

Real-Time Techniques for Beryllium Analysis in Soils - 9372

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ABSTRACT

The U.S. Army Corps of Engineers (USACE) is addressing radiological and chemical contamination by following requirements of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) at the Luckey site. The Luckey site is part of the Formerly Utilized Sites Remedial Action Program (FUSRAP). From 1949 to the early 1960s, the Brush Beryllium Company, as a contractor to the Atomic Energy Commission, used the Luckey site for beryllium (Be) processing to support the national defense program. Under FUSRAP authority, USACE conducted a CERCLA remedial investigation (RI) of the Luckey site to characterize site conditions and to determine the nature and extent of contamination. The results of the RI indicated that in addition to the typical FUSRAP radiological soil contaminants, the Luckey site soils were also contaminated with Be. As part of the site characterization efforts, an experimental system for rapid Be analysis, known as Laser-Induced Breakdown Spectroscopy (LIBS), was deployed. The LIBS system used at the time showed considerable promise, and the beryllium data that were produced by the LIBS were instrumental for determining the nature and extent of surface soil Be contamination at the site. The Luckey site is now approaching remedial design and remedial action implementation. The RI data sets have indicated that Be contamination will be the driver for remediation across much of the site. There is a pressing need for a field-deployable beryllium analytical technique that can provide quality beryllium data at concentrations around the site cleanup goal (131 parts per million [ppm]). The original prototype LIBS system is no longer available. At the request of USACE-Buffalo District, Argonne National Laboratory (Argonne) reviewed two alternative systems: a recently commercialized optical fluorescence technique and a commercial LIBS system. A data collection program was designed to explore the performance of these two systems, as compared to standard off-site laboratory beryllium analyses. Forty surface soil samples were collected in August 2008 at the Luckey site from areas determined from the RI data to span the likely range of Be concentrations expected during remediation work (from around 10 ppm up to several thousand ppm). These samples were split, and analyses were performed by using a standard laboratory procedure, the optical fluorescence technique and the LIBS system; the results were used to establish accuracy, comparability, and detection limits for the two innovative methods. Multiple sub-sample replicates were also obtained from the laboratory sample with Be concentration closest to the action level to evaluate method precision. The results from this study will be used to design a remedial strategy that can be driven by real-time analyses while excavation work is underway – an approach that is consistent with the Environmental Protection Agency's Triad approach.

INTRODUCTION

In recent years, the Environmental Protection Agency (EPA) has encouraged the use of the Triad approach for streamlining and expediting hazardous waste site characterization and remediation [1]. The Triad approach is composed of three major components: systematic project planning, dynamic work strategies, and real-time measurement systems. While the Triad is applicable to all phases of the cleanup process, it offers the greatest potential for cost savings when incorporated into remedial strategies. The U.S. Army Corps of Engineers (USACE) Buffalo District actively incorporates the Triad into its cleanup

programs as appropriate, including at sites that are being addressed as part of Formerly Utilized Sites Remedial Action Program (FUSRAP).

One such site is the Luckey site. The Luckey site is approximately 16.2 hectares (40 acres) in size and is located near Luckey, Ohio, approximately 35.4 kilometers (22 miles) southeast of Toledo, Ohio. From 1949 to the early 1960s, the Brush Beryllium Company, as a contractor to the Atomic Energy Commission, used the Luckey site for beryllium (Be) processing to support the national defense program. Under FUSRAP authority, USACE conducted a Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) remedial investigation (RI) of the Luckey site to characterize site conditions and to determine the nature and extent of contamination. The results of the RI indicated that in addition to the typical FUSRAP radiological soil contaminants, the Luckey site soils were also contaminated with Be. As part of the RI efforts, two prototype Laser-Induced Breakdown Spectroscopy (LIBS) systems were deployed at the site: a bench-top unit for analyzing soil samples for Be, and a back-pack system that was capable of in situ measurements of surface soil Be.

The Luckey site is now approaching remedial design and remedial action implementation. The RI data sets have indicated that Be contamination will be the driver for remediation across much of the site. The USACE intends to use a Triad approach going forward; in that context, the site has a pressing need for a field-deployable Be analytical technique that can provide quality beryllium data at the site cleanup goal (131 parts per million [ppm]). Unfortunately the original prototype LIBS systems are no longer available. Two alternatives were identified: a recently commercialized optical fluorescence technique and a commercial LIBS system. A data collection program was designed to explore the performance of these two systems for Be analysis as compared to standard off-site laboratory Be analyses. The results from this study will be used to design efficient remedial design data collection programs and a remedial strategy that can be driven by real-time analyses while excavation work is underway, which is consistent with EPA's Triad approach.

