TITLE: RCRA METALS ANALYSIS BY LASER-INDUCED BREAKDOWN SPECTROSCOPY:
DETECTION LIMITS IN SOILS

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Characterization, Monitoring and Sensor Technology -
Integrated Program

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RCRA Metals Analysis by Laser-Induced Breakdown Spectroscopy

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Acknowledgments

The authors wish to cite the considerable contributions of the research team assembled for this work at LANL. Much of the data in this report were acquired by Thomas Gamble. Aaron Eppler contributed the work on barium and assisted with the scanning electron microscopy. Leeann Foster contributed the data for beryllium. Thomas Kos made most of the spectral assignments.

This work is funded through the Characterization, Monitoring and Sensor Technology Integrated Program, DOE EM-541.

Introduction

The goal of the Technical Task Plan (TTP) that this report supports is research, development, testing and evaluation of a portable analyzer for RCRA and other metals. The instrumentation to be built will be used for field-screening of soils. Data quality is expected to be suitable for this purpose. The data presented in this report were acquired to demonstrate the detection limits for laser-induced breakdown spectroscopy (LIBS) of soils using instrument parameters suitable for fieldable instrumentation. The data are not expected to be the best achievable with the high pulse energies available in laboratory lasers.

The instrumentation will be based on the method of laser-induced breakdown spectroscopy [1]. In the LIBS method, sample atomization and excitation is provided directly by a laser spark. Time consuming and hazardous sample preparation is eliminated. The spark is produced by focusing pulses of laser light on the material to be analyzed to generate a small microplasma. Because plasma temperatures initially exceed 10,000K, the material in the plasma is efficiently vaporized, reduced to its elemental constituents, and the resulting atoms electronically excited.

Advantages of LIBS for field-based analyses of soils are:

- 1) Materials can be analyzed directly in the field. Little or no sample preparation is required. Adulteration of the sample by improper handling is minimized or eliminated entirely.
- 2) Rapid analysis. A complete spectrum can be obtained in a single laser shot. The technique is as rapid as the repetition rate of the laser and detection apparatus allow.
- 3) Simplicity. Skilled operators are not required.
- 4) Portability. Lasers with the necessary pulse energy for LIBS that weigh less than two pounds are now available. Compact detection systems are also available. One complete apparatus developed in our laboratory, including power supplies, detection apparatus and a portable computer is the size of a small suitcase. The active sampling unit, which includes the laser head and optics is handheld.
- 5) Simultaneous multi-element analysis. All elements in the microplasma are electronically excited and can be detected simultaneously, in principle.
- 6) Spatial discrimination. The analytical region for LIBS from a single laser pulse is the size of the induced spark. In practice, with lasers of convenient size, this region can be as small as $.01 \text{ mm}^3$ or as large as 0.5 mm^3 . Larger regions are analyzed by rastering of the laser beam.
- 7) Remote detection. The spark is produced by focused optical radiation. Thus, only optical access to the sample is required. In work to be done for this TTP, the utility of delivery of the laser light using a fiber optic cable will be investigated. In other work we are conducting, we believe LIBS spectra can be obtained at distances as great as 80 feet from the material to be analyzed.
- 8) Sensitivity. Detection limits should be suitable for field-screening data for many elements of interest.

This report presents our work to date on the detection limits for several elements in soils using LIBS. The elements targeted in the Technical Task Plan are antimony, arsenic, beryllium, cadmium, chromium, lead, selenium and zirconium. Data for these elements are presented in this report. We also have included other data of interest to potential customers for the portable LIBS apparatus. These data are for barium, mercury, cesium and strontium. Data for uranium and thorium will be acquired during the tasks geared toward mixed waste characterization.

Table 1 summarizes our results.

Table 1. Summary of 3s detection limits for selected elements in soils using laser-induced breakdown spectroscopy. Instrument parameters are as noted. Concentrations using X-ray fluorescence spectroscopy were obtained by Reference 5.

