Move to second location
0930 - 0937	Push probe to 8.8 feet (refusal) – Penetration #2
0939 – 0956	Activate LIBS system, retract and obtain LIBS data for about 3 rods Probe window dusted near end of data collection, wiped clean
1005	Move to third location
1057 - 1115	Push probe to 12.5 feet (refusal) – Penetration #3
1125	Activate LIBS system, retract and obtain LIBS data for brief time
1127	Still retracting, but LIBS signal not being obtained
1200	Probe exits ground. It appeared that the probe punctured through a highly acidic, sludge material. The external housing and the internal probe were both immediately turning green from the acidic sludge. The probe was quickly removed, cleaned and washed.
1410	Moved to fourth location
1427 – 1445	Push probe to 15.5 feet (refusal) – Penetration #4
1445 - 1459	Activate LIBS system, retract and obtain LIBS data for about 3 rods
1460	All power on Sandia Site lost
1526	Hooked up generator for truck and LIBS unit
1550 - 1600	Push probe to 10.5 feet (refusal) – Penetration #5
1600 - 1611	Activate LIBS system, retract and obtain LIBS data for about 2 rods – outer lens dusted
1623 - 1628	Re-Inserted probe into same hole as Penetration #5 to 7.8 feet- Penetration #6 - Due to the dusting of the window on the previous push, this push conducted without any airflow over the window
1629 - 1638	Activate LIBS system, retract and obtain LIBS data for about 3 rods Outer lens did not get dusted.
1710	Pack up LIBS hardware
1730	Leave Sandia Site

2.2.6 Sandia Site Test – Location of Penetrations: The locations of the penetrations referred to during Day #3 are provided in Figure 59. The chromium data from the borehole shown in the Figure was shown previously in Figure 57.

Figure 59: The location of the LIBS penetrations on Day #3

2.2.7 Sandia Site Test – LIBS Data: As described in the procedures above, it was a typical practice to test the LIBS unit prior to subsurface deployment on a chrome standard, such as a chrome plated washer, and also a pressed sample of the Sandia surface soil. Figures 60 shows the LIBS spectra of the chrome standard, which will also contain iron lines, and the Sandia surface soil. *Each of these curves represent a single spectra.* It should be noted that the surface soil concentration was determined to be about 30 ppm. and the soil spectra does exhibit small peaks in the chromium region.

Figure 60: A spectra of a chrome washer and Sandia soil (displaced for clarity) taken with the system at the ground surface prior to penetration

2.2.8 LIBS Spectra for each penetration:

LIBS data for chromium was obtained in all of the penetrations conducted on Day #3 of the field test. Figures 61 through 66 show an example LIBS single spark spectra and a graph depicting the qualitative chromium level as a function of depth obtained for each of the penetrations made on Day #3. The qualitative data shown was determined by evaluating the peak height of one of the chromium peaks after baseline subtraction. Not all of the sampling locations contained high levels of chromium, but we did obtain good spectra for each location. (Note: All of the data was obtained with the laser operating at 10 Hz, a 1200 grooves/mm grating with a 2 microsecond delay and 32 microsecond detection window for the detector. Again, all of the spectra were obtained with a single spark)

Figure 61(a): Example spectra from Penetration #1 with a chrome standard comparison. Note the absence of chromium contamination

Figure 61(b): Qualitative chromium level as a function of depth for penetration #1.

Figure 62(a): Example spectra from Penetration #2 with a chrome standard comparison. Note the strong chromium contamination.

Figure 62(b): Qualitative chromium level as a function of depth for penetration #2.

Figure 63(a): Example spectra from Penetration #3 with a chrome standard comparison. Note the strong chromium contamination.

Figure 63(b): Qualitative chromium level as a function of depth for penetration #3.

Figure 64(a): Example spectra from Penetration #4 with a chrome standard comparison. Note the medium chromium contamination.

Figure 64(b): Qualitative chromium level as a function of depth for penetration #4.

Figure 65(a): Example spectra from Penetration #5 with a chrome standard comparison. Note the absence of chromium contamination.

Figure 65(b): Qualitative chromium level as a function of depth for penetration #5

Figure 66(a): Example spectra from Penetration #6 with a chrome standard comparison. Note the absence chromium contamination

Figure 66(b): Qualitative chromium level as a function of depth for penetration #6.

2.2.9 Sandia Site Test – Calibration Procedure:

In order to calibrate the data from the Sandia site, we obtained a bucket of soil from the test location and spiked it to different chromium levels using chromic acid, the most likely source of the contamination at the site. After the soil was spiked, a portion was evaluated utilizing standard laboratory techniques and a portion was evaluated with the LIBS system in the lab. The field data was then re-evaluated using the calibration and the plots updated to reflect quantitative numbers. Table 14 shows the different spike levels and the standard GFAAS/ICP laboratory data for the spiked samples and the base soil.

Table 14: The spiked levels and actual levels for the Sandia calibration set

Sample	Added Concentration, ppm	Actual Concentration, ppm
Sandia Baseline Soil	0	30
Sandia Soil #101	50	77
Sandia Soil #102	100	130
Sandia Soil #103	200	220
Sandia Soil #104	300	300
Sandia Soil #105	500	390
Sandia Soil #106	1000	890
Sandia Soil #107	2000	1840
Sandia Soil #108	5000	4560
Sandia Soil #109	25	54

Using the LIBS/CPT probe in the laboratory, the calibration soils were evaluated with the same system parameters as used in the field. Figure 67 shows the LIBS spectra of the spiked Sandia samples (normalized to the Ca peak), and it is clear that the LIBS spectra correlate well with the various chromium levels. The two varying peaks are the 425.45nm and the 427.49 nm Cr peaks.

Figure 67: LIBS spectra of the spiked Sandia calibration standards

Figure 68 is a graph that shows that the calibration model created using the data from Figure 69. Since the data falls on the 1:1 line, it can be used to accurately predict the unknown concentration of chromium in the Sandia soil. The specific information on the data analysis techniques developed and used for this effort will be discussed in the next section.

Figure 68: The PLS predicted value as a function of actual Cr concentration.

Using the PLS calibration model, the chromium concentration as a function of depth for Rods #2 and Rods #4 are shown in Figure 69 and Figure 70, respectively. Rod 2, specifically, shows a very well defined chromium-rich layer at about 8 feet. As seen, the depth resolution of the data is well below 0.1 foot.. In general, the LIBS system is obtaining spark data with a resolution of < 1mm. In practice, however, the data will be discarded and/or averaged, resulting in a reduced depth resolution closer to 3-4 mm. This depth resolution level is most likely more than adequate for characterization and remediation activities. It should also be noted, in both Figure 69 and Figure 70, that the system will have gaps in the data that correspond to the removal of rods. Reduction of the size of this gap was not addressed during this effort, but can be reduced by minimizing the movement between rods.

The data from Penetration #2 can be compared to the historical data shown in Figure 57, since the sampling locations were in very close proximity. Figure 69 shows a Cr concentration of nearly 1200 ppm at 8 feet below the surface and Figure 57 shows very similar numbers with a level of about 2000 ppm at 10 feet. In addition, we had been detecting spectra with Cr peaks in Penetration #3 prior to coming in contact with an acidic sludge at about 11 feet. It is apparent that along the line formed by Penetration #2, #3 and the borehole, there is a chromium-rich layer at about 8-10 feet in depth.

Figure 69: Quantitative Cr concentration as a function of depth for Penetration #2

Figure 70: Quantitative Cr concentration as a function of depth for Penetration #4.

2.2.10 Sandia Site Test Performance:

In general, the performance of the system was very good. The issues with the laser delivery system that occurred in the previous field test were non-existent, with the alterations made for this test completely solving the problems. Dusting of the probe was the primary issue that was not completely resolved. The early designs of the probes were heavily dependant upon the use of an airflow to protect the last lens on the probe. The most recent design, however, helped minimize the requirements but it still utilized a small flow that was expected to help reduce window fouling. As it turns out, we still did create dusting of the window which reduces the laser energy and the spark emission collection. On the last push of Day #3, however, we had just enough time to re-enter the previous hole and take data without any airflow at all. The push resulted in no dusting of

the final window, thus, the issue of dusting may simply be resolved by not using any air at all. The latest optical design lowered the energy density on the last window considerably and moved it as far as possible away from the spark, so minor incidental dusting may be tolerable. Future efforts in this area will have to explore this issue.

2.2.11 Cost Data:

Based on the Sandia Site test, a cost analysis was performed for the deployment and operation of a CPT/LIBS system. This analysis was conducted by the DOE as part of the Innovative Technology Summary Sheet (ITSR). An excerpt from this Draft is presented in Appendix C.

2.3 LIBS Data Analysis

2.3.1 Standard LIBS data analysis:

In the simplest terms, the concentration of an analyte is obtained as shown in Figure 71. A LIBS spectrum is obtained, it is evaluated with a calibration model that relates the characteristics of the spectrum with the concentration of the analyte within the sample, and a concentration is calculated.

QUANTITATIVE ANALYSIS

Figure 71: The quantitative analysis of LIBS spectra utilizes a calibration model

The standard method of determining the analyte concentration from a LIBS spectrum is based on the use of the ratio of two peaks from the sample, one from the element of interest and another from a prominent component in the sample, as shown in Figure 72 where peak A is the standard and peak B is from the analyte of interest. 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 the entire spectrum may not be constant for a given concentration of contaminant. As shown along the top of Figure 72, the spectral intensity can change for multiple runs or for individual sparks, thus simple observation of just the peak areas or heights of the analytes of interest may be misleading. 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 72: The typical method of calibrating LIBS data is to ratio the area or heights of the analyte emission and that of another element in the spectra.

As shown in Figure 73, the typical calibration data is obtained by using a series of soils with varying concentrations of the analyte of interest. The soil samples are then evaluated by a standard method and with LIBS analysis. Once the spectra are obtained, they may be pre-processed by averaging or baseline correcting, for example, then the ratio of the peak areas are determined. All of this data can then be used to construct the lower graph in Figure 73 which relates the area ratios to the concentration, which can then be used to evaluate a sample with an unknown concentration simply by determining

the areas of the representative peaks. The peak area ratios are usually determined for an average spectrum that is an accumulation of a large set of sparks, typically 10 – 100. The use of numerous sparks co-added or averaged helps minimize the variations associated with single sparks.

Figure 73: Typical method for calibrating LIBS for quantitative analysis

This method has a number of shortcomings when it is used for in-situ field measurements. The primary concern with using the peak ratio method in the field, is that very little is often known about the compositional variations of the soil. Compositional variations can cause the calibration method to fail and often provide data that is highly erroneous. This will occur, for example, when the element that is being used as the reference changes drastically. One of the issues in the Luckey FUSRAP effort, which is

detailed in Appendix A, was that the calibration for beryllium was based upon the ratio of a beryllium peak to a nearby aluminum peak. It was apparent that in certain areas of the test site, the composition of the soil changed to a low-aluminum composition. Since the area calculation was automated, this produced values for beryllium that were off scale. This deviation of the soil composition from that used in the calibration model will cause most data analysis techniques to falter, but the issue was in the ability of the user to know when the data was not good. Since only two peaks are used, it is difficult to get a clear picture of what might be going wrong or simply that the data may not be valid.

2.3.2 Multivariate LIBS Data Analysis:

At the start of the cooperative effort with the EERC, it was mutually agreed that we would cooperate on the development of new data analysis techniques that would attempt to improve upon the present methods. The key was in the ability to have a data analysis system that could be used to calculate the concentration of an analyte in an unknown soil, but also be able indicate when the soil was not adequately modeled by the calibration set. This would allow the data to be evaluated under a different model or be discarded.

Partial least squares (PLS) regression is a technique which has been applied in molecular spectroscopy applications²⁰. However, it has not been widely applied in atomic spectroscopy due to the limited number of wavelength channels usually measured. For example, conventional atomic spectroscopic techniques such as ICP or GFAAS typically utilize a single analyte peak along with a baseline region to measure analyte concentration. For well characterized sample matrices such as those encountered in the analytical laboratory, single peak analyte prediction is more than adequate. In the case of field screening measurements for ex- and in-situ subsurface contamination characterization, little knowledge is obtained on the sample matrix prior to analysis. Therefore, application of more statistically robust methods such as PLS or principle components regression (PCR) can provide an added confidence to field screening measurements. PLS has many inherent advantages compared to univariate regression methods. All relevant variables are included in the PLS model which implies that

calibration even in the case of interferences is possible. PLS also makes possible outlier detection during the prediction of new unknown samples. Outlier detection identifies samples not accounted for by the PLS model, which will not be predicted, in contrast to the case in univariate calibration, where one cannot distinguish whether a sample is of the same kind as the calibration set or not. Additionally, when applying field techniques such as LIBS, instant feedback as to the quality of the data being collected allows the proper weight to be applied to the data when using it to make decisions involving more detailed site characterization and cleanup. Field analytical instruments are typically operated by technicians who may not have the expertise to examine and interpret raw data while on site. Conventional calibration techniques for LIBS call for expert personnel to ascertain the quality of data collected. Development of multivariate calibration techniques for LIBS allows instant feedback to the instrument operator that is easily interpreted by technician level personnel on the quality of the data collected and the prediction of analyte quantities.

The data analysis method consists of three primary phases: 1) calibration, 2) validation, and 3) prediction; and Figures 74, 79 and 80 detail the steps comprising these three phases. The calibration phase models the relationship between the spectral and chemical characteristics of the soils. As shown in Figure 74, the calibration phase starts with the fabrication of a soil sample set that represents the soil type that will be evaluated in the field. The set is split, with a portion being used to evaluate with standard chemical analysis techniques, and a portion evaluated by LIBS. It is important that the LIBS unit be operated with the same parameters that will be used in the field. As mentioned above, the present techniques often co-add or average numerous spectra. A problem with this method is that information is lost when this is done. For the present application, depth resolution will be lost if 100 spectra are averaged together, since we are moving vertically during the analysis. In addition, spark quality information is being lost since “bad” sparks are simply averaged into the data. A key component to the multivariate modeling is that each spark will be evaluated individually.

Figure 74: Details of the calibration phase for the LIBS data analysis method

After the LIBS emission spectra of a set of soils with different analyte concentrations are obtained, they will be pre-processed (i.e. baseline correction, wavelength check/calibration, mean centering) and evaluated using multivariate modeling techniques with the concentration values determined by the laboratory technique. In the PLS regression, independent variables (e.g., spectra) are arranged in a rectangular matrix (X), where each row corresponds to a sample and each column to a specific wavelength. The dependent variable (e.g., concentration) is arranged in a vector (Y). The concentration vector Y has a number of elements equal to the number of rows (samples) in X .

The result of the PLS algorithm is a model of the rectangular matrix X given by a (low) number of latent variables, each being characterized by a score vector and a loading vector. The scores and loadings obtained from PLS allow any spectrum in the set to be approximately reconstructed depending on the number of latent variables included in the

spectrum reconstruction. From a mathematical perspective, the loadings can be viewed as an orthonormal basis for the multidimensional vector space that describes the set of spectra (calibration space). The scores obtained for each sample spectrum are thus the amount of each loading needed to reconstruct the spectrum.

This can also be explained with the use of Figure 75. The PLS regression will evaluate the set of spectra and determine the loadings and scores for the soils as a function of the analyte concentration. As shown in Figure 75, the loadings represent a series of components that, when weighted by the scores, can be used to reconstruct the original spectra. Depending upon the quality of the loading and score set, the original spectra may not be reconstructed perfectly, resulting in a residual. If the model is perfect, the residual will be zero.

Figure 75: The loading and scores represent the principle components and the weight of each component of the original spectra.

As shown in Figure 75, there can be a number of loadings, or latent variables, that will be determined by the model. An example of this is shown in Figure 76, where the first three principle components of the spectrum of a chromium contaminated soil model the sample very well. It is seen that the 1st principle component models the chromium and the 2nd and 3rd components model the base soil. It is often the case that one of more of the loadings model the noise of the spectra, thus it can be readily removed from the analysis. For this data set, the scores for the first principle component relates very well to the chromium concentration in the soils. as shown by Figure 77.

Figure 76: An example of (a) a chromium- contaminated soil spectrum and (b) the principle components of a Cr-contaminated soil

Figure 77: The correlation of the 1st principle component to the Cr concentration

In order to evaluate the number of latent variables needed to provide a PLS model for the sample set which estimates analyte quantities, the prediction residual error sum of squares (PRESS) is computed. Figure 78 shows the PRESS results for a Pb in soil calibration developed for a LIBS unit. The number of latent variables which may best approximate the calibration space is usually taken to be where the a plot of PRESS versus number of latent variables reaches a global minimum. In the example given, this is at 17 latent variables. Therefore, the calibration space contains 17 loadings or dimensions. Scores for each sample are then computed by projection of each sample on to each loading. Thus each spectrum is then estimated by a sum of the loadings weighted by their respective scores.

Figure 78: An example of a PRESS vs. number of latent variable plot for a Pb-contaminated soil.

