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Cone Penetrometer for Subsurface Heavy Metals Detection

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INTRODUCTION

Surface and subsurface contamination of soils by heavy metals, including Pb, Cr, Cu, Zn, and Cd, has become an area of concern for many industrial and government organizations (1). Conventional sampling and analysis techniques for soil provide a high degree of sensitivity and selectivity for individual analytes. However, obtaining a representative sampling and analysis from a particular site using conventional techniques is time consuming and costly (2). Additionally, conventional methods are difficult to implement in the field for in situ and/or real-time applications. Therefore, there is a need for characterization and monitoring techniques for heavy metals in soils which allow cost-effective, rapid, in situ measurements.

Laser-induced breakdown spectroscopy (LIBS) has been used to successfully measure metals content in a variety of matrices (3–15) including soil (16,17). Under the Department of Energy (DOE) Federal Energy Technology Center (FETC) Industry Program, Science & Engineering Associates (SEA) is developing a subsurface cone penetrometer (CPT) probe for heavy metals detection that employs LIBS (18). The LIBS–CPT unit is to be applied to in situ, real-time sampling and analysis of heavy metals in soil. As part of its contract with DOE FETC, SEA is scheduled to field test its LIBS–CPT system in September 1997.

OBJECTIVES

The overall objectives of this project are to evaluate potential calibration techniques for the LIBS–CPT instrument and to provide a preliminary evaluation of the LIBS instrument calibration using samples obtained from the field.

Laboratory Calibration of the LIBS Instrument

The objectives of this activity are 1) to investigate methods of preparing soil mixtures in the laboratory which approximate soil samples that are encountered during in situ analysis and 2) to test new calibration procedures for the LIBS instrument. Information on available field test sites for the LIBS instrument will be surveyed to gather information on soil physical and chemical properties. A field site will be selected, and soil mixtures will be prepared in the laboratory to represent field conditions. The Energy & Environmental Research Center (EERC) will prepare a suite of soil samples which provides statistical representation of the range of sample matrix effects parameterizing on the following variables: grain size, moisture, pH, humic matter, and heavy metals. The heavy metals in the matrix will give statistical representation of the metals present at the field test site, Cr, As, Cd, Cu, Pb, Mg, Mn, and Zn. This set of samples along with a complete set of data will be submitted to SEA for use in calibrating the LIBS–CPT probe. EERC personnel will then obtain a representative sampling of soil from the test site. The set of samples collected in the field will be characterized in the EERC laboratories for the variables listed above. Particular attention will be paid to the determination of metals content, since this is the most important aspect of the calibration and validation. The metals in soil will be determined by inductively coupled argon plasma spectroscopy (ICAP), graphite furnace atomic absorption spectroscopy (GFAAS), and/or wavelength-dispersive x-ray fluorescence (WDXRF) in the EERC laboratories. A random sampling of the data collected at the EERC will be validated using an external laboratory. A random selection from the original calibration set and the samples obtained from the field will be provided to SEA without any data. SEA will analyze the samples using the calibrated LIBS–CPT probe and submit the data to the EERC. EERC personnel will compute calibration statistics and report the precision and accuracy of the calibration to SEA. If necessary, calibration techniques will be adjusted until an acceptable level of precision and accuracy is achieved.

Preliminary Development of Multivariate Models

Activities under this subtask are to investigate methods of correcting LIBS instrument responses for sample matrix effects, with the goal of obtaining calibration techniques which can be used under a variety of soil chemical and physical property conditions. Multivariate statistical analysis techniques such as principal component analysis (PCA) will be applied to the data collected during the laboratory calibration and validation to obtain information on the matrix effects which most influence the quantitation of heavy metals in the soil. Different calibration techniques will be evaluated in order to develop a data analysis technique which provides a robust means of analyzing the data obtained from the LIBS–CPT probe to extract quantitative or semiquantitative data on heavy metals which is insensitive to sample matrix effects. Statistical outlier detection methods will also be applied in the data analysis to develop diagnostic techniques for application to data in the field, allowing quality control of reported heavy metal quantities.