Analyte	Analyte Line (Å)	Internal Standard	Internal Standard Line(s) (Å)	3s Detection Limit	Calculated Blank Conc.	XRF Conc. (ppm)	Comments
As I	2349.84	Fe II	2395.408 + 2395.627	705	46		
As I	2860.44	Fe I	2872.334	1,512	675		
Ba II	4554.03	None	None	63	Not applicable	325.7±21.5	Contaminated Soils
Be II	3130.42+3131.07	Ca II	3179.33	2			
Cd I	5085.822	Fe I	5110.357	73	176		Spherical focusing lens
				141	552		Cylindrical focusing lens
Cr I	4254.35	Fe I	4250.787 + 4250.12	23	32	13.7±9.0	125 mJ laser pulse energy
				67	46		20 mJ laser pulse energy
				64	59		Cylindrical focusing lens
Cr I	3578.69	Fe I	3570.097 + 3570.25	60	361		125 mJ laser pulse energy
				56	45		20 mJ laser pulse energy
Cr I	3593.49	Fe I	3570.097 + 3570.25	27	128		125 mJ laser pulse energy
				93	78		20 mJ laser pulse energy
Cr I	3605.33	Fe I	3570.097 + 3570.25	28	-11		125 mJ laser pulse energy
				103	281		20 mJ laser pulse energy
Pb I	4057.6	Fe I	3997.392 + 3998.053	14	75		125 mJ laser pulse energy
Pb I	4057.6	Fe I	4063.594	18	70		125 mJ laser pulse energy
				9	51		Peak Fit Data
Pb I	4057.6	Fe I	3997.392 + 3998.053	21	45		Cylindrical lens
Sr II	4077.71	Fe I	4202.032	30	35	70.5±8.7	
Sr II	4215.52		4202.032	24	29		
Sr I	4607.33	Fe I	4476.0206	80	46		
Zr II	3438.23	Fe I	5 lines around 3526.2	104	60	325±15.3	
	3572.47			86	41		

Experiment

A schematic of the LIBS apparatus is shown in Figure 1. The laser used was a Quanta Ray DCR-11. This laser has donut-mode beam profile in the far-field. The energy of the laser pulses was kept at 125 mJ for all data except where noted. A 100 mm focal length spherical lens was used to focus the laser beam on the surface of the soil sample pellets for most of this work. For some experiments, the spherical lens was replaced with a 100 mm focal length cylindrical lens to create a long spark. In both cases, a motor-driven translation stage moved the pellet under the laser beam to present a fresh surface on every laser shot. Figure 2 is a picture obtained with a 100x microscope showing the track left by the laser. Under the conditions used it is clear that the large underlying crystalline structure of the soil largely remains intact. The laser-induced plasma is created from the material that resides on the surface of the soil particles.

Samples were prepared as follows. Local soil was gathered by removing the top two inches of the soil surface with a shovel, including the vegetative layer. Approximately 1 liter was collected. This soil was passed through a series of sieves. The fraction passing through a number 25 sieve, (nominal aperture size is 710 μm), was retained for the spiked samples.

Spiked samples were prepared by the following procedure. All glassware was cleaned using the standard EPA cleaning procedure except Type II water was used for rinsing instead of tap water. Aliquots of atomic absorption standards were diluted with acid to 10 ml in a volumetric flask. Acid solutions used for dilution were prepared to match the matrix of the undiluted standard. These acids were either 0.3M HCl or 0.3M HNO₃. 10 g of sieved soil was transferred to a beaker (20 or 50 ml total volume). The diluted aliquot was added to the beaker and stirred to completely wet the soil. The volumetric flask was then refilled with 10 ml of the appropriate acid and this rinse was added to the beaker. Most samples were then completely dried in a 40°C drying oven. The drying period was 48 hours. The Sb, Hg and As samples were air dried under ambient conditions in a fume hood. Drying of these three classes of samples took 4 days.

After drying, each 10 g sample was ground by hand with a porcelain mortar and pestle. 4 g of the sample was pressed into a pellet using 20 tons of pressure applied for 10 minutes. No binder was used. The unused 6 g of soil was stored in a screw cap polyethylene container for archival purposes.