Referring back to Figure 74, once the multivariate model has been determined that relate the spectra to the chemistry, then prediction algorithms can be applied. The next stage of the data analysis method development is the validation of the model. Figure 79 shows the steps in this phase. In this instance, a second set of samples are evaluated with the LIBS system and the standard laboratory method. The spectra are input into the prediction algorithm which outputs a concentration value along with data quality indicators. There are a number of different indicators, with one example being the residual. A high residual will indicate that the model cannot adequately reconstruct or predict the spectra input. If the results from the LIBS and standard technique agree well, then the model is validated. If there are inconsistencies, the model may need to be modified or the validation soils are not represented well by the soils used in the calibration/model development.

The last area to be discussed is the prediction phase. In the prediction phase, an unknown sample is evaluated with the LIBS system, processed and evaluated by the model algorithms. As Figure 80 shows, an advantage to this multivariate analysis is that

Figure 79: Details of the validation phase for the LIBS data analysis method

method will produce the information on whether the unknown spectra “fits” the model. This type of information cannot be ascertained by univariate calibration.

The data obtained during the Sandia test provides a good example of the use of the data quality indicators. Figure 81 shows the quantitative results for Penetration #2 where a high concentration layer of chromium was detected. Figure 82 shows the

Figure 80: Details of the prediction phase for the LIBS data analysis method

corresponding residual and Figure 83 the data quality the for that data set. A data quality value of 1 and a residual of 0 indicates that the spectra was perfectly modeled by the calibration algorithm. A low residual will typically correspond to a high spectrum quality, but that is not always the case. For example, at a depth of 8 feet, where the Cr value was at its highest, it is seen that the residual is low, but not 0. The Spectrum Quality, is also less than perfect at a value of about 0.75. This may reflect a sample that was high in chromium concentration, thus the principle components relating to chromium would factor highly in the prediction, but was in a slightly different matrix than the soils used for the model construction, thus there was a slight residual and spectrum quality was lowered. Based on the results of the very next penetration, where it was pushed through a

sludge-like acidic material, the matrix of the soil at the depth of 8 feet in Penetration #2 may have been a more of a sludge than dry soil. Another observation is the few data points that show a very high residual in Figure 82. It is seen that the few residuals near 1 occur at the beginning of a new rod. The detector on the LIBS/CPT system often “misses” the first several sparks for some unknown reason. These missed sparks result in a spectra that is usually far different than the rest of the sparks. As a result, the prediction could not occur and a high residual would be attained. There are many other factors involved, but this shows the additional analysis that can be attained with the multivariate technique.

Figure 81: The concentration as a function of depth for penetration#2 from the Sandia test

Figure 82: The spectrum residual as a function of depth for penetration #2 from the Sandia test

Figure 83: The spectrum quality as a function of depth for penetration #2 from the Sandia test

An example of how this information is used to reject low quality spectra or spectra that are not well modeled is shown in Figure 84. The figure shows spectra from those taken in-situ for Penetration #2 at Sandia with the LIBS/CPT probe. The upper spectrum shows one selected on the basis of the spectrum quality test and the lower spectrum shows one rejected on the basis of the spectrum quality test. Note that a conventional LIBS calibration based on the area under the Cr peak would have predicted a concentration for the sample which was rejected by the spectrum quality test.

2.3.3 Comparison of Standard vs. Multivariate with LIBS /CPT Data:

A comparison of the conventional approach and the improved multivariate approach was conducted on the Sandia Test data. As discussed in the Sandia test description, the calibration was accomplished by collecting LIBS instrument response data for samples of Sandia soil spiked with chromium. Chromium concentrations in each of the soil samples to be used for calibration were verified by conventional analysis techniques and Table 14 listed the amount of Cr added to the baseline soil for each of the calibration samples along with the actual concentration.

Figure 84: An example of spectrum that were accepted and rejected by the multivariate data analysis method.

The LIBS data on each of the calibration samples was collected and it consisted of 250 spectra where each corresponded to the emission from a single laser spark. For the conventional approach, an average spectrum for each concentration of the 250 single spark spectra was calculated to develop the instrument calibration for Cr. For the conventional approach, the peak area of the Cr peak at 425.45nm was used for the analyte and the area of an Fe peak at 438.36 nm was used as the reference. The calibration derived from the sample set provided an extremely non-linear relationship between instrument response and Cr concentration as depicted in Figure 85. The data for a second Cr peak at 427.49 nm was also used and the results were identical to that shown in Figure 85.

Figure 85: Predicted versus actual Cr concentration for conventional LIBS/CPT calibration approach (Sandia soil samples)

An improvement in the calibration for the LIBS/CPT instrument was accomplished by the application of the multivariate calibration techniques. For the application of the LIBS/CPT to measurement of Cr in soil, a full spectrum calibration model was developed using the Sandia soil calibration set listed in Table 14. The improved LIBS calibration based on PLS regression which used the entire measured spectrum (700 to 1000 wavelength data points) for each sample to predict analyte concentration, whereas the conventional LIBS calibration techniques relied on a single analyte peak (typically 15 to 25 wavelength data points) to predict the concentration in samples. Figure 86 shows a LIBS calibration model for Cr in Sandia soil using PLS regression. Comparison of the conventional versus the PLS approach to calibration shows a significant improvement in the ability of the LIBS/CPT to estimate the quantity of Cr in Sandia soil over a wide range of concentrations (i.e. 15 to 4500 ppm).

Figure 86: Predicted versus actual Cr concentration for improved LIBS/CPT calibration approach (Sandia soil samples)

A similar study was conducted on some soils doped with Pb using a small, portable LIBS instrument. In this instance the calibration again showed an improvement when PLS was used. Figure 87 shows a comparison of the calibration and Figure 88 shows the error for each data point for the two methods.

Figure 87: A comparison of conventional and PLS calibration techniques for Pb in soil

Figure 88: A comparison of conventional and PLS calibration errors for Pb in soil for the data in Figure 87.

3.0 Conclusions

There are a number of brief conclusions which can be drawn from this effort concerning the LIBS system design, the probe design, the data analysis techniques and the overall performance of the system. The goal of this effort was to develop a commercially viable system that can detect for the presence and/or concentration of heavy metals in the subsurface. The following conclusions address whether these goals were met with this prototype development and what improvements could be made to reach the intended goal.

LIBS system design: The LIBS system, which consisted primarily of the laser, laser delivery articulated arm, spectrometer and detector, was well suited for the intended application. The components were effectively packaged for field use and all performed as expected for this prototype version. For a commercial system, however, we would look to re-design some aspects and update some components to reflect either newer technology or better hardware than what was available at the time of the prototype development. In addition, the overall size and weight of the system should be reduced to better suit field deployment of this system with other devices. As shown in the report, the LIBS hardware consumed much of the available space in the truck.

The laser and the laser packaging, for example, was originally designed to launch into optical fibers. When the hollow waveguide laser delivery system was adopted, the articulated arm system was required to deliver the laser to the penetrometer. The arm is a rugged device, but would be inappropriate for a continuously used field system with operation by field technicians. The maintenance required for alignment in the field would not be advantageous, thus a re-designed launch that delivers the laser directly down the probe without the use of a sophisticated delivery arm would be more acceptable. Due to the use of the hollow waveguides, we obtained much more laser power at the soil surface than we originally anticipated, thus a lower power, smaller laser could be used.

Another LIBS system improvement would be to utilize a newer detector system that does not require as much support electronics. There are commercially available detectors with identical performance that can be used that do not require external

electronics. The hardware shown in Figure 11, therefore, would be eliminated. We have also concluded that the new multivariate data analysis developed may reduce the requirements of both the detector and the size of the spectrometer. Work done by the EERC with a smaller, less expensive LIBS system, supplied to them by SEA under an equipment loan agreement, showed that lower resolution spectra can be effectively evaluated with the more robust data analysis technique. The multivariate model can better handle peaks that overlap, thus a smaller, cheaper spectrometer may be used. A second generation LIBS system, therefore, could be designed that reduces the number of containers to two, one for the laser and a second for the spectrometer, detector and computer.

LIBS Probe Design: The final probe design for this system proved to be effective in obtaining LIBS spectra in the subsurface. The single piece design that integrated, and pre-aligned, all of the optics was a critical aspect of its success. The probe design exploited several innovative components that we believe were instrumental in the success of the probe. The most important innovation of this effort was the use of the hollow waveguides for the laser delivery. This simple waveguide enabled the delivery of very high laser powers to the probe, more than could have been expected from an optical fiber or a laser mounted in the penetrometer. The end result was simple system that exhibited a very good lens-to-sample working range. The second innovation was the use of side-looking fibers which exhibited excellent emission collection efficiency and were immune to changes in lens-to-sample distance. The only outstanding issue which must be developed further is use of air for keeping the dust off the optics. A result of the successful field test at Sandia indicate that elimination of the airflow may be the answer to this issue, but must be investigated further.

Data Analysis Technique: The use of multivariate techniques for the evaluation of the LIBS spectra was another positive result of this effort. The key to this method of analysis was that it enabled the evaluation of each spark individually so that outliers could be identified. The removal of sparks that do not surpass a quality threshold will improve performance and minimize misleading results. Another conclusion from the development

of this methodology was that the hardware performance requirements could be relaxed – specifically the detection system. As stated above, the improved capability of the multivariate technique to “pull out” the principle components from the soil spectra, reduce the resolution requirements of the spectrometer.

One of the shortcomings of the data analysis methods developed and used for this effort – and this is also true for the standard methods – is that there must be a knowledge of the soil type prior to effective LIBS analysis. In the future, we must work towards isolating the effects of soil characteristics on the LIBS signal and develop field analysis techniques that apply to multiple types of soils, thus true “unknowns” could be evaluated. In addition, as our field experience with the system increases, a well defined user interfaces for the software should be developed.

Overall System Performance: Based on the field test at the Sandia CWL, this LIBS/CPT heavy metal subsurface analysis system development was a success. The system was capable of detecting the concentration and vertical extent of chromium over a wide range of concentrations with a standard CPT rig. In field and lab testing the system could evaluate both Pb and Cr at concentrations well below the EPA’s SSL’s indicated in the introduction.

At this point in the system development, improvements to the system will occur as more field deployments are conducted. The commercial success of this system will hinge upon reducing the size, weight, and overall complexity of the system. We have identified the majority of the challenges in front of us to make the commercialization of this technology a reality. As a result of this effort, SEA has developed a field portable LIBS system that can be used to evaluate surface samples. Basic information on this unit, which is being sold under the SPARK I.D.TM name, is provided in Appendix D.

References

- 1 Allen, H.E., Haung, C.P., Bailey G.W., Bowers, A.R., Metal Speciation and Contamination of Soil, Lewis Publishers, Boca Raton, 1995
- 2 Heavy Metal soil contamination at U.S. Army Installations: Proposed Research and Strategy for Technology Development, R.M. Bricka, et. al., Technical Report TA7 W34 no. IRRP-94-1, March 1994.
- 3 This information obtained from the WWW at <http://www.pnl.gov/stcg/needs.stm>
- 4 This information obtained from the WWW at <http://www.pnl.gov/stcg/needs.stm>
- 5 This information obtained from the WWW at http://wylie.inel.gov/INEELSTCG/num_nam.asp
- 6 This information obtained from the WWW at <http://www.doeal.gov/stcgweb/96pxdd2.htm>
- 7 This information obtained from the WWW at <http://www.srs.gov>
- 8 This information obtained from the WWW at <http://www.pnl.gov/stcg/subsurf/riss15.stm>
- 9 This information obtained from the WWW at <http://www.srs.gov>
- 10 Recommendations on the Development of Chemical Sensors and Field Deployable Instrumentation for DOE Needs
- 11 Source: Market Study to Determine Needs and Present Usage of Chemical Sensor Systems for Environmental Analytical Applications, Final Report, The Unimar Group, Ltd. May 1996. Submitted to CMST Crosscutting Program, DOE, Ames, IA 50011-3020
- 12 (Bratton, et al., 1993; Gildea, et al., 1995; Montgomery, et al., 1996; Farrington and Bratton, 1997).
- 13 This information obtained from the WWW at <http://aec-www.apgea.army.mil:8080/prod/usaec/et/scaps/heavym.htm>.
- 14 Private communication, Mr. Brian Miles, USAWES
- 15 Data taken from "Guide to ARC Optical Systems" Acton Research Corporation
- 16 Data taken from a 3M Specialty Optical Fibers Specification Sheet
- 17 "Analysis of solids using Laser-Induced Breakdown Spectroscopy and Double-

-
- Pulse Excitation”, A.E. Pichahchy, H.K. Thornquist, D.A. Cremers, S.J. Saggese, to be published.
- 18 “Chromium Geochemistry in Calcareous Soils, G.L. Stein USDOE, ER/WM OTD and Sandia National Labs, December 8, 1994
- 19 ibid, page 41
- 20 The following references apply:
- R. Westerholm and H. Li, A Multivariate Statistical Analysis of Fuel-Related Polycyclic Aromatic Hydrocarbon Emissions from Heavy-Duty Diesel Vehicles *Environmental Science & Technology*, vol. 28, pp. 965-972, 1994.
- E.V. Thomas and D.M. Haaland, Comparison of Multivariate Calibration Methods for Quantitative Spectral Analysis *Analytical Chemistry*, vol. 62, pp. 1091-1099, 1990.
- E.V. Thomas, A Primer on Multivariate Calibration *Analytical Chemistry*, vol. 66(15), pp. 795A-804A, 1994.
- S. Sekulic, M.B. Seasholtz, Z. Wang, and B.R. Kowalski, Nonlinear Multivariate Calibration Methods in Analytical Chemistry *Analytical Chemistry*, vol. 65, pp. 835A-845A, 1993.
- G.D. Schrieve and A.H. Ullman, Carbon Number Prediction from Herschel-Infrared Spectra Using Partial Least-Squares Regression *Applied Spectroscopy*, vol. 45, pp. 713-714, 1991.
- M.M.A. Ruyken and J.A. Visser, On-Line Detection and Identification of Interferences in Multivariate Predictions of Organic Gases Using FT-IR Spectroscopy *Analytical Chemistry*, vol. 67, pp. 2170-2179, 1995.
- Y. Li-shi and S.P. Levine, Fourier Transform Infrared Least-Squares Methods for the Quantitative Analysis of Multicomponent Mixtures of Airborne Vapors of Industrial Hygiene Concern *Analytical Chemistry*, vol. 61, pp. 677-683, 1989.
- X. Hong-kui, S.P. Levine, and J.B. D'Arcy, Iterative Least-Squares Fit Procedures for the Identification of Organic Vapor Mixtures by Fourier Transform Infrared Spectrophotometry *Analytical Chemistry*, vol. 61, pp. 2708-2714, 1989.

-
- W.G. Hansen. Group information- and application of PCA/PLS. In: *Near Infra-Red Spectroscopy- Bridging the Gap Between Data Analysis and NIR Applications*, eds. K.I. Hildrum, T. Isaksson, T. Naes, and A. Tandberg. New York: Ellis Horwood, 1992.pp. 29-34.
- D.M. Haaland, R.G. Easterling, and D.A. Vopicka, Multivariate Least-Squares Methods Applied to the Quantitative Spectral Analysis of Multicomponent Samples *Applied Spectroscopy*, vol. 39(1), pp. 73-84, 1985.
- D.M. Haaland and E.V. Thomas, Partial Least-Squares Methods for Spectral Analyses. 1. Relation to Other Quantitative Calibration Methods and the Extraction of Qualitative Information *Analytical Chemistry*, vol. 60, pp. 1193-1202, 1988.
- D.M. Haaland and E.V. Thomas, Partial Least-Squares Methods for Spectral Analyses. 2. Application to Simulated and Glass Spectral Data *Analytical Chemistry*, vol. 60, pp. 1202-1208, 1988.
- P. Geladi and B.R. Kowalski, Partial Least-Squares Regression: A Tutorial *Analytica Chimica Acta*, vol. 185, pp. 1-17, 1986.
- A. Garrido Frenich, M. Martinez Galera, J.L. Martinez Vidal, and M.D. Gil Garcia, Partial Least-Squares and Principal Component Regression of Multi-Analyte High-Performance Liquid Chromatography with Diode-Array Detection *J.Chromatography*, vol. 727, pp. 27-38, 1996.
- F.X. Garcia, L. De Lima, and J.C. Medina, Determination of Methanol and Methyl tert-Butyl Ether in Gasoline by Infrared Spectroscopy using the CIRCLE Cell and Multivariate Calibration *Applied Spectroscopy*, vol. 47, pp. 1036-1039, 1993.
- I.E. Frank and J.H. Friedman, A Statistical View of Some Chemometrics Regression Tools *Technometrics*, vol. 35, pp. 109-135, 1993.
- A. Espinosa-Mansilla, F. Salinas, M. del Olmo, and I. de Orbe Paya, Determination of Synthetic Food Antioxidants in Multicomponent Mixtures Using UV-Visible Spectrophotometry and Partial Least-Squares Calibration *Applied Spectroscopy*, vol. 50, pp. 449-453, 1996.
- J.B. Cooper, K.L. Wise, J. Groves, and W.T. Welch, Determination of Octane Numbers and Reid Vapor Pressure of Commercial Petroleum Fuels Using FT-Raman

Spectroscopy and Partial Least-Squares Regression Analysis *Analytical Chemistry*, vol. 67, pp. 4096-4100, 1995.