The project is broken down by task as follows:

Task 1 – Laboratory Calibration of the LIBS Instrument
    Task 1.1 Definition of laboratory-prepared soil sample matrix
    Task 1.2 Laboratory preparation of soil samples
    Task 1.3 LIBS data collection
    Task 1.4 Data reduction and analysis

Task 2 – Validation of LIBS Calibration
    Task 2.1 Field sample collection
    Task 2.2 Field sample characterization
    Task 2.3 LIBS data collection
    Task 2.4 Data reduction and analysis

Task 3 – Development of multivariate models for subsurface matrix effects on the LIBS calibration.

ACCOMPLISHMENTS

Available literature pertaining to metals in soils, analysis of metals in soils, LIBS applications, spectral signal processing, and multivariate analysis of spectral data has been collected and is under review. A complete listing of the literature database used in this work at the time of this report in Appendix A.

Task 1 – Laboratory Calibration of the LIBS Instrument

In order to obtain data which allow laboratory preparation of soil mixtures that represent the field site, activities for Task 1 during this reporting period involved 1) survey of available field sites, 2) gathering information on the range of soil heavy metals content in possible field sites, 3) evaluation of ICAP, GFAAS, and WDXRF analytical methods for quantitation of metals in soils, and 4) definition of procedures for laboratory-prepared soil mixtures.

EERC personnel have contacted several organizations controlling access to candidate sites for field testing of the LIBS–CPT system. Table 1 lists sites which are currently under consideration.

TABLE 1

Field Sites Under Consideration

Site and Location	Comments	Controlling Organization
Miles Crossing, Butte, MT	Nearby sites are under evaluation	University of Montana
Opportunity Pond, Butte, MT	30'-90' thickness of processed, unconsolidated metals tailings, smelter wastes, etc.	ARCO
Berkeley Pit, Butte, MT	Superfund site	ARCO
Anaconda Smelter, Anaconda, MT	Smelter site, tailings pile	ARCO
Smelter Waste Sites, MT	Smelter and flotation tailings wastes sites	Montana Bureau of Mines
Molycorp Mine, Mountain Pass, CA	Noble metals and Pb mine tailings and waste	Molycorp Mining
Homestake Gold Mine, Lead, SD	Mine tailings	Homestake Gold Mine
Uravan Uranium Mine & Smelter, Uravan, CO	Mine tailings, smelter wastes, etc.	Uravan Mining
Triumph Mine, Haley, ID	Perched flotation, metals-rich tails pile, located in the high desert, dry soil conditions	Idaho Department of Environmental Quality
Kellog/Wallace Smelter, ID	Smelter wastes	Idaho Geological Survey

Data on metals content in soils from the Silver Bow and Mill Creek areas near Butte, Montana, were supplied by Dave Cremers of Los Alamos National Laboratory (LANL). Data were supplied on 60 samples. Data on each sample analysis were given for Zn, Pb, Mn, Fe, Cu, Cr, Cd, As, and Ag by ICAP and LIBS. Additionally, every other sample (even number samples in sequence) was analyzed by a second laboratory using ICAP and GFAAS. A reference value for each analyte was calculated as the average of the available data from ICAP and/or GFAAS. Concentration ranges for each analyte were calculated from the reference value for all samples and also for the two subsets of Silver Bow and Mill Creek sites. Concentration minimums, maximums, and ranges are reported in Table 2.

TABLE 2

Analyte Concentration Ranges for Montana Soil Samples

	Silver Bow Site			Mill Creek Site			Overall		
Analyte	Min., mg/kg	Max., mg/kg	Range, mg/kg	Min., mg/kg	Max., mg/kg	Range, mg/kg	Min., mg/kg	Max., mg/kg	Range, mg/kg
Zn	327	16,467	16,140	387	4270	3883	327	16,467	16,140
Pb	147	1977	1830	235	582	347	147	1977	1830
Mn	379	3320	2941	75	2253	2178	75	3320	3245
Fe	11,400	46,700	35,300	14,367	49,500	35,133	11,400	49,500	38,100
Cu	339	2557	2218	413	3490	3077	339	3490	3151
Cr	4	21	17	4	18	14	4	21	17
Cd	3	41	38	2	25	23	2	41	39
As	88	1670	1582	316	1590	1274	88	1670	1582
Ag	2	90	88	3	9	6	2	90	88

Information obtained from the EERC laboratories indicates that the reporting limits of quantitation for ICP–GFAAS and WDXRF for each of the target analytes are adequate for verification of the LIBS calibration. Lower limits of quantitation obtained in the EERC laboratory are listed in Table 3.