A survey was conducted using a Los Alamos soil sample, NIST soil samples (NIST Standard Reference Materials 2709, 2710 and 2711) and a sample containing 3.57% antimony and 0.66% arsenic (Canadian Certified Reference Materials Project, Antimony Ore CD-1),

Reference lines were chosen from those iron lines which clearly have no spectral interference and appear in the same spectrum as the analyte. Primary interfering elements are titanium and chromium. Since many of the transitions involved in the analyte lines have unknown upper energy levels, no attempt was made to match the excited state energy levels of the iron and that of the analyte. Small improvements in precision might be obtained by a careful choice of the reference line.

Spectra were calibrated in wavelength by acquiring LIBS spectra of iron (Bureau of Analyzed Samples, Ltd., Spectroscopic Standard SS50B). In some cases, metallic lead, copper and aluminum were also used to calibrate wavelengths. Two different gratings were used in the 1 meter spectrograph depending on the wavelength. A 3600 l/mm grating was used for some of the data and gave wavelength accuracies of $\leq 0.15\text{\AA}$. With a 1200 l/mm grating accuracy of the wavelength calibration was found to be $\leq 0.4\text{\AA}$. Iron lines were identified in the soil spectra by comparison with the LIBS spectrum of pure iron.

Calibration curves were prepared by using the net integrals. LIBS spectra of samples ranging from 0 to 1000 ppm were used. In the case of arsenic, the range ran to

10,000 ppm. Detection limits were calculated from the slope of the calibration curve and using the standard deviation of the blank. The blank was prepared in the same manner as the spiked soil samples.

As a general rule, the precision of the measurements stays within a narrow range as a function of concentration for samples above the detection limit. For concentrations decreasing below the calculated detection limit, the precision also decreases. This indicates that inhomogeneously distributed material is the primary source of noise at low sample concentrations. This is not surprising given the small sample volume of the laser spark. Standard laboratory methods of analysis eliminate this by homogenizing the sample taken from a relatively large volume. The homogenization effects a mechanical signal averaging. Since LIBS measures the distribution of analyte on a microscopic scale, the averaging must be done computationally. Figure 3 illustrates the distribution of trace analytes in NIST Reference Soil 2710 observed by scanning electron microscopy. The white areas are deposits of various lead, barium and zinc compounds. A survey of other areas with the scanning electron microscope showed that the trace elements reside in discrete, concentrated sites as in the figure.

Figure 1. Schematic of the laboratory LIBS apparatus. The sample is mounted on a motorized translation stage and translated as the laser fires.

Figure 1.

Figure 2. A microscopic view of the track left by the laser spark in soil. The smallest division of the superimposed scale is .002".

Laser Ablation Track Using a Spherical Focusing Lens

Figure 3. Scanning electron micrograph of a thin section prepared from NIST Standard Reference Material 2710. The large triangular piece at the lower right is feldspar. Most of the material that appears in white contains lead phosphate. Some arsenic and zinc also are present. The substrate for the piece towards the upper left, which has heavy surface contamination, appears to be quartz.

NIST 2710

10 MICRONS

ARSENIC

The most intense lines for arsenic listed in the NIST data tables are ionic lines [2]. We have not observed these lines in our survey scans. This is due to either spectral interference, low line sensitivity, or both, depending on the line. Also, because of the low sensitivity of the instrumentation used below about 2300Å, the atomic lines commonly used in ICP (1890.4, 1937.6, 1937.0, 1972.0 and 2288.1Å) could not be observed [3]. In addition, the 2288.1Å As I line is unsuitable for use in the presence of high cadmium concentrations. In anticipation of the necessity of observing arsenic in the presence of other RCRA elements, the 2288.1Å line was not chosen for further investigation.

We have observed several atomic lines. Observed were: 2288.12Å, 2349.84Å, 2780.22Å, and 2860.44Å. In addition, we observed As II at 2830.359Å, 2831.164Å and 2884.406Å. The first two lines of these were too weak to be useful; the 2884.406Å line has a strong nearby interference from Fe II 2883.702Å.

With these considerations, two As I lines were used to prepare calibration curves. These were the 2349.84Å and 2860.44Å lines.

Figure 4 shows a LIBS spectrum obtained from Los Alamos Soil spiked with arsenic to give 999 ppm (+ blank concentration). Figure 5 shows the spectral region of the Fe II lines used for the internal reference. The peak labeled Fe II 2395.627Å may also have intensity from Fe II 2395.408Å.