J.B. Cooper, P.E. Flecher, T.M. Vess, and W.T. Welch, Remote Fiber-Optic Raman Analysis of Xylene Isomers in Mock Petroleum Fuels Using a Low-Cost Dispersive Instrument and Partial Least-Squares Regression Analysis *Applied Spectroscopy*, vol. 49, pp. 586-592, 1995.

J.P. Conzen, J. Burck, and H.J. Ache, Determination of Chlorinated Hydrocarbons in Water by Fiber-Optic Evanescent Wave Spectroscopy and Partial Least-Squares Regression *Fresenius J Anal Chem*, vol. 348, pp. 501-505, 1994.

APPENDIX A

Use of LIBS Measurement Technology at the Luckey, Ohio FUSRAP Site to Characterize Beryllium in Surface Soils

Interim Report of Activities

By

Steve Saggese

Tom Kendrick

Nora Tocci

**Science & Engineering Associates, Inc. (SEA)
6100 Uptown Blvd., NE
Albuquerque, New Mexico 87110**

February 16, 1998

***Worked performed under contract to the
US Department of Energy
Federal Energy Technology Center
FETC Contract No. DE-AR21-95MC32089***

TABLE OF CONTENTS

1.0	INTRODUCTION	1
2.0	SITE BACKGROUND	1
3.0	DESCRIPTION OF OVERALL SITE ACTIVITIES	3
4.0	LIBS INSTRUMENTATION	3
5.0	LIBS FOR SOILS ANALYSIS	6
6.0	LIBS CALIBRATION.....	7
7.0	FIELD SAMPLING QUALITY ASSURANCE (QA).....	10
8.0	SITE SPECIFIC LIBS ANALYSIS METHODOLOGY	11
9.0	FIELD ACTIVITIES – WEEKLY SUMMARY	13
10.0	MEASUREMENT RESULTS	19
11.0	LESSONS LEARNED.....	23
12.0	CONCLUSIONS	26
13.0	ACKNOWLEDGEMENTS.....	27
14.0	REFERENCES.....	28
	APPENDIX A: EXAMPLE DATA FILES	A-1
	APPENDIX B: SEA PRESS RELEASE	B-1

1.0 INTRODUCTION

Science & Engineering Associates, Inc. (SEA) was requested to support a laser induced breakdown spectroscopy (LIBS) field measurement program for beryllium (Be) contamination at a Formerly Utilized Sites Remedial Action Program (FUSRAP) site in Luckey, Ohio. To facilitate the required measurements, SEA coordinated with Los Alamos National Laboratory (LANL) to transition two prototype LIBS-based instruments, developed and built by LANL from their research program, into tools useable in a routine field measurement program. SEA then used these instruments to complete a six-week characterization of the surface soil at the Luckey site for Be contamination. This report provides a summary of the activities undertaken to complete this effort and a presentation of the overall results of the characterization.

SEA's goals for this field effort were to:

1. Successfully transition the Backpack and TRACER prototype instruments into an ongoing site characterization,
2. Provide accurate, timely characterization of the surface beryllium contamination to FUSRAP,
3. Evaluate the instrument and method performance in a "real world" scenario
4. Develop an understanding of the sample throughput rate under "real world" conditions,
5. Investigate the efficacy of the data analysis methodology.

To accomplish this effort, SEA was funded by the DOE Oak Ridge FUSRAP program through the Federal Energy Technology Center (FETC). SEA supported LANL personal and equipment through a User Facility Agreement 96-01. While on-site at Luckey, SEA worked under the auspices of Bechtel National Inc. (BNI) and Science Applications International Corporation (SAIC).

2.0 SITE BACKGROUND

The Luckey site is located approximately 1 mile north of the town of Luckey, Ohio, which is a rural agricultural community, approximately 22 miles southeast of Toledo, OH. An aerial photograph of the site is shown in Figure 1. In 1942 the Defense Plant Corporation (DPC) built a magnesium reduction facility at the site to produce magnesium metal for the war effort. Beginning in 1949, the

Figure 1: Aerial photograph of the Luckey Site

Brush Beryllium Company (BBC), under contract to the Atomic Energy Commission (AEC), leased the entire site to produce beryllium products, primarily beryllium hydroxide. Beryllium production was discontinued at the site in 1958, and the site underwent a decontamination of the buildings and surplus equipment in 1959. Available records indicate that the facility produced between 40,000 and 144,000 pounds of beryllium for the AEC. Liquid wastes from beryllium operations were stored in lagoons on the site. Closing operations included constructing an 8.5-acre dike-enclosed landfill on the northeast corner of the property. The hazardous material from the lagoons was reportedly moved to the landfill, which was capped, graded, and seeded. In 1961, the site was then sold to a private corporation, Aluminum and Magnesium, Inc., a division of Vulcan Materials Company, until ownership changed to the Goodyear Tire & Rubber Co. in 1968. At this time, Goodyear began production of urethane foam products for the automobile industry and the site has been used in this capacity ever since. The current occupant manufactures a urethane coated auto wheel product.

Contamination of the site with radionuclides (primarily uranium, thorium, and their associated decay products) may have occurred by several different means. Prior to arrival at the Luckey site, the beryl ores were crushed and ground at the Middlesex Sampling Plant located in Middlesex, NJ. This AEC facility also processed uranium ores. It is believed that the beryl ores were contaminated by residual uranium ore material remaining in the crushing equipment. In addition to this source, 1,000 tons of scrap steel, intended to be used to react with chlorine off-gas from a magnesium reduction process, were sent to the Luckey site in 1951 from the Lake Ontario Storage Area (LOSA). Much of this steel was from surplus drums previously used to contain pitchblend uranium ores, and thus contained residual radioactive contamination. Because the radiological constituents were

incorporated into the feed materials of the processes operating at the site, they are likely to be distributed in much the same manner as the Be contamination.

3.0 DESCRIPTION OF OVERALL SITE ACTIVITIES

In order to better understand the role of the LIBS measurements conducted, it is helpful to understand the goals of this portion of the characterization activities and how they relate to the overall site characterization. Four stages were defined to complete the characterization of the type and extent of AEC related contaminants present at the site. *Stage 1* consisted of pre-mobilization activities related to gathering historical and other available information, such as aerial photographs, site drawings, and historical documents and records. *Stage 2* consisted of the initial on-site reconnaissance activities, including several walk-over type surveys. These surveys included geophysical measurements to detect and characterize various subsurface features (i.e. buried metallic objects, abandoned trenches, waste disposal pits), a gamma walk-over to characterize the extent and magnitude of near surface radiological constituents, and the LIBS walk-over to characterize the extent and magnitude of any significant Be contamination on the surface. Various other characterization activities were conducted during this stage, including the characterization of the background conditions near the site, assessing the general levels of hazards that the workers may expect to face in the following more intrusive characterization stages, and determining which of the many possible constituents are actually of concern at this site. It is the *Stage 2* LIBS measurements that this report documents.

Stage 3 will be primarily concerned with evaluating and interpreting the results of the Stage 2 investigations, and planning a more invasive characterization effort to be completed in Stage 4. This *Stage 4*, intrusive sampling, has the goal of determining the lateral and vertical extent of contaminated materials, i.e. determining the boundaries of the affected materials. This will permit an estimation of the volumes of soil materials that must be remediated, as well as determining the possible disposal options. Additionally, ground water monitoring will be instituted at the site to assess possible migration of the constituents of concern by this pathway.

4.0 LIBS INSTRUMENTATION

4.1 Basic LIBS Systems

Laser induced breakdown spectroscopy (LIBS) is a field deployable analytical technique well suited to screening level measurements of a wide variety of elemental contaminants. Unlike X-Ray fluorescence, which is limited to elements

with a relatively high atomic number, LIBS can be used quite successfully on many elements with low atomic numbers, such as beryllium.

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. At the present time, there are various types of LIBS instruments being developed for field applications, such as hand-held devices, van mounted systems, and truck mounted cone penetrometer systems.

Regardless of the deployment technique, all LIBS systems contain the same basic components. As shown in Figure 2, a LIBS system consists of a laser source to produce the plasma, a method of delivering and focussing the laser beam onto the sample, 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.

Figure 2: A basic LIBS arrangement

An emission spectrum is obtained by focusing the high power laser on the sample surface to produce a local plasma. 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. Elemental analysis is conducted by observation of the wavelength, intensity, and temporal characteristics of the emission lines. For the present effort at the Luckey Site, two prototype LIBS instruments developed by LANL were deployed by SEA; a Backpack model and a van-mounted system called TRACER.

4.2 LIBS Backpack system

A photo of the LIBS Backpack instrument is shown Figure 3. A 30 mJ Nd:YAG pulsed laser (Kigre model MK-480, 0.5 Hz) is mounted in the lower portion of the hand-held probe. The probe also houses an optical lens system to focus the laser beam at the surface of the soil to create a plasma spark and direct the spark light emission to an optical fiber (C-Technologies). The optical fiber then transmits the

Figure 3: LIBS Backpack instrument

spark light from the probe tip to a 1/8 meter spectrometer (Thermo Jarrel-Ash Model Monospec-18) that is mounted on the Backpack frame. The spark emission light is dispersed by the spectrometer and a cooled CCD camera (Santa Barbara Instruments Group Model ST-6) is used to record the spectral information. The Backpack frame also contains the laser power supply and a 12 VDC gel-cell battery that supplies power to the system. A palm-top computer attached to the users arm (Hewlett-Packard Model 200 LX) is used to operate the system, graphically display the resultant LIBS spectra, display the calculated

Be concentration, and provide a permanent record of the measurement results. For this effort, a cart, shown in Figure 4, was assembled to provide another means for deploying the Backpack hardware.

Figure 4: The backpack hardware was also deployed via a field transportable cart

4.3 TRACER system

The second instrument used was the *Transportable Remote Analyzer for Characterization & Environmental Remediation* (TRACER). This system uses a significantly larger laser with a higher sustainable pulse repetition rate and a higher resolution spectrometer. Figure 5 shows a photo of the TRACER system in operation at the Luckey site. The single container system utilizes a 100 mJ pulsed-infrared laser (Laser Photonics Model YQL-102 Nd:YAG), a 0.5 meter spectrometer (Chromex Model 500is), and a cooled, intensified CCD detector (Oriel InstaSpec). A lunch-box style personal computer provides a platform to operate the custom software that interfaces with each of the major system components. Unlike the Backpack system that evaluates the soil surface *in-situ*, the TRACER unit evaluate soils placed within a glass vile.

Figure 5: The TRACER system being used at the Luckey Site

5.0 LIBS FOR SOILS ANALYSIS

When evaluating soils, the spectrograph is tuned to the wavelength(s) where the element of interest has an emission. Figure 6(a) and 6(b) show LIBS spectra determined for a NIST soil sample from a Montana Superfund Site with high heavy metals contamination. Figure 6(a) shows the spectral region for lead (Pb), and Figure 6(b) for chromium (Cr).

Figure 6a: Typical LIBS emission spectra for a Pb contaminated soil

Figure 6b: Typical LIBS emission spectra for a Cr contaminated soil

6.0 LIBS CALIBRATION

6.1 Background

The basis for quantitative analysis with LIBS is that the intensity of the analyte emission peak is proportional to the concentration of the analyte in the sample. Thus a larger analyte concentration produces a larger emission peak. Calibration of the technique then relies on developing a relationship between the analyte peak intensity and analyte concentration of the sample medium. This relationship is

determined empirically through the use of standards. The standards are prepared by adding known amounts of the analyte element to a sample matrix representative of the materials to be measured. Typically three or four standards, each of a different analyte concentration, are used to develop the calibration curve, which for most elements over the lower concentration ranges is a linear relationship. As the concentration of an analyte is increased, however, it is common for the peak height to stabilize and not increase with concentration due to self absorption. The key for effectively using LIBS is to utilize emission peaks that do not saturate over the concentration range of interest. Thus, a strong emission peak for an analyte may be used for low concentrations and a weaker peak may be used for higher concentrations.

Figure 7: The reduction in the Pb peak with a reduction in concentration

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.

Calibration curves for conducting quantitative analysis are constructed by plotting the ratio of the peak areas for the analyte of interest and a standard element vs. the

concentration of the analyte in the soil. Figure 8 shows a calibration curve for a Pb-spiked sample using an Fe line as an internal standard.

Figure 8: Typical calibration curve for a LIBS system

6.2 Calibrations for Luckey Effort

The standard soils used for the LIBS measurements were prepared by Mountain States Analytical Laboratory and were provided to SEA by the host contractor, Bechtel National, Inc. These standards materials were the same standards used in the performance assessment of the LIBS instrumentation that was conducted by the LANL group prior to the field measurement activities.

The standards were developed by using a large quantity of blended soil obtained from a location known to be free of significant Be contamination near the Luckey site. This background soil was determined by laboratory analysis to have a beryllium concentration of 0.7 ppm. A known quantity of Be standard solution (Be Atomic Absorption Standard Solution) was added to each of three aliquots of the background soil, resulting in additional standards with concentrations of 10, 100, & 1,000 ppm Be.

Using these three standards and the background soil, the Be calibration curve was developed using the ratio of the beryllium peak to the aluminum peak. For the measurements performed at the Luckey Site, the spectral region was chosen to include the emission line from the Be(II) once-ionized doublet at 313.1nm and the aluminum line at 309.3 nm which was used as the reference. This scheme was chosen by the LANL researchers during their initial feasibility study as being the

most accurate. The least squares linear regression, slope and offset of this regression were then stored in computers for use during the actual measurements.

Concern existed at the outset of the field planning process regarding the effect of moisture on the measurement results. One result of the LANL feasibility effort was that there was an effect on the performance of the LIBS TRACER unit when the soil was wet. Due to this fact, the standard soils were dried for calibration of the TRACER system, and the TRACER field procedure included a soil drying step.

The Backpack, on the other hand, is configured to allow analysis of either dry or wet sample material, but the signal strength was somewhat dependent on moisture. Since there would be no practical way to ensure that the *in-situ* soil sample to be analyzed by the Backpack system remain dry, the alternative approach was adopted, where the soil surface was controlled to be moist. A spray bottle, filled with ordinary tap water, was used to moisten the soil surface immediately before the measurement was conducted. Correspondingly, the Backpack calibration was conducted using the soil standards prepared with 30 weight percent moisture content.

7.0 FIELD SAMPLING QUALITY ASSURANCE (QA)

To assure that the quality of the measurements were maintained at acceptable levels, three different categories of QA measurements were made. These categories - spikes, blanks, and field duplicates - accounted for at least 5% of the samples analyzed on a daily basis. In general, the procedures specified the analyses in groups of twenty, with the tenth analysis being a blank (the 0.7 ppm standard), the twentieth analysis being a field spike (the 1,000 ppm Be standard), and one of the twenty locations measured was immediately re-measured as a field duplicate. If the field logistics dictated an analysis group of less than twenty measurements, then the analysis group was always ended with the field spike.

For the Backpack system, if any of the field spike results deviated by 50% from the known value, then the instrument was considered out of calibration and the results of the previous twenty samples were thrown out. The unit would then undergo a calibration procedure and the twenty samples evaluated again. For the TRACER system, which is considered to have a higher accuracy and precision, the results were required to be within 25% of the known value to be considered valid.

As an additional QC measure, the LIBS field results were correlated with off-site laboratory analysis. In order to accomplish this, a series of 50 locations were selected for a correlation sample set. These locations were prepared for sampling by clearing a twelve inch square of grass or other vegetation and smoothing the soil. The Backpack system was then used to obtain 10 sparks that were

distributed evenly over the area to be sampled, and the average Be concentration was measured. Following the Backpack measurement, a sample was collected for TRACER analysis by scraping a thin layer of soil from the sample area. The last step was to prepare and collect a sample for off-site laboratory analysis. The soil was broken-up over the twelve inch by twelve inch location to a depth of approximately one inch. This material was then blended and an aliquot of approximately 50 g was obtained by the cone and quarter method.

8.0 SITE SPECIFIC LIBS ANALYSIS METHODOLOGY

8.1 Backpack LIBS system

As shown in Figure 3, the probe of the Backpack system is placed directly onto the surface to be analyzed. Since grass covered most of the areas on the site not occupied by buildings, pavement, and railroad tracks, the grass needed to be removed to gain access to the underlying soil. This was accomplished by cutting-out a small square of sod approximately six inches on a side with a garden trowel. The underlying soil was smoothed, and moistened if needed to prepare the surface for measurement. The trowel was cleaned with soapy water between each measurement location to prevent cross-contamination. The surface of the probe was also cleaned with soapy water in between every measurement to control the potential for cross contamination.

Because of the relatively low sustainable repetition rate of the small Kigre laser, a total of ten sparks were analyzed for each measurement location. The individual spectra from each spark were co-added, resulting in one spectra that is processed for a final result. The instrument operator moved the position of the hand-held laser head between each spark to avoid sampling exactly the same location for all ten sparks.

The Backpack measurement results from the previous day's field activities were provided to BNI at the morning planning meetings. The results were provided in two different formats, an ASCII data file formatted to BNI specifications and a file in Microsoft Excel TM format. Appendix A gives an example of the Excel TM data format for a typical Backpack data set.