TABLE 3

Lower Limits of Quantitation for Laboratory Methods[a]

Analyte	ICAP–GFAAS, μg/g	WDXRF, μg/g
As	0.4[b]	7
Cd	0.03[b]	5
Cr	0.1[b]	2
Cu	6	4
Fe	8	4
Ni	0.8[b]	
Pb	0.2[b]	7
V	4	
Zn	3	4

[a] There is no upper quantitation limit in practice.

[b] Limits based on analysis by GFAAS.

A procedure for producing laboratory-prepared mixtures of soil and heavy metals consisting of an initial preparation of the baseline soil, followed by addition of known concentrations of heavy metals, has been defined.

The soils will be dried under N_2 at 105°C until marble-sized samples do not retain shape following release after application of light squeezing pressure. A sieve test of each sample will determine a rough size distribution. Samples will be reconstituted and stirred to make them as homogeneous as possible prior to analysis. Particle sizes retained on a No. 5 mesh (4 mm) will be collected, ground, and added back to the sample to ensure that background data on the elements will be obtained from the total sample.

Preparation of samples spiked with heavy metals can be accomplished by two methods. The first involves addition of solid salts of the metals to soil followed by thorough mixing in a tungsten carbide shatterbox. This produces a finely divided mixture of fairly uniform particle sizes, i.e., a powder with reasonably homogeneous distribution of metals. The second method involves dissolving salts of the metals in water, stirring the solid and dissolved metals gently for 2 hours, and allowing the water to evaporate. This produces a soil matrix with relatively unchanged particle sizes and a homogeneous distribution of metals. This latter method also provides for a more natural distribution of metals on the soil matrix, i.e., allowing for natural phenomena as ion exchange, recrystallization, and redox to occur. Although slight alteration in soil characteristics may occur, the changes would not be expected to be significant with regard to the behavior of the soil toward analysis by the LIBS instrument.

A sample of the baseline soil before spiking with additional heavy metals will be analyzed by ICAP and/or GFAAS to determine background levels of elements of interest. In addition, the spiking solution will also be analyzed by ICAP–GFAAS methods. These levels will be considered when evaluating analytical data obtained for spiked samples.

For example, a spiked sample of soil containing quantitative amounts of the elements listed in Table 4 to be used in testing can be prepared as follows:

TABLE 4

Preparation of Standard Contaminant Element-Impregnated Soil

Element	Salt	Spike Liquor Concentration, mg salt/L	Soil Concentration (from spike), μg M/g soil
As	NaH_2AsO_4	219	100
Cd	$Cd(NO_3)_2$	53	25
Cr	$Cr(NO_3)_3$	229	50
Cu	$Cu(NO_3)_2$	295	100
Fe	$Fe(NO_3)_3$	216	50
Pb	$Pb(NO_3)_2$	160	100
Zn	$Zn(NO_3)_2$	579	200

One liter of an aqueous solution containing seven selected metal and metalloid contaminants can be prepared using the weights of reagent-grade salts (anhydrous). Five hundred milliliters of the solution is mixed with 500 g of soil, and the mixture is stirred gently for 2 hours. The water is evaporated at 105°C, and the dry metals-impregnated soil is tumbled at slow speed (to minimize crushing and abrasion) overnight. The samples are then ready for analysis.