Figure 6 is a calibration curve for the As I 2349.84Å line using the Fe II lines as a reference. The calibration curve is linear except for some possible curvature at 10,000 ppm. Using the slope of a linear fit to the points, the calculated 3s detection limit is 705 ppm.

The relative standard deviations of the points between 1000 ppm and 10,000 ppm range between 10% to 21%. The relative standard deviation for the 300 ppm sample, (which has a concentration below the detection limit), is much greater. Detector noise is 0.084 counts absolute using the same region of interest as the arsenic line. The noise on the signal for the 300 ppm sample is 1.74 counts absolute; for the blank, 1.88 counts. The primary source of noise is not the detector. Rather it comes from fluctuations in the plasma emission.

The samples were made by spiking the soil with aliquots of known amounts of analyte. The method of standard additions can be used to calculate the amount of arsenic in the blank that is present in the same matrix as the added analyte. Doing so, we obtain a value of 47 ppm As in the Los Alamos soil samples. This is above the general range of concentrations found in the soils in this area of 1.2 to 11 ppm, as determined by laboratory X-ray fluorescence spectroscopy [4].

A calibration curve for As I 2860.44Å using Fe I 2872.334Å as an internal reference resulted in a detection limit of 1500 ppm.

Figure 4. LIBS spectrum of soil near As I 2349.84Å. The upper trace was obtained from a sample spiked with arsenic. The net concentration of the spiked soil is 999 ppm plus background. The lower trace is the spectrum obtained from a soil blank.

Figure 5. LIBS spectrum of soil near Fe II 2395.627Å. This spectrum is an expansion of the same spectrum used for figure 4. The upper trace is the spectrum obtained from the soil blank. The lower trace was obtained from the sample spiked with arsenic. The iron "line" is actually an unresolved pair of lines at 2395.408Å and 2395.627Å.

Figure 6. Calibration curve for As I 2349.84Å. The net integral of the As I line divided by the net integral due to the Fe II lines at 2395.408Å and 2395.627Å is plotted. Precision bars are 1 standard deviation of 10 replicate measurements. Each measurement was obtained by averaging the results of 100 spectra where each spectrum was taken from a different point on the sample.

As I 2349.84Å Calibration Curve

CHROMIUM

The most sensitive lines we have identified for LIBS detection of chromium in soil are Cr I 4254.35Å and Cr I 3593.49Å. Detection limits for these two lines are 23 ppm and 28 ppm, respectively, based on three standard deviations of the blank.

Figure 7 is the LIBS spectrum for a sample spiked with chromium to produce a concentration of 41.4 ppm (+ background level). There are no resolvable spectral interferences for the Cr I 4254.35Å line. A very weak shoulder due to titanium appears to the red. The figure also shows the two unresolved Fe I lines at 4250.12 and 4250.79Å which were used as internal reference for the calibration curve.

Figure 8 is a pair of calibration curves for the Cr I 4254.35Å line. Data for the two curves were acquired using different laser pulse energies. This was done to investigate the reduction in sensitivity which results from decreased irradiance. This transition of chromium is a resonance line with an excited state at $23,500\text{ cm}^{-1}$. The curvature in both calibration curves indicates self-absorption at high concentrations. Figure 9 shows linear fits to the same data using only those samples with concentrations below 225 ppm. The 3s detection limits derived from these linear fits are 23 ppm and 67 ppm for laser pulse energies of 125 mJ and 20 mJ, respectively. A similar reduction in sensitivity with lower laser pulse energy occurs without using the Fe internal reference. Relative standard deviations for the data points above the detection limit range from 20% to 31% for a laser pulse energy of 20 mJ and from 17% to 37% for a laser pulse energy of 125 mJ.

The calculated concentration of the blank using standard additions is 32 ppm and 46 ppm for the 125 mJ and 20 mJ data, respectively. The value obtained by laboratory X-ray fluorescence spectroscopy was 13.7 ± 9.0 based on two measurements [5].