8.2 TRACER LIBS System

The TRACER instrument was set-up in a small rental trailer. Whereas the Backpack instrument is designed to conduct *in-situ* measurements, the TRACER is designed to accept a dried granular sample of approximately 1 to 1.5 grams. The soil samples were dried in a microwave oven, within the sample vials, prior to analysis. To meet the necessary industrial hygiene requirements, the drying procedure and all other sample handling needed to be performed in a ventilation hood. As the host contractor, Bechtel National, Inc., provided the hood facility, which consisted of a plywood enclosure connected by duct work to a portable, high volume fan/HEPA filtration system.

TRACER samples were collected using a laboratory spatula. Where grass or other vegetation was present at the soil surface, it was removed to expose the upper-most soil layer. A two to four gram sample of the soil was collected into a 35 mm diameter plastic petri dish. The lid was secured with vinyl tape, and the location ID, date and time recorded on the sample container, and in a field notebook. Collection of the sample in a petri dish facilitated the required radiological survey of the sample materials prior to being handled in the trailer set-up for the TRACER measurements.

Following release by the radiological control technician, the petri dishes were transferred to the TRACER trailer for sample preparation. Approximately 0.5 to 1 grams of the soil sample was transferred into a labeled 4 dram analysis vial using a lab spatula. The vials were then placed in a microwave oven for drying. Following the drying step, any clumps that had formed were broken up with a spatula to produce a granular material suitable for analysis. The spatula was cleaned with isopropyl alcohol between each sample to prevent cross contamination.

Unlike the Backpack, the laser system used in the TRACER allows a high pulse repetition rate. Thus a total of 300 sparks, in six groups of 50 each were analyzed for each sample. The analysis scheme co-adds the spectra from the 50 sparks in a group, and then processes a measurement result for each of the six groups, as well as an average for the full 300 sparks

As with the Backpack measurement results, the TRACER results from the previous day's field activities were provided to BNI at the morning planning meetings. The results were provided in two different formats, an ASCII data file formatted to BNI specifications and a file in Microsoft Excel TM format. Appendix A, gives an example of the Excel TM data format for a typical TRACER data set.

9.0 FIELD ACTIVITIES – WEEKLY SUMMARY

The work schedule adopted for the Luckey site was four 10-hour days per work week. Accordingly, SEA adopted this work schedule to be compatible with the supporting field activities. In addition to conducting LIBS analysis, SEA was involved in marking the location of the sampling points and attending daily meetings called by BNI concerning on-site activities and planning. Table 1(a) – (g) summarize the LIBS measurement progress during the field work. SEA mobilized to the site on 23 September and left the site on 7 November. The following sections summarize the activities on a weekly basis.

9.1 Weekly Summary

Week #1 (23 September to 25 September)

The LIBS team, consisting of the SEA site personnel and program manager, along with the LANL researcher that helped develop the prototypes, mobilized to the Luckey Site. The initial two days were spent unpacking, setting up and calibrating the equipment and completing the required site-specific training.

In addition, the SEA team met with BNI and SAIC personnel to discuss the field procedures that SEA had developed and to determine the specifics of how the LIBS characterization would best fit into the ongoing site activities. From this meeting, it was mutually agreed that during this stage of the characterization the LIBS instruments would be used to define areas of significant Be contamination, and thus exclude these areas from the requirement to be sampled for Be assay at an off-site laboratory. Because the TRACER instrument exhibits a lower method detection limit (MDL) than the Backpack Instrument (TRACER MDL = ~10 ppm, Backpack MDL = ~ 50 ppm), the plan was to start with Backpack measurements in areas suspected of having high Be levels and work outward until the measurements results indicated values below 100 ppm. This zone of < 100 ppm Be would be sampled for on-site TRACER analyses. This would allow the Backpack to be used effectively as a first cut screening tool, and make efficient use of the analysis capacity of the more sensitive TRACER unit.

The 40 acre Luckey Site was sectioned off into 50 meter major grids with 10 meter minor grids, thus there were 25 sampling locations per major grid. In some of the major grids the Be contamination was thought to be rather low. In such cases, only 12 or 13 sampling locations were used. At this point in time, only the 50 meter major grids were marked off, and the minor grids would have to be marked off as the work progressed. The total number of sampling locations onsite for LIBS was set at 1200.

During this meeting, the requirements of the lab trailer for the TRACER unit were finalized. The trailer was not ready for TRACER deployment and a ventilated hood had to be fabricated and qualified, thus the LIBS analysis was initially limited to the Backpack unit.

Table 1(a): Week #1 activities

Date	Number of Backpack Measurements	Number of Tracer Measurements	Comments
9/23/97	-	-	Travel to site
9/24/97	-	-	Equipment set-up – Backpack, checkout, calibration
9/25/97	-	-	Site specific training, Meeting with Site Operations

Week #2 (29 September to 3 October)

One of the issues discussed the previous week concerned the specific depth location that the LIBS would be used to evaluate. In general, should the unit be used to evaluate the top surface or several inches below the surface? On the first day of planned field measurements, 29 September, the Backpack system was used to determine whether or not there was a specific horizon in the near surface soil that exhibited a significant increase in Be concentration, indicating an air fall depositional feature. If an air fall depositional feature existed, then the top surface Be concentration may not be indicative of the bulk soil below. The results indicated that there was a consistent pattern in that the Be concentration generally increased with depth to the 4 inches examined. Based on these results it was determined that the LIBS measurements would be obtained from the soil surface where it was free from vegetation, or from the soil immediately below the root zone of the grass or other vegetation.

Routine measurements of the sampling grid were started 30 September in the area immediately to the north of the main factory building using the Backpack system mounted on the cart. The minor grids were not all marked off ahead of time and the early part of the week was spent getting this area staked off. Difficulties with spectral shifts attributable to temperature build-up in the cart housing and mechanical shock led to the decision to reconfigure the Backpack system to the backpack frame for the remainder of the field measurements.

As shown in Table 3, the daily sampling rate at the grid nodes increased through the week from an average of 34 on the first two days to an average of 65 on the second two days of the week even with a suspension of Backpack operation on 3 October due to rain. This daily rate increase is attributable to the switching of the deployment from the cart to the Backpack and the pre-marking of the minor grid sampling locations.

Table 1(b): Week #2 activities

Date	Number of Backpack Measurements	Number of Tracer Measurements	Comments
9/29/97	14	-	Evaluation of soil profiles, vertical extent
9/30/97	27	-	Begin routine Backpack measurements in Investigational Area #7
10/1/97	41	-	Minor grid marking
10/2/97	69	-	
10/3/97	62	-	

Week #3 (6 October to 9 October)

On 6 October and 7 October the weather grew unseasonably warm. During the mornings, the temperature was cool and the Backpack temperature was stable, but in the afternoon the temperature would increase substantially causing the spectral shifts in the Backpack system. The spectral shifts were minor (i.e. several nanometers) but the present prototype software on the Backpack could not account for the changes, thus the unit drifted out of calibration. When this occurred, the system required more frequent calibration, leading to low sample throughput rates.

Following completion and qualification of the dust control hood, the first series of TRACER samples were processed for analysis by drying on 8 October. This coincided with an increase in the sample throughput rate for the Backpack measurements as the warm temperatures subsided. On 9 October the TRACER analysis was begun in the afternoon and the Backpack was only used a half day due to rain.

Table 1(c): Week #3 activities

Date	Number of Backpack Measurements	Number of Tracer Measurements	Comments
10/6/97	21	-	Temperature problems with Backpack
10/7/97	29	-	Temperature problems with Backpack
10/8/97	46	-	Temperature stable, TRACER facilities completed
10/9/97	26	36	Rain suspends Backpack measurements

Week #4 (13 October to 16 October)

At the start of the new fiscal year, the FUSRAP program was shifted from the US DOE to the US Army Corps of Engineers. As a result, BNI found it necessary to plan for a work stoppage at the site if issues regarding funding and the authority to proceed with the field work were not resolved in a timely manner. The best estimates at the time indicated that a shut-down would only last a week or two. Obviously, this would have had a dramatic effect on the ability of SEA to complete the LIBS measurements within the allotted time frame and budget.

SEA was under contract with the US DOE Federal Energy Technology Center (FETC) to perform this scope of work, not US DOE FUSRAP. In light of this, it would have been possible for SEA to continue to work so long as this did not require any of the support (such as health physics and industrial monitoring) that BNI and the other site subcontractors had been providing for the LIBS measurement task. This could be accomplished if the only tasks performed by SEA were analysis of TRACER samples that had been collected and released by the radiological control technician. Given this option, an all out effort was made to collect as many TRACER samples as possible, and suspend operation of the Backpack until the situation was resolved, or a two week backlog of TRACER samples could be generated.

By the end of the week, the DOE/Corps of Engineer situation was successfully resolved, and the Backpack measurements were once again initiated. By the last day of the week, 16 October, the Backpack was used a full day and the TRACER had a heavy backlog of samples already sent through health and safety, thus the sample total for the day was the highest to date at 190.

Table 1(d): Week #4 activities

Date	Number of Backpack Measurements	Number of Tracer Measurements	Comments
10/13/97	-	69	Focus on TRACER sampling
10/14/97	-	83	Focus on TRACER sampling
10/15/97	44	-	
10/16/97	86	104	Potential stop work planning

Week #5 (20 October to 23 October)

This week exhibited a consistent throughput for the LIBS instruments with a total of 503 samples evaluated. Near the end of the week, the focus was shifted towards the TRACER since the grid nodes accessible to the Backpack were decreasing. In areas of high Be levels, the decision was made by BNI to limit exposure to the LIBS site personnel, thus the TRACER would be used for all of the sampling in these areas.

Table 1(e): Week #5 activities

Date	Number of Backpack Measurements	Number of Tracer Measurements	Comments
10/20/97	75	84	
10/21/97	82	75	
10/22/97	27	59	
10/23/97	-	101	Focus on TRACER sampling

Week #6 (27 October to 30 October)

Again, this week was focused on using the TRACER, therefore, the Backpack was used sparingly and a fair amount of time was spent acquiring TRACER samples.

Table 1(f): Week #6 activities

Date	Number of Backpack Measurements	Number of Tracer Measurements	Comments
10/27/97	-	-	Focus on TRACER sampling
10/28/97	-	84	Focus on TRACER sampling
10/29/97	50	81	
10/30/97	13	82	

Week #7 (3 November to 7 November)

For this week there was only 1.5 days available for LIBS analysis due to the requirement to survey the equipment prior to shipping. Since the equipment was shipped on 6 November, two days was required to perform a swipe check of the equipment for Be contamination. Thus the short time was spent finishing up some Backpack accessible locations and performing TRACER measurements. As Table 1 indicates for 4 November, when the samples are available and prepared, the TRACER throughput jumped to 131 measurements for that single day. The instruments were found to be free of Be contamination and SEA shipped out at the end of the week.

Table 1(g): Week #7 activities

Date	Number of Backpack Measurements	Number of Tracer Measurements	Comments
11/3/97	25	--	Rain suspends Backpack measurements

Date	Number of Backpack Measurements	Number of Tracer Measurements	Comments
11/4/97	-	131	Survey equipment for Be contamination
11/5/97	-	-	Survey equipment for RAD and Pack-up equipment
11/6/97	-	-	Ship equipment
11/7/97	-	-	Travel home

Although it was originally planned to spend a day or two inside of the factory buildings with the Backpack system, this activity did not take place. The original intent was to evaluate the ability of the Backpack to detect Be contamination on the walls, floors, and structural elements of the buildings. Logistics between the FUSRAP project and the current building occupants, coupled with a need to suspend use of the LIBS equipment by noon of 4 November to accommodate the sample turn-around time required by the Be smear samples on the equipment were the factors primarily responsible. It is anticipated that this activity will be completed during Stage 4 of the characterization activities.

9.2 LIBS Sampling Rate

Figure 9 shows the cumulative sample number as a function of time for the LIBS effort. Overall, the LIBS team evaluated 1664 soil samples, which included the QA samples discussed previously. The rate is seen to have been effected by the weather conditions and the availability of support equipment. As shown in the Figure, the initial rate during startup was approximately 39 samples/day using only the Backpack with two personnel in the field. After the TRACER came on line with the availability of a trailer and fume hood, the rate jumped to 111 samples/day, with one person on the TRACER and a two person field crew collecting TRACER samples and performing Backpack measurements. At the closing of the effort, the focus was transitioned to primarily accumulating TRACER samples, thus the backpack was used sparingly and the rate dropped to about 78 samples/day.

Figure 9: The LIBS cumulative sampling of the Luckey Site

10.0 MEASUREMENT RESULTS

10.1 Off-site Laboratory Correlation

To determine the correlation for the LIBS field measurements relative to standard laboratory techniques, a series of 50 soil samples were analyzed by both LIBS units on-site and then evaluated off-site at a government approved analytical laboratory. The locations of the correlation samples were chosen to represent a range of Be concentrations so that the LIBS instruments could be adequately evaluated. As of the writing of this report, there were a couple of missing lab data points or duplicates, but there are 43 locations that are common to the lab, TRACER and backpack.

Figure 10 (a) and 10 (b) show that the correlation between the LIBS TRACER and Backpack versus the laboratory analysis, respectively. As shown, there is a linear correlation between the two techniques and the regression coefficient has a value of $r = 0.949$ for both the TRACER the Backpack, thus the LIBS instruments are well suited for use as a screening tool at this site. There are a couple of data points where the correlation is rather poor and the reasons for this are discussed in

the Lessons Learned Section. Only one sample, the same sample for the TRACER and the Backpack, was not used in the regression.

Figure 10(a): The Be concentrations determined with the TRACER vs. Laboratory (42 samples plotted, 1 thrown out)

Figure 10(b): The Be concentrations determined with the Backpack vs. the laboratory analysis (42 samples plotted, 1 thrown out)

10.2 Contour Map

All of the Backpack and TRACER measurement results were compiled and a contour map (Figure 11) was prepared to provide a general picture of the distribution of the Be abundance on the site. As previously stated, the results were provided to BNI on a daily basis so that the contour map could be constructed to identify areas of high Be contamination and trends. Figure 11 shows the contour map of the Be contamination determined with the LIBS instruments for the on-site samples.

The map axes are labeled with the site coordinate system in meters. The major buildings and other concrete structures are represented by black, and the parking areas and other paved areas are shown in light gray. Unimproved roads, fences, and other site features are shown by the thin black lines. The red areas represent significant Be contamination and the dark blue areas represent the lowest Be abundance, generally background concentrations.

It is interesting to note that the significant areas of Be contamination shown in the north central part of the site (517350, 199530) and the northeastern corner, correspond to areas devoid of vegetation. Moreover the area in the northeast corner corresponds to the location identified in historical records as being used for land disposal of sludge's and other solids removed from the lagoons to the south of the main factory building. The map also shows moderately elevated Be concentrations for much of the eastern half of the site, with some high spots evident along abandon rail road beds immediately to the south of the main factory building.

The open area in the pavement south of the main factory building encloses an electrical power transformer. An examination of aerial photos at the site indicates that the pavement to the south of the main factory building postdates the AEC related activities. These data indicate the possibility of significant Be contamination underlying the pavement.

As stated in the site description, the south side of the main building had lagoons that were capped with several feet of topsoil. As shown on the contour plot, the regions of topsoil coverage show minimal, if any, Be contamination. The LIBS analysis, however, does show a slight increase in the Be concentration where the topsoil coverage ends, thus indicating that there will potentially be subsurface contamination in this area under the topsoil cover.

**Contour Map of Measured Beryllium Abundance in Surface Soils
At the Luckey Ohio FUSRAP Site**

Figure 11. Contour map of the Luckey site showing the measured Be concentration distribution. Blue indicates areas of low or background levels of Be, and red indicates areas of significant Be concentration.

11.0 LESSONS LEARNED

In addition to the specific task at hand (i.e. the characterization of the Luckey Site for Be-contamination) SEA was gaining experience on the field deployment of LIBS technology. Based on this experience, we have learned a number of lessons on field deployable instrument design, data analysis, and deployment methodology.

11.1 Instrument Designs

As previously stated, the prototype Backpack and TRACER units were designed and fabricated by LANL personnel several years prior to this effort, and they are one-of-a-kind instruments. For both systems, the Luckey effort would be the most rigorous test to-date for field applicability. In general, both systems worked quite well, considering that they were not designed specifically for this task.

11.1.1 Backpack For the Backpack, the design issues were related to 1) ease of cleaning, 2) environmental effects, and 3) data handling capability. None of these issues were great hindrances, however, improvements could be made in future hardware designs to optimize the system performance.

1) Backpack Ease of Cleaning For the backpack, the laser was situated at the end of a “staff” which could be placed onto the ground at the sampling location. A lens was used in front of the laser to focus the laser beam onto the ground. In order to minimize the damage to the focussing optic due to particulates kicked up by the spark, it was necessary to clean the sample area in front of the lens after every set of ten sparks. This process did not take very long to perform, but if it wasn’t done correctly, the laser could easily damage the focusing lens. Movement of the lens further away from the sample and altering the design of the staff where the laser interacts with the soil would help alleviate this problem.

2) Environmental Effects on Backpack Operation The Backpack instrument was not designed to be an all weather system; therefore, it was not protected against rain. While this could be, and was to some extent, remedied in the field by rain shields for the equipment, the more serious problem presented by the rain was to interfere with the measurement process itself. With more than a light rain, the moisture content of the surface soil began to elevate rapidly, resulting in a significant portion of the available laser energy being absorbed by the water. This resulted in an overall reduction of light output from the spark and a poor signal to noise ratio.