Task 3 – Development of Multivariate Models for Subsurface Matrix Effects on the LIBS Calibration

LIBS spectra collected by SEA during Phase I of its contract with DOE FETC (18) were supplied to the EERC by Steve Saggese of SEA. Several LIBS data sets were made available: 1) a set of clean LANL soil spiked with varying levels of Cu over the range of 0 to 1000 μg/g added above baseline soil Cu concentration; 2) spectra of four different National Institute of Standards and Technology (NIST) standard reference material (SRM) soils, for Pb, Cr, and Cu/Zn spectral regions; 3) spectra of 100 μg/g Cr on LANL soil taken using different detector gate delays after the laser pulse; and 4) spectra of the 100 μg/g Cr on LANL soil using different detection time window lengths. Also among the data were three sets of 70 LIBS spectra of clean LANL soil spiked with varying amounts of Cr over the range of 0 to 1000 μg/g added to the baseline Cr level in the LANL soil. For the Cr-spiked samples, ten spectra for each concentration in the series (0, 25, 50, 100, 300, 500, and 1000 μg/g added Cr) were collected by coadding emissions produced by 100 laser sparks to produce each spectrum, resulting in a total of 70 spectra in each calibration set. Three different laser pulse energies (35, 75, and 150 mJ) were used to produce three sets of 70 spectra each of the Cr-spiked samples.

The three sets of Cr-spiked samples (i.e., 35, 75, and 150 mJ) were chosen as the subject of a preliminary study of the application of spectrum analysis techniques. The data received were LIBS spectra as described above where each spectrum is the result of coadding optical emissions produced by 100 laser sparks. The spectra were submitted as optical emission intensity at each of 1024 data points. Each of the 1024 data points in the spectrum comes from an individual pixel in the photodiode array detector. The LIBS spectra were preprocessed prior to analysis. Because of the fact that some of the pixels showed no response at the extreme ends of the spectrum, each spectrum was truncated by eliminating the first and last five data points in each spectrum, resulting in 1014 data points on each sample. After truncation, each spectrum was automatically baseline-corrected using a standard algorithm whose iteration results in a best-fit straight line being calculated through the baseline and subtracted from the spectrum. To separate the baseline data points from those which are associated with peaks in the spectrum, a threshold value for the baseline noise is assumed; it is also assumed that any points less than zero in the result are part of the baseline, and the standard deviation of these points is calculated. Any points greater than the threshold are considered part of a peak in the spectrum and eliminated from further iterations. When the number of points in the baseline are distributed evenly about zero, the algorithm terminates. Once the spectrum has been truncated and baseline-corrected, a wavelength axis is computed for each spectrum by computation of a best-fit line relating the pixel number to reference wavelengths for three peaks. Peaks used were pixel 351, which corresponds to a Cr peak at 425.42 nm, pixel 622, an Fe transition at 427.17 nm, and pixel 670, another Cr emission at 427.48 nm. A typical spectrum from the Cr-spiked sample set after preprocessing is shown in Figure 1.