A similar set of data was taken for the Cr I lines in the 3600Å region. Figure 10 is a spectrum for chromium spiked soil in this spectral region. Three lines appear in this region: Cr I 3578.69Å, Cr I 3593.49Å, and Cr I 3605.33Å. The best results were obtained with the line at 3593.49Å. Not uncoincidentally, this is the line with the least amount of spectral interference. 3s detection limits using this line were 28 ppm for data using 125 mJ of laser pulse energy and 93 ppm for data taken with 20 mJ of laser pulse energy. Relative standard deviations for samples above the detection limit range from 8% to 21% for the 125 mJ data and 13% to 24% for the 20 mJ data.

Figure 7. LIBS spectrum of soil near Cr I 4254.35Å. The upper trace was obtained from a sample spiked with chromium. The net concentration of the spiked soil is 41.4 ppm plus background. The lower trace is the spectrum obtained from a soil blank.

Wavelength (Å)

Figure 8. Calibration curves for Cr I 4254.35Å. The net integral of the Cr I line divided by the net integral due to the two unresolved Fe I lines at 4250.12Å and 4250.79Å is plotted. Precision bars are 1 standard deviation of 10 replicate measurements. Each measurement was obtained by averaging the results of 100 spectra where each spectrum was taken from a different point on the sample.

Cr @4254.35Å CALIBRATION CURVE vs. LASER PULSE ENERGY

Figure 9. Calibration curves for Cr I 4254.35Å. This is an expanded view of the calibration curve presented in Figure 8. The lines are least squares fits to the data below 250 ppm Cr.

Cr I 4254.35Å CALIBRATION CURVE

Figure 10. LIBS spectrum of soil near 3580Å. The upper trace was obtained from the same sample as that used to obtain Figure 7. The lower trace is the spectrum obtained from a soil blank.

CADMIUM

The strongest line listed in the NIST tables is Cd I 6438.47Å. A LIBS spectrum of this region showed that Ca I 6439.07Å strongly interferes when spectral resolution is 2Å. The Ca I line persists for 100 μs so using time discrimination will not aid in eliminating this interference. A 100 ppm Cd soil sample could not be discerned on the side of the Ca peak. The other peaks which would appear in this region--6359.98Å, 6354.72Å and 6464.94Å--are Cd II transitions and were not observed.

There are a number of other slightly weaker spectral lines, all of equal intensity in the NIST tables. We chose the 5085.822Å line to construct a calibration curve. This line is atomic and as a rule of thumb it is often easier to detect atomic transitions with LIBS. Also, this line is in the visible and detector sensitivity can be expected to be higher in this region. Figure 11 is a spectrum of 500 ppm Cd in soil. There is some spectral interference from titanium at 5085Å.

Figure 12 is a calibration curve for Cd I 5085.822Å using Fe I 5110.357Å as an internal reference. The bounds used to calculate the net integral for cadmium encompass both the Ti I 5085.33Å and Ti I 5087.07Å lines. Fluctuations in these titanium lines could result in elevated detection limits. The 3s detection limit using this calibration curve is 73 ppm. This value is limited by the noise in the emission from the plasma. Relative standard deviations for each sample range from 10% to 19% for concentrations greater than the detection limit.

The titanium interference underlying the Cd line results in an apparent high level of Cd in the blank. We measure an apparent level of 176 ppm compared to the general value of ≤ 2 ppm for Los Alamos soil determined by X-ray fluorescence spectroscopy. A multivariate calibration could help reduce these effects of titanium interference.

A common technique used in this laboratory to decrease the effect of sample inhomogeneity is to use a "long spark". To produce the long spark, a cylindrical lens is used instead of a spherical lens to focus the laser beam onto the soil surface. As long as the irradiance is the same in both cases, the longer spark helps reduce the effect of sample inhomogeneities in the size range of 100 μm to 1 mm. Because of limitations in the pulse energy achievable in the laser used for this work, the irradiance could not be kept as high as that for the spherical focusing lens. The resulting detection limit using a cylindrical lens, 141 ppm reflects the reduced irradiance.