In addition to the rain effects, the Backpack was effected by temperature fluctuations. The temperature swing from the cool morning to the hot afternoon would cause shifting in the spectral curve. This shift was probably due to mechanical alignment changes from thermal expansion differences of the instrument. If a variation occurred in the location of spectra on the CCD camera,

as would occur due to thermal effects, then the emission peaks would be incorrectly evaluated. This can be solved by two methods, 1) altering the software to “find” the peaks of interest regardless of the pixel locations, or 2) actively cool the spectrometer and detector to minimize the thermal gradients causing the peak shift. The former solution is preferable because the addition of cooling would primarily add weight to a system which cannot afford much more hardware. The spectral shifts encountered were not large enough to cause any concern on the overall system design, simply altering the software to account for slight shifting would solve the problem.

3) Data Handling Capability In general, the software used to run that instrument and evaluate the data was rather basic, primarily due to the fact that it is being run on a palm top computer with minimal memory and capabilities. Improvements could be made in the software running the system to help on hardware performance diagnostics (i.e. detector temperature monitoring), spectral peak analysis to minimize temperature effects, and the ability to save more information on the spark raw data and analysis for review. None of these issues would be difficult to implement in future designs and they would enhance the usability and performance of the system greatly.

11.1.2 TRACER For the TRACER instrument, the overall design was very efficient. Once the trailer was set-up, the single package unit enabled us to get working quickly and efficiently. The issues regarding the TRACER were related to 1) the sample preparation required and 2) the laser/sample interactions within the vial.

1) TRACER Sample Preparation The amount of time and effort which went into getting the sample obtained, checked for radioactive contamination, transferred to the sampling vials and dried was often a limiting factor in the sampling rate for the TRACER. Since the TRACER unit resided outside the exclusion zone in a laboratory trailer, a radiation scan of the samples had to be performed prior to releasing the samples to the LIBS trailer. This step in the process, which involved other site personnel that were often busy with other tasks, would slow the TRACER analysis process down. This step also required SEA to be dependent upon other site personnel. The solution for this would be to repackage the system such that it could be located in the exclusion zone, thus eliminating the extra sample handling.

2) TRACER Laser/Sample Interaction One of the more elegant features of the TRACER is the ability to sample the soil without introducing Be-contaminated dust into the environment. This is accomplished by inserting the soil sample into a sealable glass vile and shooting the laser through the glass to sample the soil. The vials were also useful for performing the drying step in the microwave oven. The authors believe, however, that there are a couple of disadvantages to this sampling method, 1) the dust created within the vial tends to

coat the inside vial wall, thus reducing the emission light intensity reaching the optical fiber pick-up, and possibly attenuating the laser light, and 2) the spark, which was designed to occur slightly above the soil within the vial, may cause segregation of the soil by particle size. In effect, the spark creates a pressure wave that “kicks up” particles within the vial. As the sparking continues, the dust within the vial increases and the laser can now directly interrogate the particles. Thus, there is reason to believe that the fine particles in the sample are preferentially interrogated. Depending on where the Be-contamination resides within the sample, this process may introduce a bias.

11.2 Deployment Methodology

The deployment methodology refers to the manner in which the LIBS instruments were used to support the customer. The natural questions to ask are: Did SEA utilize the resources to their fullest potential? Did SEA provide the customer the information they desired in a timely manner? Can the overall performance be improved in this regard? This field experience was extremely enlightening in this area, and several lessons in how LIBS instruments should be used were learned.

At the root of the discussion of whether the customer’s needs were satisfied is the definition of “real time”. Clearly the several weeks to a month or more that has occurred for some of the results sent to off-site laboratories is not adequate to meet the needs of the personnel charged with directing the characterization activities. Fast information helps the project team make intelligent decisions about where to expend valuable resources and, perhaps more importantly, it enables informed decisions to be made regarding health & safety issues. “Real time” measurements would enable them to most effectively conduct their duties. For this Stage 2 effort, the authors believe that the next day submission of results adequately supported the field personnel.

For situations similar to that at the Luckey Site, the authors feel that the TRACER unit, with its next day turn-around of results and higher sustainable sample throughput rate, provides a better solution than does the one day-result availability from the Backpack. This has partly due to the fact that for many of the decisions regarding where to sample next, or to determine what health & safety measures are to be implemented, are applied to a relatively large area of the site, and not based on one or two measurement results.

In general, the authors feel that if the site to be characterized is well supported, meaning that there are trailer facilities and support personnel for sample collection and health & safety, then a TRACER unit would have a higher sample throughput rate than the Backpack system. The time spent walking over the site, collecting samples and transferring them to the trailer-based TRACER would be a more efficient use of the site personnel and the environmental concerns (i.e. temperature fluctuations, precipitation) would not be an issue.

On the other hand, if the site is not well serviced and/or there needs to be only a quick evaluation of the site, then the battery operated Backpack offers a better solution. The Backpack design would enable a single person the ability to quickly obtain results without having to deal with support trailers or waste disposal. For the Luckey Site, the Backpack design would also be suited for the evaluation of the buildings, due to its ability to access a variety of areas.

The design and implementation of the LIBS instruments should be evaluated fully before deployment so that the best option can be utilized to support the requirements of the specific characterization or remediation effort.

12.0 CONCLUSIONS

As stated in the introduction, SEA had a number of goals for this field effort, all of which have been achieved.

1. Successfully transition the Backpack and TRACER prototype instruments into an ongoing site characterization

Since these prototypes were designed and fabricated by LANL to be general purpose instruments, and are the only instruments of their type in existence, we must praise their prior efforts on the development of LIBS systems that could be readily deployed into an ongoing field characterization without extensive hardware modifications. The primary issues for the Luckey deployment that SEA addressed concerned the development of field procedures that would provide accurate results and could be integrated into the Sampling and Analysis Plan and the Health and Safety Plan for the site. Field procedures were developed in cooperation with LANL for this effort. For the TRACER, SEA worked closely with the site personnel to establish the methods to effectively obtain samples, get them checked for radioactive contamination, and establish an effective trailer configuration to enable efficient analysis – all without adversely effecting the ongoing site activities.

2. Provide accurate, timely characterization of the beryllium contamination to FUSRAP

The overall performance of both LIBS instruments in this application was very favorable. The methodology utilized allowed a rapid, in-field determination of the extent and magnitude of Be contamination over the site. The results of the Be characterization were provided to BNI the morning after they were taken. This timeframe worked well with BNI's data reporting requirements. By the time SEA had left the site, the local BNI site personnel had received results for 1200 sample locations.

3. *Evaluate instrument and method performance in a “real world” measurement scenario.*

In general, the instrument performance was very good and the methods used were adequate for the Stage 2 effort. After this experience, the authors feel that the backpack methodology might not have been the most appropriate for this site, since there was adequate support for the TRACER instrument. If the two field personnel worked solely on the TRACER sampling, the throughput probably would have been better, since the analysis schedule would not have been slowed down by weather related complications. The backpack is more appropriate for sites that do not have the health & safety or logistical support, such as when a quick survey occurs prior to full deployment by a characterization team.

4. *Investigate the efficacy of the data analysis methodology.*

The data analysis methodology worked better than we expected. The internal reference method is appropriate when the soil type does not change drastically from the calibration samples and this appears to be the case for the Stage 2 measurements at Luckey. The correlation to the laboratory samples was high with r values of approximately 0.94 for both the backpack and TRACER. The authors do feel, however, that improvements can be made in handling variations in soil type, microsampling, and “bad” sparks. These issues can be addressed in the data analysis methods and by improved system design.

5. *Develop an understanding of the sample throughput rate under “real world” conditions.*

It was anticipated that the sample throughput would be relatively low for the first few days, but would increase as the SEA team became accustomed to the site conditions and work practices of the site. This trend is observable in Figure 9, however the sample throughput of the Backpack system did not achieve the consistency that was anticipated. As mentioned previously this was due in part to temperature problems and rain delays. The throughput of the TRACER was very good and could have been increased with the addition of a technician to support the sample collection in the field and sample preparation.

13.0 ACKNOWLEDGEMENTS

SEA acknowledges the support of Dave Cremers and Monty Ferris of LANL for the equipment and technical support, and the support of BNI and SAIC personnel at the Luckey Site. In addition, the authors thank Karen Cohen and Rick Griffiths of FETC for enabling the support for this work.

14.0 REFERENCES

“Sampling and Analysis Plan FOR The Luckey Site”, Final DOE/OR/21950-1024, USDOE-OROO-FUSRAP, August, 1997

“Fiber Optic/Cone Penetrometer System for Subsurface Heavy Metals Detection”, Phase I Draft Report, DOE Contract DE-AR21-95MC32089, , Saggese, S.J., Science & Engineering Associates, January 1995.

“Detection of Metals in the Environment Using a Portable Laser-Induced Breakdown Spectroscopy Instrument”, Cremers, et.al., Applied Spectroscopy, Volume 50, Number 2, 1996.

“Transportable laser-induced breakdown spectroscopy (LIBS) instrument for Field-based soil analysis”, Cremers, D.A., et.al., SPIE Volume 2835, page 190, 1996.

APPENDIX A: EXAMPLE DATA FILES

Example Data File for Backpack Measurement Results

Example Data File for TRACER Measurement Results

Example Excel Data File for Backpack Measurement Results

Site ID	Location ID	Sample ID	Sample Type	Date Collected	Time Collected	Analyte Element	Method
111LUC	09CJ00	09CJ00	REG	10/9/97	11:34:53	Be	LIBS-B
111LUC	09CP00	09CP00	REG	10/9/97	11:40:58	Be	LIBS-B
111LUC	09CU00	09CU00	REG	10/9/97	11:46:28	Be	LIBS-B
111LUC	09CZ00	09CZ00	REG	10/9/97	11:48:54	Be	LIBS-B
111LUC	09DE00	09DE00	REG	10/9/97	11:53:30	Be	LIBS-B
111LUC	09DJ00	09DJ00	REG	10/9/97	11:56:39	Be	LIBS-B
111LUC	09DP00	09DP00	REG	10/9/97	12:00:09	Be	LIBS-B
111LUC	N/A	BLANK1	FDB	10/9/97	12:05:12	Be	LIBS-B
111LUC	N/A	SPIKE1	FS	10/9/97	12:09:26	Be	LIBS-B
111LUC	10CF00	10CF00	REG	10/9/97	14:41:03	Be	LIBS-B
111LUC	10CK00	10CK00	REG	10/9/97	14:43:43	Be	LIBS-B
111LUC	10CQ00	10CQ00	REG	10/9/97	14:47:11	Be	LIBS-B
111LUC	10CV00	10CV00	REG	10/9/97	14:50:55	Be	LIBS-B
111LUC	10DA00	10DA00	REG	10/9/97	14:53:42	Be	LIBS-B
111LUC	10DF00	10DF00	REG	10/9/97	14:56:25	Be	LIBS-B
111LUC	10DK00	10DK00	REG	10/9/97	15:00:44	Be	LIBS-B
111LUC	10DG00	10DG00	REG	10/9/97	15:06:31	Be	LIBS-B
111LUC	10DB00	10DB00	REG	10/9/97	15:09:19	Be	LIBS-B
111LUC	10CW00	10CW00	REG	10/9/97	15:12:38	Be	LIBS-B
111LUC	N/A	BLANK2	FDB	10/9/97	15:17:28	Be	LIBS-B
111LUC	10CR00	10CR00	REG	10/9/97	15:20:21	Be	LIBS-B
111LUC	10CL00	10CL00	REG	10/9/97	15:23:10	Be	LIBS-B
111LUC	10CG00	10CG00	REG	10/9/97	15:28:11	Be	LIBS-B
111LUC	10CG00	10CG00	DUP	10/9/97	15:31:48	Be	LIBS-B
111LUC	10CH00	10CH00	REG	10/9/97	15:35:38	Be	LIBS-B
111LUC	N/A	SPIKE2	FS	10/9/97	15:40:19	Be	LIBS-B

Site ID	Location ID	Be Concentration	Analyte Units	Method Detection Limit	MDL Units	Date Measured	Time Measured	Data File Name
111LUC	09CJ00	180	ppm	50	ppm	10/9/97	11:34:53	09CJ00RW.B
111LUC	09CP00	60	ppm	50	ppm	10/9/97	11:40:58	09CP00RW.B
111LUC	09CU00	70	ppm	50	ppm	10/9/97	11:46:28	09CU00RW.B
111LUC	09CZ00	-20	ppm	50	ppm	10/9/97	11:48:54	09CZ00RW.B
111LUC	09DE00	70	ppm	50	ppm	10/9/97	11:53:30	09DE00RW.B
111LUC	09DJ00	300	ppm	50	ppm	10/9/97	11:56:39	09DJ00RW.B
111LUC	09DP00	350	ppm	50	ppm	10/9/97	12:00:09	09DP00RW.B
111LUC	N/A	0	ppm	50	ppm	10/9/97	12:05:12	BLANK1BW.B
111LUC	N/A	1350	ppm	50	ppm	10/9/97	12:09:26	SPIKE1SW.B
111LUC	10CF00	180	ppm	50	ppm	10/9/97	14:41:03	10CF00RW.B
111LUC	10CK00	50	ppm	50	ppm	10/9/97	14:43:43	10CK00RW.B
111LUC	10CQ00	90	ppm	50	ppm	10/9/97	14:47:11	10CQ00RW.B
111LUC	10CV00	20	ppm	50	ppm	10/9/97	14:50:55	10CV00RW.B
111LUC	10DA00	10	ppm	50	ppm	10/9/97	14:53:42	10DA00RW.B
111LUC	10DF00	0	ppm	50	ppm	10/9/97	14:56:25	10DF00RW.B
111LUC	10DK00	0	ppm	50	ppm	10/9/97	15:00:44	10DK00RW.B
111LUC	10DG00	50	ppm	50	ppm	10/9/97	15:06:31	10DG00RW.B
111LUC	10DB00	20	ppm	50	ppm	10/9/97	15:09:19	10DB00RW.B
111LUC	10CW00	30	ppm	50	ppm	10/9/97	15:12:38	10CW00RW.B
111LUC	N/A	-30	ppm	50	ppm	10/9/97	15:17:28	BLANK2BW.B
111LUC	10CR00	30	ppm	50	ppm	10/9/97	15:20:21	10CR00RW.B
111LUC	10CL00	70	ppm	50	ppm	10/9/97	15:23:10	10CL00RW.B
111LUC	10CG00	160	ppm	50	ppm	10/9/97	15:28:11	10CG00RW.B
111LUC	10CG00	230	ppm	50	ppm	10/9/97	15:31:48	10CG00DW.B
111LUC	10CH00	140	ppm	50	ppm	10/9/97	15:35:38	10CH00RW.B
111LUC	N/A	1180	ppm	50	ppm	10/9/97	15:40:19	SPIKE2SW.B

Example Excel Data File for TRACER Measurement Results

Site ID	Location ID	Sample ID	Sample Type	Date Collected	Time Collected	Analyte Element	Method
111LUC	05ED00	05ED00R	REG	10/2/97	9:21	Beryllium	LIBS-T
111LUC	05EP00	05EP00R	REG	10/2/97	9:12	Beryllium	LIBS-T
111LUC	05EH00	05EH00R	REG	10/2/97	9:42	Beryllium	LIBS-T
111LUC	05EC00	05EC00R	REG	10/2/97	9:45	Beryllium	LIBS-T
111LUC	05EI00	05EI00R	REG	10/2/97	9:24	Beryllium	LIBS-T
111LUC	05EI00	05EI00D	DUP	10/2/97	9:24	Beryllium	LIBS-T
111LUC	05ES00	05ES00R	REG	10/2/97	9:37	Beryllium	LIBS-T
111LUC	05ET00	05ET00R	REG	10/2/97	9:30	Beryllium	LIBS-T
111LUC	05EK00	05EK00R	REG	10/2/97	10:12	Beryllium	LIBS-T
111LUC	N/A	BLANK1B	FDB	N/A	N/A	Beryllium	LIBS-T
111LUC	05EA00	05EA00R	REG	10/2/97	10:39	Beryllium	LIBS-T
111LUC	05ER00	05ER00R	REG	10/2/97	10:02	Beryllium	LIBS-T
111LUC	05EB00	05EB00R	REG	10/2/97	9:51	Beryllium	LIBS-T
111LUC	04FG00	04FG00R	REG	10/2/97	9:57	Beryllium	LIBS-T
111LUC	05EU00	05EU00R	REG	10/2/97	9:08	Beryllium	LIBS-T
111LUC	04FA00	04FA00R	REG	10/2/97	9:37	Beryllium	LIBS-T
111LUC	04FI00	04FI00R	REG	10/2/97	9:54	Beryllium	LIBS-T
111LUC	05EG00	05EG00R	REG	10/2/97	9:55	Beryllium	LIBS-T
111LUC	04FY00	04FY00R	REG	10/2/97	10:42	Beryllium	LIBS-T
111LUC	N/A	SPIKE1S	FS	N/A	N/A	Beryllium	LIBS-T
111LUC	05EE00	05EE00R	REG	10/2/97	9:18	Beryllium	LIBS-T
111LUC	05EE00	05EE00D	DUP	10/2/97	9:18	Beryllium	LIBS-T
111LUC	05EQ00	05EQ00R	REG	10/2/97	10:05	Beryllium	LIBS-T
111LUC	05EJ00	05EJ00R	REG	10/2/97	9:15	Beryllium	LIBS-T
111LUC	05EF00	05EF00R	REG	10/2/97	10:15	Beryllium	LIBS-T
111LUC	04FJ00	04FJ00R	REG	10/2/97	9:49	Beryllium	LIBS-T
111LUC	04FK00	04FK00R	REG	10/2/97	10:01	Beryllium	LIBS-T
111LUC	04FC00	04FC00R	REG	10/2/97	9:42	Beryllium	LIBS-T
111LUC	04FE00	04FE00R	REG	10/2/97	9:45	Beryllium	LIBS-T
111LUC	05EN00	05EN00R	REG	10/2/97	9:27	Beryllium	LIBS-T
111LUC	N/A	BLANK2B	FDB	N/A	N/A	Beryllium	LIBS-T
111LUC	04FR00	04FR00R	REG	10/2/97	10:28	Beryllium	LIBS-T
111LUC	05EL00	05EL00R	REG	10/2/97	9:58	Beryllium	LIBS-T
111LUC	04FM00	04FM00R	REG	10/2/97	10:04	Beryllium	LIBS-T
111LUC	05EM00	05EM00R	REG	10/2/97	9:39	Beryllium	LIBS-T
111LUC	N/A	SPIKE2S	FS	N/A	N/A	Beryllium	LIBS-T