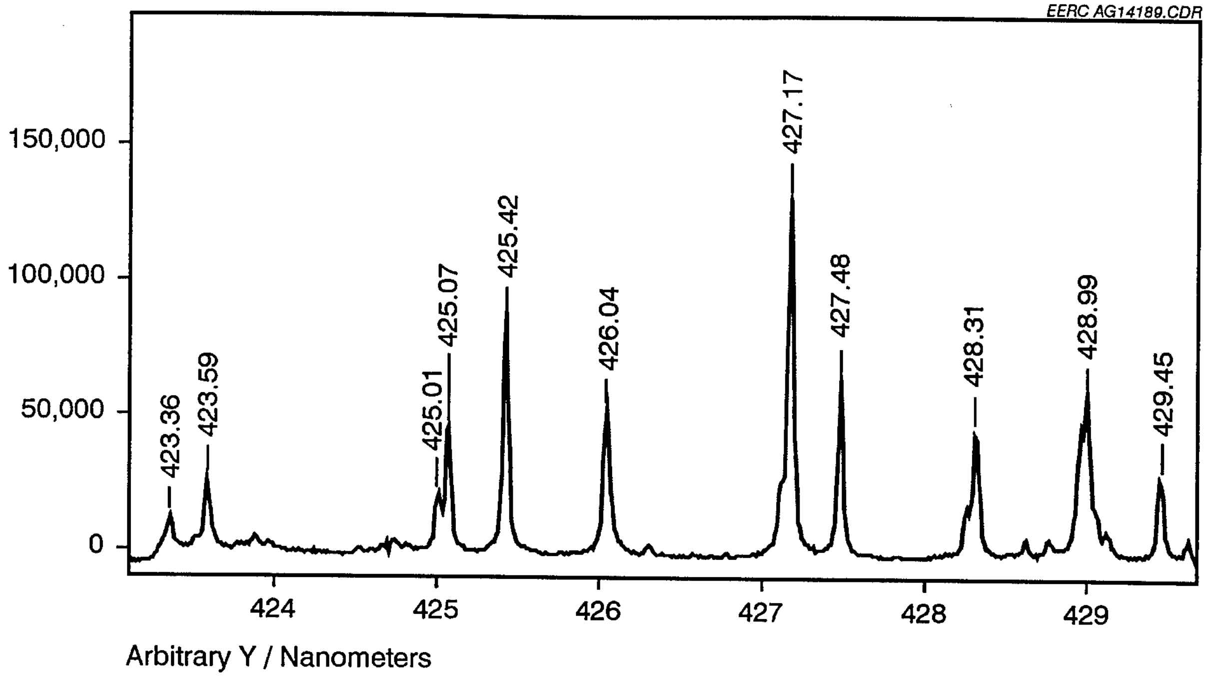

Figure 1. LIBS spectrum of soil spiked with 300 mg/g Cr taken using a 150-mJ laser pulse.

PCA was then applied to each data set as follows. First each set of 70 spectra was mean-centered by computing the mean spectrum for the set and subtracting the mean spectrum from each member of the set. Then a set of principal components and scores was determined from a singular value decomposition (SVD) and calculation of associated eigenvalues for the instrument responses on each sample in the set. A well-known property of this sort of calculation is that the SVD produces a set of orthogonal vectors which are the principal components (or factors). The factors can be considered a set of basis vectors for a space (call it the principal component space) in which to model the variance of the data set under analysis. Modeling the measured samples in the principal component space is done by projection of the samples onto the basis vectors (factors). The resulting magnitudes (eigenvalues) equate to the "amount" each basis vector contributes to reconstruction of the original data.

The calculations described above were applied to the 35-, 75-, and 150-mJ subsets of the Cr-spiked samples data. At the time of this report, only a preliminary analysis of the calculated data was completed on the 150-mJ laser pulse energy samples. As expected, the majority (>93%) of the variance in the data set occurs in the spectral regions associated with Cr emissions, since the same soil was spiked with varying amounts of Cr. Therefore, the first three principal components capture over 99% of the variance in the data set. Figure 2 depicts the first principal component of the data set. As can be seen, the spectrum is made up almost entirely of peaks associated with Cr. This implies that the scores for each sample associated with the first principal component should have good correlation with Cr concentration.

Figure 3 shows the second principal component (multiplied by −1 in the figure for clarity) which is seen to contain almost all the spectral features of the soil without the Cr peaks. Analysis of linear combinations of the second and third principal components (not shown) resulting