The commonly used ICP lines 2144.9Å, 2288.0Å and 2265.0Å are inappropriate for this application. The Cd II 2144.9Å line is interfered by high iron concentrations, like those found in soils [3]. The Cd I 2288.0Å line should not be used with high arsenic concentrations. The limitation on this line may not be severe if it is known from other data that the arsenic concentration is low. Finally, the Cd II 2265.0Å line has a weak interference from the aluminum doublet at 2269Å.

The facilitators for this project have recently requested that we try to improve the detection limit for cadmium to about 10 ppm. We are investigating other cadmium emission lines for this purpose.

Figure 11. LIBS spectrum of soil near Cd I 5085.82Å. The upper trace was obtained from a sample spiked with cadmium. The net concentration of the spiked soil is 298.99 ppm plus background. The lower trace is the spectrum obtained from a soil blank.

Figure 12. Calibration curve for Cd I 5085.82Å. RATIO is quotient of the net integral of the Cd I line divided by the net integral for Fe I 5110.357Å. Precision bars are 1 standard deviation of 10 replicate measurements. Each measurement was obtained by averaging the results of 100 spectra where each spectrum was taken from a different point on the sample.

Cd I 5085.82Å CALIBRATION CURVE

LEAD

Figure 13 is a spectrum of a 100 ppm Pb sample (+ background concentration) in the neighborhood of the 4057.81Å line. The line has nearby interferences from manganese on both the blue side and, more severely, on the red side. The strength of the line however overcomes the interference and results in a good detection limit. Using the Fe I lines at 3997.392Å and at 3998.053Å as an internal reference, the 3s detection limit was found to be 15 ppm. Using Fe I at 4063.6Å the 3s detection limit was 17 ppm. Relative standard deviations for samples with concentrations from the detection limit to 1005 ppm are in the range 7% to 19% for the data using the Fe I 4063Å reference line. RSDs for the data using the Fe I lines near 3998Å are in the range of 8% to 17%. The difference in precision between the two data sets is probably insignificant. The calculated background concentration is about 75 ppm using standard additions. The specific soil used in these experiments was not analyzed for lead by X-ray fluorescence spectroscopy. However, in a survey of soils around Los Alamos the lead concentration was found to be from 18 ppm to 56 ppm [4]. The higher value obtained from the LIBS data is probably due to the weak manganese interference found near the lead line.

Figure 13. LIBS spectrum of soil near Pb I 4057.81Å. The trace with the largest lead peak was obtained from a sample spiked with lead. The net concentration of the spiked soil is 298.99 ppm plus background. The trace with the lower concentration of lead is the spectrum obtained from a soil blank.

Wavelength (Å)

STRONTIUM

There are three strong strontium lines which show strong emission using LIBS. These are Sr II 4077.71Å, Sr II 4215.52Å and Sr I 4607.33Å. Figures 14 through 16 show the LIBS spectra obtained from spiked soil at each of these wavelengths. The residual intensity in the blank is due to the background strontium level in the soil used. There is a possible very weak interference to the red of the 4077Å line. The 4215.52Å has a slight spectral interference from Fe I at 4217.56Å. The 4607.33Å line also has a very weak, but unidentified, peak which overlaps on the red edge. In no case is the spectral interference particularly limiting. The calibration curves for these lines show curvature at high concentrations, indicative of the onset of self-absorption in the plasma. Below about 325 ppm the calibration curves are effectively linear. Using these data the 3s detection limits for 4077.71Å, 425.52Å and 4607.33Å are 30, 24 and 80 ppm, respectively. The calculated level of the blank is 35, 29 and 46 ppm when using these three lines. The value obtained by XRF was 70.5 ± 8.7 ppm [5].

Figure 14. LIBS spectrum of soil near Sr II 4077.71Å. The upper trace was obtained from a sample spiked with strontium. The net concentration of the spiked soil is 25.4 ppm plus background. The lower trace is the spectrum obtained from a soil blank.

Figure 15. LIBS spectrum of soil near Sr II 4215.52Å. The upper trace was obtained from a sample spiked with strontium. The net concentration of the spiked soil is 25.4 ppm plus background. The lower trace is the spectrum obtained from a soil blank.