Example Excel Data File for TRACER Measurement Results

Site ID	Location ID	Be Conc. (ppm) Shot # 1	Be Conc. (ppm) Shot # 2	Be Conc. (ppm) Shot # 3	Be Conc. (ppm) Shot # 4	Be Conc. (ppm) Shot # 5	Be Conc. (ppm) Shot # 6	Average Be Conc. (ppm)
111LUC	05ED00	37	38	37	36	35	35	36
111LUC	05EP00	188	111	127	109	157	133	138
111LUC	05EH00	39	37	30	34	44	45	38
111LUC	05EC00	45	36	40	34	35	40	38
111LUC	05EI00	239	259	300	255	262	271	264
111LUC	05EI00	242	234	213	212	218	228	225
111LUC	05ES00	56	72	49	47	51	47	54
111LUC	05ET00	104	91	89	95	98	101	96
111LUC	05EK00	24	19	20	21	17	19	20
111LUC	N/A	23	21	24	17	11	18	19
111LUC	05EA00	42	38	43	40	41	38	40
111LUC	05ER00	49	50	49	47	48	58	50
111LUC	05EB00	22	27	21	25	22	26	24
111LUC	04FG00	32	25	30	36	42	46	35
111LUC	05EU00	42	43	41	44	46	55	45
111LUC	04FA00	18	17	14	17	17	17	17
111LUC	04FI00	47	53	51	52	55	50	51
111LUC	05EG00	75	99	150	119	235	76	126
111LUC	04FY00	270	238	237	224	218	201	231
111LUC	N/A	1412	1042	1153	1099	1111	1112	1155
111LUC	05EE00	67	86	83	107	161	287	132
111LUC	05EE00	85	97	120	82	111	99	99
111LUC	05EQ00	27	22	29	27	25	24	26
111LUC	05EJ00	77	64	80	71	60	65	70
111LUC	05EF00	55	50	53	44	54	45	50
111LUC	04FJ00	73	71	66	70	69	77	71
111LUC	04FK00	19	12	11	16	17	13	15
111LUC	04FC00	28	29	22	21	24	26	25
111LUC	04FE00	35	67	27	30	29	30	36
111LUC	05EN00	53	50	55	50	53	56	53
111LUC	N/A	17	14	23	30	26	26	23
111LUC	04FR00	38	40	34	37	36	36	37
111LUC	05EL00	31	24	25	24	28	25	26
111LUC	04FM00	57	58	51	65	55	50	56
111LUC	05EM00	31	28	24	26	28	26	27
111LUC	N/A	1072	887	834	1008	960	963	954

APPENDIX B: SEA PRESS RELEASE

DOE Technology Used to Characterize Beryllium Contaminated Site

Science & Engineering Associates, Inc (SEA) of Albuquerque, NM has teamed with researchers at Los Alamos National Laboratory (LANL) to deploy prototype field instruments at a Luckey, Ohio site. The Luckey Site was used during the early 1950's by the Brush Beryllium Company to operate and maintain a beryllium manufacturing plant for the AEC. As a result of these operations and others since then, the 40 acre site was placed on the Formerly Utilized Sites Remedial Action Program (FUSRAP) list for cleanup.

In order to provide data to the remediation team on the beryllium contamination at the soil surface, SEA fielded a team with technology based on Laser Induced Breakdown Spectroscopy (LIBS). The LIBS technique uses a focused, high peak power laser to rapidly heat the soil. The "spark" produced emits light of certain wavelengths and intensities that can be correlated back to the concentration of contaminants - in this case beryllium. As shown in the pictures, two separate instruments were deployed for this initial 6 week surface characterization. The Backpack LIBS unit, which contains a small

spectrometer, optics and batteries in a single backpack and a laser in a "walking stick" arrangement, can be transported around the site to access the surface over uneven and heavily foliated terrain. The analysis can be conducted by placing the laser directly onto the surface. A small wrist mounted computer controls the instrument and analyzes the data in real time.

The second LIBS unit is slightly larger but has greater sensitivity. This van mounted instrument, named TRACER, was primarily used to evaluate soil samples that were below the detection limit of the backpack. In addition, it was used to evaluate samples taken from suspected highly contaminated areas to minimize personnel exposure. As shown in the Figure at right, the LIBS instruments located "hot spots" of Be-contaminated soils where the contamination was high.

SEA was funded for this effort by the

Federal Energy Technology Center (FETC) and the Oak Ridge DOE FUSRAP program under contract #DE-AR21-95-MC32089. The FUSRAP program is presently being operated by the U.S. Corp of Engineers. The hardware used for this effort was developed and supplied by LANL. SEA is presently developing a number of different systems for elemental analysis based on this technology. For more information, contact Dr. Steven Saggese of SEA at (505) 880-9862 or e-mail at sjsaggese@seabase.com.

**Aerial Photo of
Luckey Site**

Beryllium Concentration Map

APPENDIX B

LIBS/CPT Workplan for DOE Hanford Deployment

Written by:

**Science & Engineering Associates, Inc.
6100 Uptown Blvd. NE
Albuquerque, NM 87110**

**Applied Research Associates, Inc.
Waterman Road RR1
South Royalton, VT 05068**

March 10, 1998

TABLE OF CONTENTS

1.	PURPOSE.....	1
2.	INTRODUCTION	1
3.	OBJECTIVES.....	2
3.1.	Background on Cone Penetration Technology.....	3
3.2.	Background on LIBS technology	4
3.2.1.	LIBS for Soils Analysis.....	6
3.2.2.	LIBS Calibration.....	8
3.2.3.	Calibration of LIBS for Ur and Cr Analysis at Hanford Site	10
3.2.4.	LIBS/CPT Analysis.....	11
3.3.	Personnel on-site for LIBS-CPT testing.....	12
3.4.	Site Selection	13
3.5.	Decontamination	13
3.6.	Penetration Closure	14
3.7.	Data Collection	15
3.8.	Data Evaluation.....	15
3.8.1.	LIBS Data Analysis.....	15
3.8.2.	CPT Data Evaluation	16
4.	FINAL REPORTING	18
5.	FIELD LOGISTICS.....	18
6.	REFERENCES	18
7.	Appendix A: Lithology Testing using CPT.....	20
8.	Appendix B: Laser Safety Certification	26
9.	Appendix C: Work Schedule	27
10.	Appendix D: Training Schedule.....	28

1. PURPOSE

The purpose of this task plan is to provide guidelines for the Laser Induced Breakdown Spectroscopy - Cone Penetrometer Testing (LIBS-CPT) to be conducted at the 300 and 100 areas of the DOE Hanford facility. This demonstration is being conducted as partial fulfillment of Contract DE-AR21-95MC32089 between Science and Engineering Associates, Inc. (SEA) and the Federal Energy Technology Center (FETC). The testing is being conducted to demonstrate the LIBS/CPT system to potential DOE users and to evaluate the cost effectiveness of the technology. The baseline technology upon which the cost effectiveness will be evaluated consists of digging trenches, obtaining physical samples, and then analyzing those samples using either screening methods or laboratory analytical techniques.

The parties involved in this project consist of Bechtel Hanford, Inc. (BHI), Science & Engineering Associates, Inc. (SEA) and Applied Research Associates, Inc. (ARA). BHI is primarily responsible for providing the infrastructure to conduct the testing. The responsibilities include all site preparation activities (e.g. surveying, site access, permitting, health and safety management, and waste disposal) necessary to perform the testing. SEA is responsible for supplying and operating the LIBS equipment. ARA, under contract to SEA, is responsible for providing the cone penetrometer test equipment and its operation. SEA and ARA have been jointly working on the integration of the LIBS and CPT for the past year and have formed an effective working team.

2. INTRODUCTION

LIBS is being developed to conduct elemental analysis on a variety of types of samples, such as soils, metals, and rocks. In the LIBS technique, a laser is focused onto a sample to produce an intense plasma (or spark). The excitation of ions in the plasma causes the emission of light of discrete wavelengths which are characteristic of the elements present. The plasma emission can be evaluated with a spectrometer and the wavelength and intensity of the light emitted will be indicative of the elements present.

For environmental remediation activities, LIBS is being investigated for the analysis of heavy metals and other contaminants in soils, both on the surface and in the subsurface. For subsurface analysis, a LIBS system can be deployed with a cone penetrometer to produce a 3-D mapping of a contaminant. This type of system is potentially less expensive than standard techniques, can produce near real time results, and does not produce any additional waste which has to be disposed.

For the present effort at the Hanford Site, the LIBS/CPT system will initially be used to investigate the concentration of Ur in the 300 Area. The goal will be to deploy LIBS in areas near where test pits have been dug and the soils analyzed. The LIBS system, therefore, can be evaluated for future use in the 300 Area as a characterization tool. Upon successful completion of this task, the LIBS/CPT system will be deployed in the 100-D Area. In the 100-D Area, sodium dichromate was used and it has been determined that there may have been substantial spills from pipelines and/or tanks. The LIBS/CPT system will be used to investigate a number of locations in the 100-D Area for high chromium content to identify source areas for chromium VI. (Note: the LIBS technique will evaluate total Cr only and will not be able to specifically identify Cr VI).

3. OBJECTIVES

The objective of the CPT/LIBS testing in the 300 Area is to determine the uranium profile of the soil berms surrounding waste ponds where disposal wastes were deposited. For the 100 Area, the LIBS/CPT system will be used identify source areas for chromium VI. The CPT, using separate standard CPT probe hardware, may also be used to identify any lithology changes that occur within the berms. Testing will be conducted for a period of three to five eight-hour days at the 300 Area and up to five days at the 100-D area, depending upon the overall performance of the system in the 300 Area.

3.1. Background on Cone Penetration Technology

The Cone Penetrometer Test (CPT) was originally developed in The Netherlands in about 1934 for geotechnical site investigations. The original cones involved mechanical measurements of the penetration resistance on a conical tip. A friction sleeve was added in 1965 (Begemann, 1965). Electronic measurements were added in 1948 and improved in 1971 (de Reister, 1971). Pore pressure probes were introduced in 1975 (Torstensson, 1975 and Wissa et al., 1975), initially as independent sensors, but were soon incorporated with the cone penetrometer instrumentation. The modern CPT probe contains the primary geotechnical sensors for tip stress, sleeve friction, pore pressure along with options of an inclinometer to measure the tilt of the probe, resistivity, soil moisture, soil pH, and redox potential. The standard 10cm² cone is used widely in Europe for geotechnical investigations due to the soft nature of many of the European soils. In the United States, significant efforts have been made to develop more robust CPT probes suitable for use in the stiffer United States soils (especially in the western states). Due to the high cost of drilling at contaminated sites, both the DOD and DOE have initiated aggressive programs to develop chemical sensors and sampling methods for the minimally intrusive CPT (Bratton, et al., 1993; Gildea, et al., 1995; Montgomery, et al., 1996; Farrington and Bratton, 1997). This demonstration is a result of one such program.

Major components of the modern cone penetrometer system are the instrumented probe, the instrumentation conditioning and recording system, the hydraulic push system, and the vehicle on which the system is mounted. The common configuration provides the reaction mass for a hydraulic push force of about 20 tons (18,000 Kg); however, due to the gravelly nature of the soil at the Hanford facility, 30 tons of reaction mass will be provided. Standardization for geotechnical applications of the cone penetration test was established by the American Society of Testing and Materials in 1986. This standard allows for a probe diameter of 1.44 or 1.75 inches (3.658 cm or 4.445 cm).

Using the cone penetrometer for environmental site characterization represents a relatively recent application of the technology. Significant advantages of the CPT include: eliminating drilling wastes and the need for treatment and disposal of drill spoils as hazardous material; providing continuous data on the subsurface stratigraphy in real time; identifying thin layers of significantly different hydraulic conductivity; minimizing the potential for crew exposure to the potentially hazardous material; reducing the possibility of cross-contamination (by pressure grouting the hole as the probe is withdrawn); and speed, when compared to conventional drilling and sampling. CPT is an excellent platform for making continuous measurements of contaminant information with depth, is useful for pushing monitoring sensors into the subsurface, for installing monitoring wells and points, and for taking gas, water, or soil samples for environmental testing.

For this 300 Area and the 100-D Area efforts, the cone penetrometer tests will be conducted using the ARA penetrometer truck. The penetrometer equipment is mounted inside a van body attached to a 10-wheel truck chassis with a diesel engine. Ballast in the form of metal weights are added to the truck to achieve an overall push capability of 60,000 lbs. Penetration force is supplied by a pair of large hydraulic cylinders bolted to the truck frame.

3.2. Background on LIBS technology

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. LIBS instruments have been primarily used in a laboratory environment and they are just now being developed for the field. At the present time, there are various types of LIBS instruments being developed for field applications, such as hand-held devices, van mounted systems, and truck mounted cone penetrometer systems.

Regardless of the deployment technique, all LIBS systems contain the same basic components. As shown in Figure 1, a LIBS system consists of a laser source to produce the plasma, a method of delivering and focussing the laser beam onto the sample, 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.

Figure 1. A typical laser induced breakdown spectroscopic (LIBS) system

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

3.2.1. LIBS for Soils Analysis

When evaluating soils, the spectrograph is tuned to the wavelength(s) of where the element of interest has an emission. Figure 2(a) through 2(c) show LIBS spectra determined for an NIST sample from a Montana Superfund Site with high heavy metals contamination. Figure 2(a) shows the spectral region for Pb, Figure 2(b) for Cr, and

Figure 2(a). LIBS spectrum of a NIST Superfund soil in the Pb spectral range

Figure 2(b). LIBS spectrum of a NIST Superfund soil in the Cr spectral range

Figure 2(c) for Cu, Zn, and Ag. Each spectra contains information on other elements. Figure 2a, for example, shows the spectral window from 402 nm to 410 nm which 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 2(c). LIBS spectrum of a NIST Superfund soil in the Cu/Zn spectral range

3.2.2. LIBS Calibration

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 3(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 3(b) shows the reduction in the Pb peak as the concentration of Pb is decreased.

Figure 3. (a) A typical LIBS spectrum for a 1000 ppm Pb-spiked soil sample.
(b) The Pb peak is reduced as the concentration of Pb is decreased.

Calibration curves for conducting quantitative analysis are constructed by plotting the ratio of the peak areas for the analyte of interest and a standard element vs. the concentration of the heavy metal in the soil. Figure 4 shows a calibration curve for a Pb-spiked sample using an Fe line as an internal standard. Using the best fit equation, the concentration of the heavy metal can be calculated by evaluating the peak areas.

Figure 4. A calibration curve for Pb in soil

3.2.3. Calibration of LIBS for Ur and Cr Analysis at Hanford Site

Research efforts are presently underway to optimize the calibration of LIBS instruments. Soil matrix effects, such as clay/sand content, moisture, and variations in particle size all play a role in the LIBS signal generation and data analysis. As a result of matrix effects, it is advantageous to produce calibration curves from the soils that will be investigated with LIBS, therefore, BHI supplied both Cr- and Ur-contaminated soils to SEA for calibration set-up.

The soils of various analyte concentrations were excavated, analyzed for the concentration of the analyte of interest, and sent to SEA. The concentration range of interest for both Uranium in the 300 Area and Cr in the 100 Area will be from background through 2000 ppm. (Note: The present action level for uranium is 350 picocuries per gram which equates to about 1029 ppm). The soils excavated from the Hanford Site, however, did not adequately represent the concentration range of interest, therefore, SEA is generating “spiked” samples. SEA will mix the soils delivered from the 300 Area and the 100 Area with known quantities of Uranium and Chromium, respectively, to generate calibration curves.

The actual calibration curves will be reported within the final report. It is anticipated that the lower quantitative detection limit in the field for Cr will be <100ppm and that for Ur will < 500 ppm.