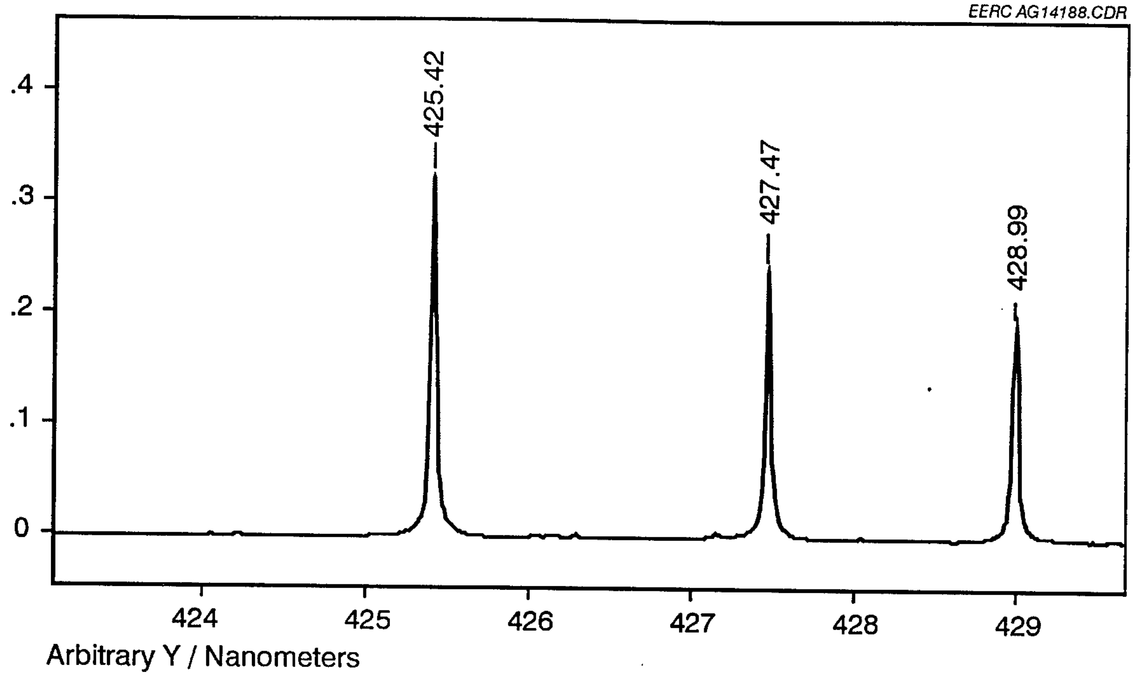

Figure 2. First principal component from PCA of Cr calibration series.

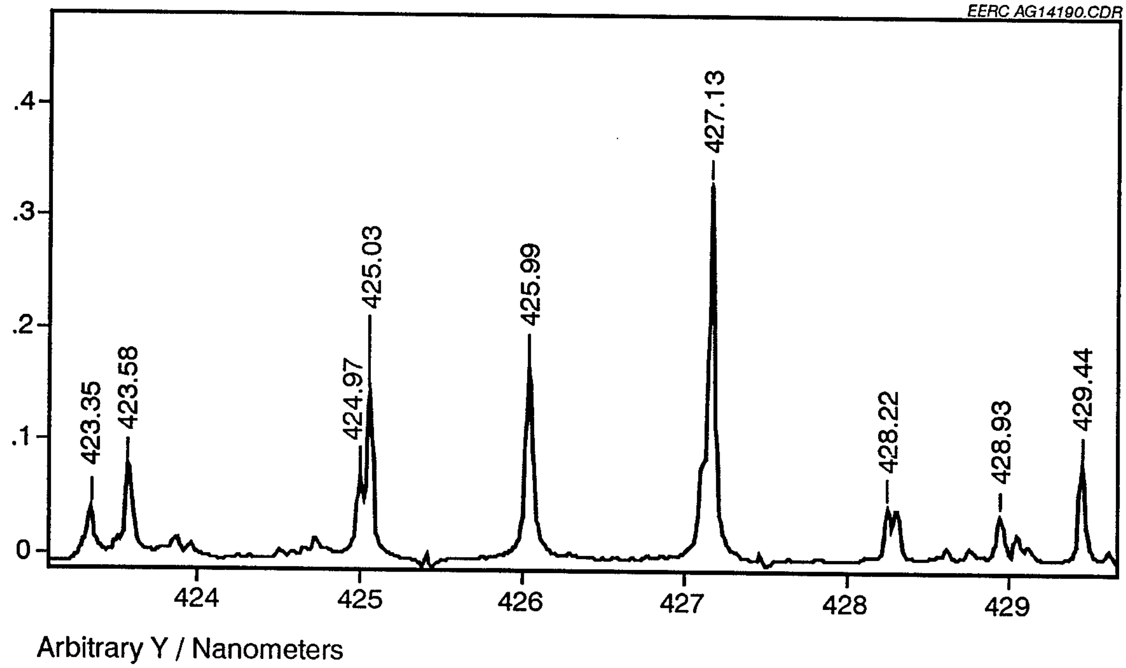

Figure 3. Second principal component from PCA of Cr calibration series.

from adding them together after premultiplication by their associated scores for each sample shows that the spectrum of the baseline soil can be reconstructed in all cases.