Figure 16. LIBS spectrum of soil near Sr I 4607.33Å. The upper trace was obtained from a sample spiked with strontium. The net concentration of the spiked soil is 25.4 ppm plus background. The lower trace is the spectrum obtained from a soil blank.

BARIUM

The data for barium was taken with soil samples of known composition. Soil samples were collected from many different areas and had very different compositions. Samples were pressed into pellets using 24 g of soil to 3 g of binder. The binder was a mix commonly used in X-ray fluorescence and has an elemental composition of 48.7% C, 42.6% O, 8.1% H and 0.6% B. Figure 17 is a calibration curve for Ba II 4554.03Å using these pellets. The detection limit using this data is estimated to be 63 ppm with a typical relative standard deviations of 5% for each data point.

Figure 17. Calibration curve for Ba II 4554.03Å. For this curve, no internal reference was used.

Ba II 4554.03Å CALIBRATION CURVE

BERYLLIUM

The instrumentation used for measurements of beryllium in soils was different from that used for the other metals analyzed in this report. The laser used had a near-gaussian spatial profile rather than a donut mode. The laser pulse energy used was the same as above and the focusing lens also had the same focal length. The detector was another intensified diode array. Time gating was used as for the other data. The spectrograph used had a resolution 1/2 that of the one used in the rest of this work.

A calibration curve for beryllium is shown in Figure 18. Points on the calibration curve were calculated from six replicates of 100 laser shots each. The figure shows data for the unresolved Be II 3130.42Å and 3131.07Å lines. The Ca II 3179.33Å line was used as an internal reference. The calibration curve is linear over two orders of magnitude. Some curvature occurs above about 200 ppm. Using a linear fit to the points from samples with concentrations below 200 ppm, the 3s detection limit is calculated to be 2 ppm. Precision ranges from 5% to 36% with the lowest precision occurring near the detection limit.

Figure 18. Calibration curve for Be II 3131Å. RATIO is the quotient of the net integral of the Be II line divided by the net integral for Ca II 3179.33Å. Precision bars are 1 standard deviation of 6 replicate measurements. Each measurement was obtained by averaging the results of 100 spectra where each spectrum was taken from a different point on the sample.

Be II 3131Å CALIBRATION CURVE

CESIUM

Some preliminary work has been done on cesium. The moderately strong line of Cs II at $4526.74\text{\AA}$ was sought and could not be found. The strongest line of the atomic species at $6973.297\text{\AA}$ was observed along with weaker lines at $6870.46\text{\AA}$ and $6983.49\text{\AA}$. The Cs I signal is clearly evident at a spiked Cs concentration of 500 ppm. Using standard additions, the cesium concentration in the blank is estimated to be 35 ppm. Measurements to develop a full calibration curve at this wavelength and a search for the more intense Cs II lines will be conducted in the near future.

MERCURY

The strongest mercury line listed in the NIST tables is Hg I 2536.52Å. Figure 19 shows the spectrum of a 1000 ppm Hg in a soil sample in the region of this line. Strong spectral interference is observed from the Fe II 2536.67Å and 2536.80Å lines. No signal due to mercury is observable.

The next strongest line for mercury is Hg I 4358.33Å. Several interfering peaks occur at this wavelength in soil. The intensities of these interferences are weak, however. A calibration curve for mercury will be obtained for this wavelength in the near future.

Figure 19. LIBS spectrum of soil near Hg I 2536.52Å. The solid curve was obtained from a sample spiked with mercury. The net concentration of the spiked soil is 999.3 ppm plus background. The dashed curve is the spectrum obtained from a soil blank.

Wavelength (Å)

SELENIUM

The strongest selenium line suitable for a portable detector listed in the NIST table occurs at 2413.5Å and is an atomic line. As shown in Figure 20, this line occurs on the side of an Fe II transition at 2413.31Å. LIBS spectra taken at this wavelength for samples of with different selenium concentrations up to 1002 ppm show no signal attributable to selenium. In ICP-AES, two lines near 1960Å are used [3]. This wavelength is not detectable with the apparatus available to us. Another commonly used line is at 2039.9Å, but this has a reported interference from Sb I 2039.77Å. The 2039.9Å line could be useful if correction for antimony can be made from other spectral information. This will be investigated in the near future.