3.2.4. LIBS/CPT Analysis

The subsurface analysis will be conducted with a special CPT deployed LIBS probe. As shown in Figure 5, the module contains a sacrificial sleeve which protects the optics used to focus the laser onto the soil and return the emission signal during the penetration process. The LIBS system is not active during the penetration portion of the push as the sacrificial sleeve covers the sensing equipment. Once the final depth or refusal is reached, the CPT equipment is retracted leaving behind the sacrificial sleeve and exposing the optics to the soil surface. The LIBS analysis is performed upon retraction of the penetrometer from the soil.

Figure 5: LIBS analysis is conducted upon retraction of the penetrometer and removal of a sacrificial sleeve.

The LIB/CPT probe head is configured as shown in Figure 6. A copper tube is used to deliver the Q-switched laser pulse down into the penetrometer rod string and two lenses and a high power mirror are used to direct and focus the laser onto the soil surface. Two optical fibers which have a 90 degree acceptance angle are used to retrieve

Figure 6: LIBS optical arrangement.

the spark emission and transmit the light back to the spectrometer in the truck. The LIBS/CPT probe is susceptible to damage due to the close proximity of dirt and debris to optical elements, therefore, the head has been designed to minimize the laser energy density on the optics and an airtube is used to keep the optics clean.

3.3. Personnel on-site for LIBS-CPT testing

The LIBS-CPT crew will consist of 4 to 5 people. The CPT portion is performed by a crew chief and a rod man with a project engineer as oversight and the LIBS testing will be conducted using a two man crew. All crew members will have current OSHA 40 hour certification, and the CPT rod man and crew chief will also have RAD2 level

training for the work in the 300 area. The LIBS crew and the CPT project engineer will be data handlers and not handle equipment.

For the 100D area work, the project engineer may also serve as the rod man. This leaves a two man crew for the CPT and also a two man crew for the LIBS.

3.4. Site Selection

The specific test locations will be selected by BHI for each site. For the 300 area the berm tops must of sufficient width (10 feet) and strength (30 tons of load) that the CPT rig can be driven upon them. The penetration point is located near the centerline of the CPT rig and therefore the test locations should be located near the center of the berm. All penetrations will be conducted to a depth of 25 feet, which is the estimated thickness of the berm, or until penetrometer refusal. All test locations will be cleared and permitted if required by BHI prior to testing.

For the 100-D Area testing, BHI will again select penetration locations. As this site is a relatively flat, site access should not be a problem and the only requirement is that the CPT rig can get to each designated test location. The depth of penetration for this area will be the maximum possible at refusal or the top of the aquifer (approximately 85 feet). ARA will use instruments on the CPT to detect the top of the aquifer. To date, SEA has not had the opportunity to test the LIBS unit at depths greater than 40 feet, but every effort will be made to enable testing at lower depths if the penetrometer can penetrate further.

3.5. Decontamination

Decontamination in the 300 area will be performed on an as needed basis to reduce waste generation. As each 1 meter rod is removed from the ground after the LIBS analysis, HP personnel will use a muslin mop and take a swab the full length of rod. (Note: The truck height allows for 1 meter lengths of rod to be removed from the soil without entering the truck). The swab will be scanned by the HP to determination if

contamination is present on the rods. If clean, the rods will be permitted to enter the truck. If dirty, the rods will be fully wiped by ARA personnel and a second swab taken by HP. This process will continue until the rods are found to be clean by the HP. When the rods are clean, they will be allowed into the truck. If the rods cannot be cleaned by ARA personnel, they will be pushed back into the ground for a depth of 6 feet, and will again be retracted using the standard testing and wiping procedures. If the rod still remains dirty, then the rods will be disconnected from the truck and will be pulled by a driller. The rods will then be sent for decontamination. All decontamination and radiation monitoring equipment that becomes contaminated is the responsibility of BHI. Decontamination in the 100-D area will be performed using the same procedures used in the 300 area.

If swabbing is ineffective, inefficient or otherwise impractical, then decontamination will be performed by steam cleaning. The steam cleaning is accomplished through a steam cleaning head located on the end of the guide tube. This unit has friction seals on both the top and bottom of the cleaning section. As the rods are pulled through this section they are washed with high pressure hot water to remove contamination. The waste water exits the unit and is stored in a collection bucket. The water spray is only applied while the rods are moving to minimize waste generation. Disposal of the waste water will be the responsibility of BHI.

3.6. Penetration Closure

The penetration hole that remains after retraction of the CPT equipment will be backfilled from the surface using bentonite pellets if required. Filling of the holes will be performed on a daily basis at the end of each day by the CPT crew. Final requirements for hole abandonment will be available from the Washington Department of Natural Resources when BHI obtains the required permits.

3.7. Data Collection

Upon retraction of the penetrometer rods, the LIBS system will be activated. The laser pulse will be delivered from the truck into the probe tip where it is focused onto the soil surface. The laser is operated in a continuous pulsed mode such that a series of spectra will be collected while the probe is being retracted. At each 1 meter length of retraction, a CPT rod must be removed. At this juncture, the LIBS data will be saved such that each rod will have a corresponding spectral file. Each spectral file will contain individual sparks that will be evenly distributed over the 1 meter length of rod (i.e. 1000 sparks will produce a resolution of 1 mm). Under normal conditions, multiple sparks will be averaged to minimize the S/N, so the resolution will be reduced. For the present effort, the spectra will be averaged over a length of 1 to 3 feet. For example, in the 300 Area SEA will attempt to obtain at least 25 discrete concentration values for Ur with a 25 foot penetration. If the data quality warrants, this will be increased.

Normal CPT data may be collected on separate pushes, if desired. As described in Appendix A, the CPT data consists of measurements of the tip stress, sleeve stress and pore pressure generated during the penetration. These values are all recorded along with a depth value by a data acquisition system mounted in the CPT rig. Data is recorded at a rate of one record for all sensors every second. For a penetration rate of 2 cm/sec this corresponds to a depth resolution of 2 cm. The raw data is stored in a .DAT file. Header information that is also stored in the .DAT file consists of the date and time, site location, crew present, and weather conditions.

3.8. Data Evaluation

3.8.1. LIBS Data Analysis

After all of the spectra from each rod have been collected and combined into a single file, the quality of each individual spark will be evaluated and only those which pass a minimum criteria will be utilized. Once the inadequate sparks have been removed,

the sparks can then be grouped and averaged to achieve the desired vertical resolution. To quantify the concentration of the element of interest, the area of its emission peak(s) will be calculated, divided by the area of an internal standard, and compared to a previously determined calibration curve. This process will produce concentration values for the contaminant that can be plotted as a function of depth. The vertical profile of the contaminant can then be evaluated by the site personnel. Since the software for data analysis is still presently under development, it is anticipated that the results will be available for evaluation by site personnel on the day following raw data collection.

3.8.2. CPT Data Evaluation

If acquired, the CPT measurements will be transformed into profiles of tip resistance, sleeve friction and pore pressure if used. A sample presentation of data is shown in Figure 7. Tip resistance is obtained by dividing the vertical force on the conical tip by the effective tip area (2.35 in²). The offset between the depth at the tip and the depth at the friction sleeve is corrected by shifting the sleeve friction profile downward so that it corresponds to the depth at the centroid of the tip. In addition to the resistance and sleeve friction, a friction ratio profile is presented for each location. This is simply the sleeve friction expressed as a percentage of the tip resistance. In uncemented soils the friction ratio can be used to determine soil type.

Figure 7. Sample CPT Presentation of Data.

The penetration pore pressure that is measured as the probe is advanced is also plotted in Figure 7. The magnitude of the penetration pore pressure is a function of the soil compressibility and, most importantly, permeability. In freely draining soil layers, the measured pore pressures will be very close to the hydrostatic pressure computed from the elevation of the water table. When low permeability soil layers are encountered, excess pore pressures generated by the penetration process can not dissipate rapidly and this results in measured pore pressures which are significantly higher than the hydrostatic pressures. Whenever the penetrometer is stopped to add another section of push tube, or when a pore pressure dissipation test is run, the excess pore pressure may begin to dissipate. When the penetration is resumed, the pore pressure quickly rises to the level measured before the penetrometer was stopped. This process causes some of the spikes

that may appear in the penetration pore pressure data. Appendix A provides more detail on CPT analysis.

4. FINAL REPORTING

A draft report will be delivered to BHI three weeks after completion of the field tests. After receipt of technical reviews and comments from DOE-Richland and BHI, a final report will be submitted to BHI within 2 weeks. The final report will address technical reviews and comments. The report will include information on the equipment used for the tests, the specific tests conducted, a daily log, the LIBS and CPT data and interpretations of the results. In addition, the report will discuss the costs to conduct the demonstration and an estimation of the cost for future analysis at the Hanford Site.

5. FIELD LOGISTICS

The required physical site conditions of each test site were discussed previously. In addition, there are necessary procedural and safety steps that need to be completed prior to implementation of any field activities. The implementation of these activities are not part of this Task Plan and are the responsibility of BHI. Listed below are several of these key activities.

- Health and Safety Plan
- Job Safety Analysis
- Initial Radiation Survey
- Radiation Survey of Leveled Areas
- Radiation Work Permit
- Air Monitoring
- Dust Control
- Excavation permit
- Equipment Protection from Radiation
- Site Preparation

6. REFERENCES

- American Society for Testing Materials, "Standard Method for Deep Quasi-Static Cone and Friction-Cone Penetration Tests of Soil," ASTM Designation: D3441, 1986.
- Robertson, P.K. and R.G. Campanella, *Guidelines for Using the CPT, CPTU and Marchetti DMT for Geotechnical Design*, Vol. II, University of British Columbia, Vancouver, BC, Canada, March 1988.
- Begemann, H.K.S., "The Friction Jacket Cone as an Aid in Determining the Soil Profile," *Proc. 6th ICSMFE*, Montreal, Canada, Vol. I, pp. 17-20, 1965.
- Bratton, W.L., J.D. Shinn, S.M. Timian, G.D. Gillispie, R. St. Germain, "The Air Force Site Characterization and Analysis Penetrometer System (AFSCAPS); Laser Induced Fluorescence Cone Penetrometer," Under Contract No. F08635-88-C-0067, SETA Subtask 8.00, Report to Air Force Armstrong Laboratory, Tyndall AFB, FL, February 1993.
- de Reister, J., "Electric Penetrometer for Site Investigations," *Journal of SMFE Division*, ASCE, Vol. 97, SM-2, pp. 457-472, February 1971.
- Farrington, S.P., and W.L. Bratton, "Measuring Fuel Contamination Using Cone Penetration Testing and High Speed Gas Chromatography," Final Report to U.S. Department of Energy, Morgantown Technology Center, Morgantown, WV, February 1997.
- Gildea, M.L., W.L. Bratton, J.D. Shinn, "Demonstration and Evaluation of the Air Force Site Characterization and Analysis Penetrometer System in Support of Natural Attenuation Initiatives," Under Contract F08635-93-C-0020, SETA Subtask 8.01.1, Report to Air Force Armstrong Laboratory, Tyndall AFB, FL, February 1995.
- Montgomery, R.L., J.C. Bianchi, J.D. Shinn, R.M. Morey, R.E. Walker, S.P. Farrington, W.C. Dickerson, S.M. Conklin, "Groundwater Remediation Field Laboratory - GRFL: Hydrogeology Characterization and Site Development," Report to Air Force Armstrong Laboratory AL/EQW-OL, Tyndall AFB, FL, June 1996.
- Torstensson, B.A., "Pore Pressure Sounding Instrument," *Proc. ASCE Spec. Conf. on In Situ Measurement of Soil Properties*, Raleigh, NC, Vol. II, pp. 48-54, 1975.
- Wissa, A.E.Z., Martin, R.T., and Garlanger, J.E., "The Piezometer Probe," *Proc. ASCE Spec. Conf. on In Situ Measurement of Soil Properties*, Raleigh, NC, Vol. I, pp. 536-545, 1975.

7. Appendix A: Lithology Testing using CPT

The penetrometer probe is of standard dimensions having a 1.75-inch diameter, 60° conical tip, and a 1.75-inch diameter by 5.27-inch long friction sleeve as shown in Figure A-1. The shoulder between the base of the tip and the porous filter is 0.08 inch long. A 1.85-inch diameter expander, located behind the top of the friction sleeve, pushes the penetration hole open and reduces the frictional drag on the push tubes behind the probe. The penetrometer is normally advanced vertically into the soil at a constant rate of 48 inches/minute, although this rate must sometimes be reduced as hard layers are encountered. The electric cone penetrometer test is conducted in accordance with ASTM D3441.

Figure A-1. Schematic of CPT Probe with Resistivity and Moisture Module

Inside the probe, two load cells independently measure the vertical resistance against the conical tip and the side friction along the sleeve. Each load cell is a cylinder of uniform cross section which is instrumented with four strain gages in a full-bridge circuit. Forces are sensed by the load cells and the data are transmitted from the probe

assembly via a cable running through the push tubes. The analog data are digitized, recorded, and plotted by computer in the penetrometer truck. A set of data is normally recorded each second, for a minimum resolution of about one data point every 0.8 inch of cone advance. The depth of penetration is measured using a linear displacement transducer mounted inside one of the push cylinders.

Electronic data acquisition equipment for the cone penetrometer consists of a computer with a graphics monitor and a rack of eight signal conditioners. Analog signals are transmitted from the probe to the signal conditioners where the CPT data are amplified and filtered at 1 Hz. Once amplified, the analog signals are transmitted to a high speed analog-to-digital converter board, where the signals are digitized; usually at the rate of one sample per second for the penetration data and 10,000 samples per second for the seismic data. The digital data are then read into memory and written to the internal hard disk for future processing.

Saturation of the Piezo-Cone

When penetration pore pressures are to be measured a pressure transducer is located behind the tip in the lower end of the probe. Water pressures in the soil are sensed through a 250 min porous polyethylene filter that is 0.25-inch high and 0.202-inch thick. The pressure transducer is connected to the porous filter through a pressure port as shown in Figure 1. The pressure port and the filter are filled with a high viscosity silicone oil.

For the pressure transducer to respond rapidly and correctly to changing pore pressures upon penetration, the filter and pressure port must be saturated with oil upon assembly of the probe. A vacuum pump is used to de-air the silicone oil before use and also to saturate the porous filters with oil. The probe is assembled with the pressure transducer facing upwards, and the cavity above the pressure transducer is filled with de-aired oil. A previously saturated filter is then placed on a tip and oil is poured over the

threads. When the cone tip is screwed into place, excess oil is ejected through the pressure port and filter, thereby forcing out any trapped air.

Saturation of the piezo cone is verified with field calibrations performed before and after each penetration test. The high viscosity of the silicone oil coupled with the small pore space in the filter prevents the loss of saturation as the cone is pushed through dry soils. Saturation of the cone can be verified with a calibration check at the completion of the penetration. Extensive field experience has proven the reliability of this technique.

Field Calibrations

Many factors can effectively change the calibration factors used to convert the raw instrument readouts, measured in volts, to units of force or pressure. As a quality control measure, as well as a check for instrument damage, the load cells and the pressure transducer are routinely calibrated in the field. Calibrations are completed with the probe ready to insert into the ground so that any factor affecting any component of the instrumentation system will be included and detected during the calibration.

The tip and sleeve load cells are calibrated with the conical tip and friction sleeve in place on the probe. For each calibration, the probe is placed in the push frame and loaded onto a precision reference load cell. The reference load cell is periodically calibrated in ARA's laboratory against instruments traceable to NIST standards. To calibrate the pore pressure transducer, the saturated probe is inserted into a pressure chamber with air pressure supplied by the compressor on the truck. The reference transducer in the pressure chamber is also periodically calibrated against an NIST traceable instrument in ARA's laboratory. Additionally, the linear displacement transducer used to measure the depth of penetration, is periodically checked against a tape measure.

Each instrument is calibrated using a specially developed computer code that displays the output from the reference device and the probe instrument in graphical form. During the calibration procedure, the operator checks for linearity and repeatability in the instrument output. At the completion of each calibration, this code computes the needed calibration factors using a linear regression algorithm. At a minimum, each probe instrument is calibrated at the beginning of each project. Furthermore, the pressure transducer is recalibrated each time the porous filter is changed and the cone resaturated. Calibrations are also performed to verify the operation of any instrument if any damage is suspected.

Pore Pressure Correction of Tip Stress

Cone penetrometers, by necessity, must have a joint between the tip and sleeve. Pore pressure acting behind the tip decreases the total tip resistance that would be measured if the penetrometer was without joints. The influence of pore pressure in these joints is compensated for by using the net area concept (Robertson & Campanella, 1988). The corrected tip resistance is given by:

$$q_T = q_c + u \left(1 - \frac{A_n}{A_T} \right) \quad (1)$$

where:

- q_T = corrected tip resistance (psi)
- q_c = measured tip resistance (psi)
- u = penetration pore pressure measured behind the tip (psi)
- A_n = net area behind the tip not subjected to pore pressure (1.911 in²)
- A_T = projected area of the tip (2.35 in²).

Hence, for the ARA cone design, the tip resistance is corrected as:

$$q_T = q_c + u (.1870) \quad (2)$$

Laboratory calibrations have verified Equation 2 for ARA's piezo-cone design.