As mentioned above, since the first principal component is made up almost entirely of features associated with Cr emissions, its score should have good correlation with Cr concentration in the soil. Therefore a comparison of the principal component number one score was made to the amount of Cr added to the LANL soil. Since the Cr concentration of the soil prior to being spiked with Cr is unknown, the spectra associated with the baseline soil were eliminated from the analysis. Data from soil samples spiked with 1000 μg/g Cr added were also eliminated from the analysis. Elimination of the 1000 μg/g Cr-spiked samples was based on the fact that the instrument response produced by these samples showed a large deviation from a linear relationship to the concentration when included with the rest of the set. Figure 4 shows the result of calculating a best-fit line relating the first principal component score to Cr concentration.

The scores used in the regression below represent the average value obtained for the ten replicate LIBS spectra collected at each Cr concentration. The average value was used because of the fact that there was considerable scatter in the score of the first principal component.

FUTURE WORK

Work over the next quarter will complete all subtasks under Task 1, namely, the definition of laboratory-prepared soil sample matrix, laboratory preparation of soil mixtures, LIBS data collection, and the associated data reduction and analysis for these activities. Under Task 2, Validation of LIBS Calibration, we will complete the field sample collection and LIBS data collection subtasks. Since Task 3 is a developmental effort calling for continued evaluation of multivariate models, work in this area will continue throughout the duration of this project.

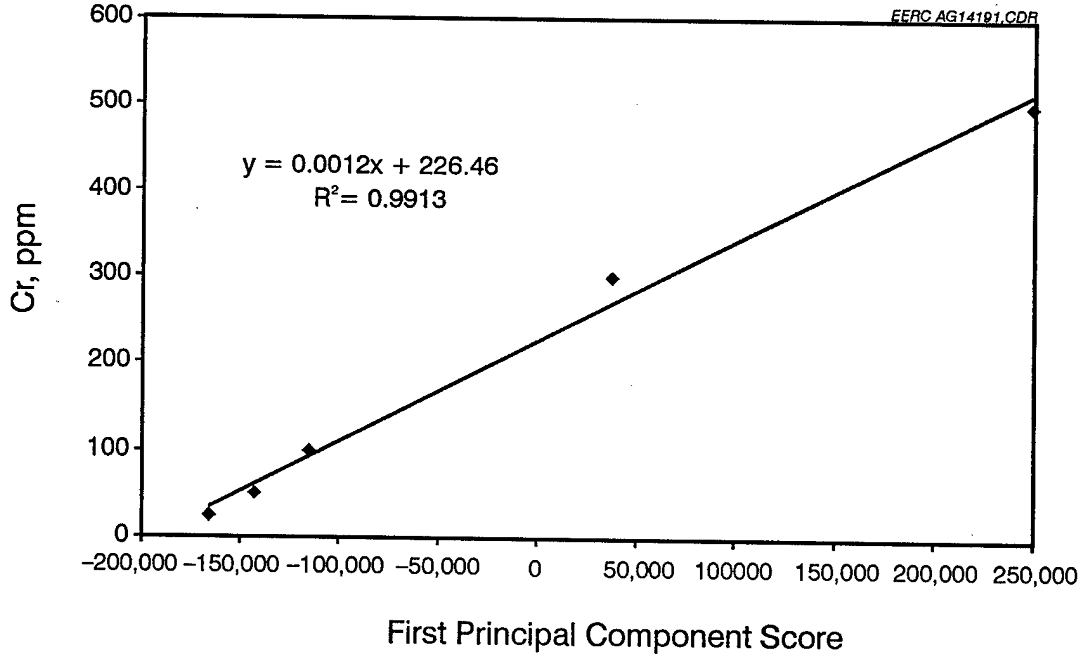

Figure 4. Comparison of PCA first principal component score to Cr concentration.

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APPENDIX A

LITERATURE DATABASE

APPENDIX A - LITERATURE DATABASE

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