Figure 20. LIBS spectrum of soil near Se I 2413.5Å. The upper trace was obtained from a sample spiked with selenium. The net concentration of the spiked soil is 1002 ppm plus background. The lower trace is the spectrum obtained from a soil blank.

Wavelength (Å)

ZIRCONIUM

Zirconium, while not a RCRA metal, had been listed as an element of interest in the 1993 call for Technical Task Plan proposals.

Figure 21 is a spectrum of a 1000 ppm Zr in soil sample in the 3500Å region. Most of the zirconium lines show some spectral interference from iron. Calibration curves were constructed for several of the zirconium lines found between 3300Å and 3600Å. The best lines of those selected for further study were the Zr II 3438.23Å and the Zr II 3572.47Å line. Detection limits were 103 ppm and 86 ppm, respectively, with relative standard deviations ranging from 13% to 20% and 15% to 19% for the 3438Å and the 3572Å lines, respectively. The large number of lines available in a single spectrum and the varying degrees of spectral overlap with iron lines suggest a multivariate calibration will greatly improve the results for this analyte.

Figure 21. LIBS spectrum of zirconium spiked soil near 3400Å. The net concentration of the spiked soil is 100 ppm plus background.

Counts

5000

10000

15000

3400

3450

3500

3550

Wavelength (Å)

3367.2

Fe I 3370.79

Zr II 3374.73

Fe I 3378.69

Ti II 3380.28

Ti I 3385.95

Fe II 3388.13

Ti II 3394.58

Zr II 3391.98

Zr II 3396.33

Zr II 3499.35, Fe I 3399.33

Ti II 3402.42

Zr II 3404.83

Fe I 3407.46

Zr II 3410.25

Fe I 3413.13

Zr I 3414.66

Fe I 3418.51

Fe I 3422.66

Fe I 3424.29

Fe I 3427.12

Fe I 3428.19

Zr II 3430.53

Zr I 3438.23

Fe I 3440.61, Fe I 3440.99

Fe I 3443.88

Zr I 3441.36

Fe I 3450.33

Fe I 3452.28

Fe I 3456.93

Zr II 3457.56

Ti II 3461.50

Zr II 3463.02

Fe I 3465.86

Fe I 3471.34

Fe I 3476.70, Fe I 3475.45

Zr II 3479.34

Zr II 3481.13

Zr II 3483.54

Fe I 3485.34

Fe I 3490.54

Fe I 3493.47

Zr II 3496.21

Fe I 3497.84

Zr II 3505.48

Zr I 3509.32

Ti II 3510.84

Fe I 3513.82

Zr I 3519.60

Fe I 3521.26

Fe I 3424.28

Fe I 3526.17

Fe I 3529.82

Fe I 3533.20

Fe I 3536.98, Ti II 3535.41

Fe I 3541.09

Zr II 3542.62, Fe I 3542.08

Zr I 3547.68

Zr I 3549.74

Zr II 3551.95

Fe I 3554.93

Zr II 3556.60

Fe I 3558.52

Fe I 3565.38

Fe I 3570.91

Zr II 3572.47

ANTIMONY

Many antimony lines have been investigated. The three lines studied in detail to date are: Sb I 2373.67Å, Sb I 2528.52Å, and Sb I 2877.92Å. For all three lines the calibration curves have a weakly negative slope as a function of increasing concentration. Negatively sloped calibration curves can occur, in principle, for analyte lines with high oscillator strength, due to self-absorption. It is unlikely that this explanation is valid for these antimony lines since the oscillator strengths are known to be low. The effect is the same whether the solution matrix from which the samples are prepared contains HCl or HNO₃. It is also the same at 2528.52Å when a curve is prepared using the data obtained for the three NIST standard reference soils.

We plan to acquire data for Sb I 2311.47Å to determine whether the effect is due to chemistry in the plasma. All three of the lines described above have some spectral interference from elements present in the soil matrix. If antimony is coupled through some reaction path to these elements, then the intensity contribution from the interfering elements may decrease with increasing antimony concentration. The line at 2311.47Å appears to be relatively free of spectral interference and may give better results.

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