A joint also exists behind the top of the sleeve (see Figure 1). However, since the sleeve is designed to have the same cross sectional area on both ends, the pore pressures acting on the sleeve cancel out. Laboratory tests have verified that the sleeve is subjected to equal end area effects. Thus, no correction for pore pressure is needed for the sleeve friction data.

The net effect of applying the pore pressure correction is to increase the tip resistance. Generally, this correction is only significant when the measured tip resistance is very low.

Numerical Editing of the Penetration Data

Any time that the cone penetrometer is stopped or pulled back during a test, misleading data can result. For instance, when the probe is stopped to add the next push tube section, or when a pore pressure dissipation test is run, the excess pore pressures will dissipate towards the hydrostatic pore pressure. When the penetration is resumed, the pore pressure generally rises very quickly to the pressures experienced prior to the pause in the test. In addition, the probe is sometimes pulled back and cycled up and down at intervals in deep holes to reduce soil friction on the push tubes. This results in erroneous tip stress data when the cone is advanced in the previously penetrated hole.

To eliminate this misleading data from the penetration profile, the data is numerically edited before it is plotted or used in further analysis. Each time the penetrometer stops or backs up, as apparent from the depth data, the penetration data is not plotted. Plotting of successive data is resumed only after the tip is fully re-engaged in the soil by one tip length (1.22 in) of new penetration. This algorithm also eliminates any data acquired at the ground surface before the tip has been completely inserted into the ground. The sleeve data is similarly treated and this results in the first data point not occurring at the ground surface, as can be seen in the tip and sleeve profiles of Figure 2.

These procedures ensure that all of the penetration data that is plotted and used for analysis was acquired with the probe advancing fully into undisturbed soil. The second part of Figure 2 illustrates the resulting soil classification and soil properties for this penetration.

8. Appendix B: Laser Safety Certification

LASER SAFETY TRAINING

Employee: Dr. Steven Saggese
Employee Number: 304
Date Certified: 1/5/98
Related Equipment: LIBS/Cone Penetrometer System

The employee listed above has completed the necessary laser safety training for the laser and equipment specified. The user will be responsible for safe system operation and ensuring that other personnel have been informed of the hazards.

Signed _____ (Signature on file)
Employee

Signed _____ (Signature on file)
Mr. Chris German, *SEA Laser Safety Officer*

9. Appendix C: Work Schedule

Task	Date(s)
Work on Modifications to Probe	Through March 20
Start field testing at ARA in VT	March 23
Finish Testing at ARA in VT	March 27
Mobilize to Hanford	April 18
System unpack/set-up	April 19
HGET Training	April 20
Mobilize to 300 Area & Set-up	April 20-morning April 21
Push LIBS	Afternoon April 21- 23
Teardown System/Remobilize to 100 Area	April 24
Push LIBS	April 27
Push LIBS (optional)	April 28
Push LIBS (optional)	April 29
Teardown System	April 30

10. Appendix D: Training Schedule

Name	HGET Training	Rad Worker 2
Wesley Bratton	4/20 at 8AM	Not required
Bryon Fisk	4/20 at 8AM	Not required
Shaun Ricker	4/20 at 8AM	Not required
Joel Borst	4/20 at 1PM	4/20 AM
Wayne Russel	4/20 at 1PM	4/20 AM
Steve Saggese	4/20 at 1PM	Not required
Tom Kendrick	4/21 at 8AM	Not required
Ames Grisanti	4/20 at 8AM	Not required

Cost Analysis

Methodology

The cost analysis of the CPT/LIBS system for subsurface heavy metals detection is based on comparison of the subject system to the baseline. The baseline method is installation of soil borings, collection of core samples, and off-site laboratory analysis.

The cost analysis will include a breakdown of the cost components associated with each technology and the conditions on which the costs are based. A cost comparison that applies each of the technologies to a hypothetical site investigation scenario will be performed to quantify the cost advantages of the CPT/LIBS system. A discussion of cost advantages of the CPT/LIBS System compared to the baseline will be included.

The cost data for the CPT/LIBS is based on information supplied by SEA and the demonstration of the system at Sandia's Chemical Waste Landfill. Cost data for the baseline technology was acquired from representatives of SNL. Other cost data was taken from R.S. Means Environmental Remediation Cost Data (ECHOS, 1998). The cost analysis will compare the CPT/LIBS system to baseline for subsurface characterization of chromium. The comparison is based on installing 3 CPT penetrations or 3 soil borings to a depth of 30 ft and the following assumptions:

CPT/LIBS System

The costs for the CPT/LIBS system are based on the following assumptions:

- The capital cost of an operational LIBS system is projected to be \$70,000 per unit and includes the sensor, and related computer hardware and software (the cost of the prototype unit was \$150,000)
- The daily cost of the LIBS system was determined to be \$280/day. To calculate a daily cost, the capital cost (\$70,000) was amortized over a 2-year useful life of the system at a real rate of 2.6% (Office of Management and Budget, 1992) and a utilization rate of 130 days/year (50% utilization).
- Site-specific calibration of the LIBS system requires 10 analytical samples and 24 man-hours of labor
- Set-up of the LIBS equipment in a CPT rig requires 8 man-hours of labor
- The CPT rig and crew will be subcontracted based on a daily rate, 2 additional LIBS operators will be required
- Costs are based on Safety Level C work conditions
- The push rate of CPT-deployed system LIBS is 90 ft/day (3 pushes to 30 ft each) based on the demonstration at Sandia
- CPT rods will be decontaminated as they are retracted from the ground and one 55-gallon drum of non-hazardous liquid will be generated per day
- Disposal costs do not consider costs for waste handling, storage, and transportation.

The primary costs associated with the CPT/LIBS system are presented in Table 1. The costs are calculated based on installing 3 pushes to a depth of 30 ft each in one work day.

Table 1 - Costs for CPT/LIBS System (Based on 3 pushes to 30 ft)

Description	Qty	Units	Unit Cost	Total Cost
LIBS system	1	day	\$280	\$280
LIBS system set-up	8	man-hrs.	\$75	\$600
Mobilization/Demobilization of CPT Rig	1	each	\$2,805	\$2,805
CPT rig (includes equipment and labor)	1	day	\$2,673	\$2,673
LIBS operation	16	man-hrs.	\$75	\$1,200
Calibration (sampling + labor)	1	ea	\$2,780	\$2,780
Consumable Supplies	1	day	\$250	\$250
Disposal of decontamination fluids	1	drum	\$150	\$150
Sub-Total:				\$10,738
General and Administrative Overhead (10%), Fee (5%), Total = 15%				\$1,611
Total:				\$12,349
Average Cost per 30 ft				\$4,116
Average Cost per Foot				\$137

Baseline Costs:

The baseline technology is installation of soil borings and continuous core samples. The costs provided for the baseline are based on the following assumptions:

- Costs are based on utilization of a hollow-stem auger drill rig to drill an 4.25-inch borehole
- Continuous core sampler will be utilized over the entire depth of the soil boring
- One sample will be collected every 2 ft for analysis at an off-site laboratory for RCRA Metals (Mercury, Chromium, Selenium, Cadmium, Silver, Lead, Arsenic, and Barium) on a 48-hour rush basis at a 100% surcharge.
- Drill cuttings will be generated at a rate of approximately one 55-gallon drum per 60 ft of 4.5-inch diameter borehole (approximately one-half drum per 30 ft)

- Drill cuttings will be disposed at a landfill as a hazardous solid (costs for waste handling, storage, and transportation are not included)
- Three soil borings to a depth of 30 ft with sampling can be performed in approximately 8 hours
- Costs are based on Safety Level C work conditions

The primary costs associated with installing soil boring to collect split-spoon samples are presented in Table 2 below. The costs are calculated based on installing 3 borings to a depth of 30 ft each.

Table 2 - Costs for Soil Boring and Split-spoon Sampling (Based on 3 borings to 30 ft)

Description	Qty	Units	Unit Cost	Price
Drill Rig Mobilization/Demobilization	1	ea	\$ 3,000.00	\$ 3,000
Drill Rig Operation (3 man crew)	8	hrs	\$ 160.00	\$ 1,280
Hollow Stem Auger Drilling (4.25 in. dia)	90	ft	\$ 16.00	\$ 1,440
Continuous Core Sampler (1.5 in. dia.)	90	ft	\$ 25.00	\$ 2,250
Laboratory Analysis (RCRA Metals)	45	ea	\$ 214.00	\$ 9,630
Disposal of Drill Cuttings	2	drums	\$ 140.00	\$ 280
Decontamination (labor)	1	hrs	\$ 160.00	\$ 160
Disposal of Decontamination Fluids	3	drums	\$ 150.00	\$ 450
Sub-Total:				\$15,490
General and Administrative Overhead (10%), Fee (5%), Total = 15%				\$2,324
Total:				\$17,814
Average Cost per 30 ft				\$5,938
Average Cost per Foot				\$198

Cost Conclusions

As presented in Table 1, the cost to install a CPT push to 30 ft with LIBS analysis is \$4,109 based on the given assumptions. This translates to an average cost of \$137/ft. In comparison, the average cost to install one soil boring to a depth of 30 ft, collect continuous core samples, and have the samples analyzed at a laboratory is \$5,938, which works out to a cost of \$198/ft. Therefore, there is a significant potential cost savings from the use of the CPT/LIBS system compared to the baseline technology. The cost for CPT/LIBS analysis under the given conditions is approximately 30 percent less than the cost of the baseline.

The technologies being compared have different capabilities, therefore a direct comparison based solely on cost is limited. Specific difference that should be noted include:

- The baseline scenario assumes that a soil sample is collected at 2 ft intervals for analysis, the CPT/LIBS system provides continual analysis over the depth of the CPT penetration. Therefore, the CPT/LIBS system provides a greater number of data points.
- The baseline scenario includes laboratory analysis for RCRA metals based on a 48-hour turn-around time. The LIBS analysis is for chromium only, (but could be used for several different metals) with results available in 24 hours. With software advances, quantitative LIBS results could be available in minutes.

APPENDIX D

*SPARK I.D.*TM

(The following is an excerpt from the SPARK I.D. User's Manual)

Overview of SPARK I.D.™ System

Figure 5 shows the SPARK I.D.™ system configuration. A general description of the function of the primary units labeled are:

Computer – The computer is used to set the parameters of the CCD camera (i.e. integration time, number of spectra to take, wavelength calibration), to initiate the data collection process, to acquire the spectra, and export the data. The computer is directly connected to the CCD controller.

CCD Controller – The CCD controller powers the CCD detector and handles all I/O from the camera. In addition, when the data collection process is initiated by the computer, the CCD controller will trigger the laser via the Integrated Cooler & Electronics (ICE) unit at the appropriate time.

Integrated Cooler & Electronics (ICE) – The ICE unit is the power supply and cooling unit for the laser head. All of the laser parameters can be set via the front panel of the ICE and the back panel provides I/O for laser triggering and safety interlocks.

Laser Head – The laser head is the source of laser energy and is within the light sealed enclosure. After exiting the head, the laser enters the Laser Delivery Optics.

Laser Delivery Optics – This system of optics and mounts accepts the laser light, expands the diameter of beam to minimize the potential for damage to the optical components, focuses the laser onto the sample, collects the plasma emission, and launches the emission into an optical fiber bundle.

Sample Chamber – The sample houses the sample during analysis. The sample chamber can be configured to evaluate soils in vials or soils pressed into pellets. For pelletized samples, the chamber has a sample spinner which will move the sample so that a fresh portion of the sample is always interrogated.

Spectrometer/CCD Detector – The emission from the spark is collected by the optical system and launched into an optical fiber bundle. The optical fiber bundle delivers the light to the spectrometer/CCD detector where the light is split into a range of wavelengths. The optical fiber bundle also includes a single fiber for delivering a wavelength calibration source.

Blower – When the Primary power switch is activated, the blower is automatically turned on. The laser/soil interaction often creates dust which can be hazardous to the optics transmitting the high power laser. To minimize the problem, the blower sucks air and fine dust out of the sample chamber and through a filter prior to exhaust.

Figure 5

SPARK I.D.™ Construction

The following section will highlight and briefly describe the function of the SPARK I.D.™ components. More specific information on the use and maintenance of each component will be provided in subsequent sections. The purpose of this section is to get the User familiar with the unit.

External Housing: Figure 6 depicts the external housing of the SPARK I.D.™ system. The blue enclosure is designed to allow for shipment of the system and routine transportation in the field. The system is equipped with 5 inch casters for ease of transport. The casters can be removed by tilting the unit carefully forwards and backwards. When tilted, the casters can be removed by depressing the locking pin on the inside edge of each caster. When the spring pin is depressed, the caster will slide off of the container. During use, the covers should be removed to allow access to both the front and back of the unit for system set-up and also to allow for proper ventilation.

Figure 6

Front View: Figure 7 shows a picture of the front view of the SPARK I.D.TM system. The laser cooler and electronics (ICE) is on the left side. The front panel of the ICE unit is used to turn the laser on and provides the indicators for the status of the laser. The large red button is an emergency shutoff or kill switch. The specifics of the front panel of the ICE are well described in the Big Sky User's Manual.

Figure 7

Above the ICE unit are a number of On/Off switches which are used for a variety of system operations. Figure 8 shows a close-up of this panel. The first switch is for activating the sample rotation stage. This stage will rotate the sample so that a fresh portion is exposed for each spark. The second switch activates a mercury/argon lamp which is used for wavelength calibration of the spectrometer. The third switch is used to activate a red laser aiming beam. The aiming beam will illuminate the sample at the location where the high power laser will spark and can be helpful during sample alignment. The next set of switches are used to set the number of laser sparks that occur during sampling. In the up position, the laser fire mode switch will activate the laser a specific number of times during sampling, with the number of pulses set by the thumb wheels. In the lower position, the switch will allow the laser to free run. This will be described in more detail in the Data Acquisition chapter.

Figure 8

On the right side of the front panel, there is a manually operated shutter for blocking the passage of the laser to the sample chamber. As shown by the labels, pushing the knob IN will block the laser beam, and pulling the knob OUT will open the shutter and allow the laser into the sample chamber. This is to be used as a safety precaution to eliminate accidental exposure, especially when the interlocks have been defeated.

Note: The laser should never be run for an extended period of time with the shutter closed.

Below the shutter is the sample door to the sample chamber and the location of the safety interlock system is indicated. At the bottom of the front panel, there is a drawer for storing the laptop computer. The computer is held securely in the drawer by a foam cutout, as shown in Figure 9. The computer can be oriented so that the connectors match the cutouts and the wires can be routed within the channels in the foam. These channels are used to support the removable work surface.

Figure 9

Back View: The back of the SPARK I.D.™ system is shown in Figure 10. On the top shelf is the air filter and blower which is used to remove dust and fine particles from the sample chamber. The exhaust system will automatically activate with the main power to assure that it is always on. It should be noted that the blower has been mounted on shock mounts to reduce the transmission of vibrations to other components.

Attached to the bottom of the top shelf, on the right side, is the CCD controller box. This unit interfaces the computer and CCD detector and provides the trigger to the laser during sampling. This unit is also powered automatically when the SPARK I.D.™ system main power switch is activated.

The spectrometer/CCD detector is on the bottom shelf and the back of the spectrometer is facing the back of the unit. The emission light enters the front of the spectrometer via an optical fiber bundle and the slit width is set by a mechanical slit inserted in front of the

fiber optic cable. The unit has been shipped with a range of slit widths from 10 microns to 150 microns. The unit was shipped with a 10 micron slit already in the spectrometer. On the back of the spectrometer is the wavelength adjustment knob which is used to set the center wavelength. The wavelength is $\frac{1}{2}$ the reading set on the wavelength adjustment knob. (i.e. for a center wavelength at 405 nm, the wavelength adjustment knob should read 810) Attached to the spectrometer is the CCD detector. This unit contains its own thermo-electric cooler (TEC) to reduce the noise floor of the detector and a fan/heatsink to remove the heat generated by the TEC.

Figure 10

From the back, to the right of the blower, it is possible to view the back panel of the ICE. Of primary importance is the water level and the lamp count. This will be discussed in a later section. On top of the ICE unit, the access port for filling the laser coolant reservoir is seen. A funnel and access tube have been provided with the unit to facilitate filling the unit with distilled water. The water coolant lines for the laser are stored along the bottom, below the drawer section. The procedure for changing the coolant water will be addressed in the Maintenance section.

The main power strip is located at the top of the back panel. All of the SPARK I.D.™ power is fed through this strip and the main power switch is located on the left.

Note: The side view was obtained when the unit was not in the rugged enclosure and all panels are removed.

Side View: Figure 11 show the side view (the right side when viewed from the front) of the instrument with the covers removed. Behind the black enclosure is the laser (along top) with the beam directed to the left towards the launch optics. The sample chamber is shown along the left side with the sample spinner situated below it. The electronics box contains the timing circuitry for the laser, the red aiming laser, and the power supply for the calibration source. Midway up the launch optics structure, the optical fiber that collects the emission can be seen protruding out towards the right. It loops around and attaches to the front of the spectrometer at the location indicated. On the shelf above the spectrometer, the calibration source is situated, with an optical fiber connection to the spectrometer below.

Figure 11

The rugged, pre-aligned optical system within the enclosure is used to expand the infrared beam, redirect it towards the sample, focus the light onto the sample, collect the emission and launch the emission into an optical fiber bundle.