REAL-TIME BERYLLIUM MEASUREMENT TECHNOLOGIES

Standard laboratory analysis for Be levels in soils uses Inductively Coupled Plasma (ICP) technologies or ICP mass spectrometry (ICP-MS). Beryllium ICP-MS analyses of soil samples yield detection limits that are less than 0.1 ppm – levels that are several orders of magnitude below the action level of concern for the Luckey site and well below background levels. The typical turn-around time for standard laboratory analyses is a couple of weeks.

At this time, there are limited proven options for conducting real-time analyses for Be in environmental samples at detection levels required by most cleanup programs. The USACE evaluated two potential real-time Be analysis systems applicable to soils as alternatives to conducting standard off-site laboratory testing. The first was an optical fluorescence technique developed originally at Los Alamos National Laboratory (Los Alamos) and commercialized by Berylliant, Inc. (Berylliant). The second was a commercially available LIBS system manufactured by Ocean Optics, Inc. (Ocean Optics).

Optical Fluorescence

The optical fluorescence technique evaluated in this study was developed by Los Alamos and is commercially available through Berylliant. Its application to wipe analyses has already been documented [2]. An ASTM standard has been developed (ASTM Standard D7202 [3]), and it has been recognized by National Institute for Occupational Safety and Health (NIOSH) (Method 7704 and Method 9110 [4]).

Details of the underlying method can be found in a paper by Minogue et al. [5]. In this setting, ammonium bifluoride (ABF) is used to dissolve the Be present in a sample. The resulting solution is filtered, a specialized fluorophore specific to Be is added, and the mixture is analyzed with a fluorometer for Be content.

In the case of soils, the primary challenge is the initial step: the dissolution of Be present in soil samples (both anthropogenic and naturally occurring). Complete dissolution of soil samples by using ABF requires heating the samples and waiting during potentially lengthy dissolution times. One of the questions addressed by the performance study was the effect that shortening dissolution times would have on dissolution efficiency and, consequently, on data quality. The expectation was that this technique would have detection limits below 1 ppm, assuming full dissolution of Be within a sub-sample.

The current protocol for Be fluorometry employed by Berylliant analyzes relatively small soil sub-samples (0.5 grams [g]). Standard soil sample sizes can range from 100 to 400 g or more in the field, depending on the size of the vertical soil interval being sampled and the geometry of the sampling device. Within-sample contaminant heterogeneity can be a significant concern if samples are not properly prepared before sub-sampling for analytical purposes. Samples that are not thoroughly homogenized can result in sub-sample analytical results that are not representative of the bulk characteristics of the original sample. The performance study addressed this potential issue through replicate sub-sampling and analysis of one selected sample.

Laser-Induced Breakdown Spectroscopy (LIBS)

LIBS uses lasers to target a sub-sample for analysis. The laser creates plasma from the target material, which produces ions and atoms in an excited state. As the plasma cools, elements within it emit characteristic wavelengths. Spectroscopy can then be used to detect these atomic emission lines and thus identify the elements present. If the system has been calibrated for the target material, inferences can be drawn about the concentrations of the elements present.

LIBS has a wide range of applications [6]. Prototype systems were developed by Los Alamos for Be analysis and were tested at the Luckey site as part of the RI work. Two different systems were deployed at the time at the site, a bench-top unit for analyzing soil samples ex situ, and a backpack unit for taking in situ measurements of exposed surface soils. At the time, comparability was evaluated by obtaining samples from some of the locations targeted by the backpack LIBS system and by splitting samples analyzed by the bench-top LIBS system. The detection limits for the two systems appeared to range between 10 and 100 ppm based on the laboratory split analyses.

A regression analysis of the paired results (laboratory versus LIBS) showed a relative weak relationship between LIBS and laboratory results over the range of concentrations of interest from a decision-making perspective; however, the LIBS data when mapped provided useful qualitative insights into the spatial distribution of surface soil Be contamination at the site. Part of the comparability problem was the lack of sample results in the range of the proposed action level (131 ppm); most samples were either highly contaminated with Be or had Be at levels not detectable by the LIBS. Figure 1 shows a map of Be results based on LIBS data for the site.

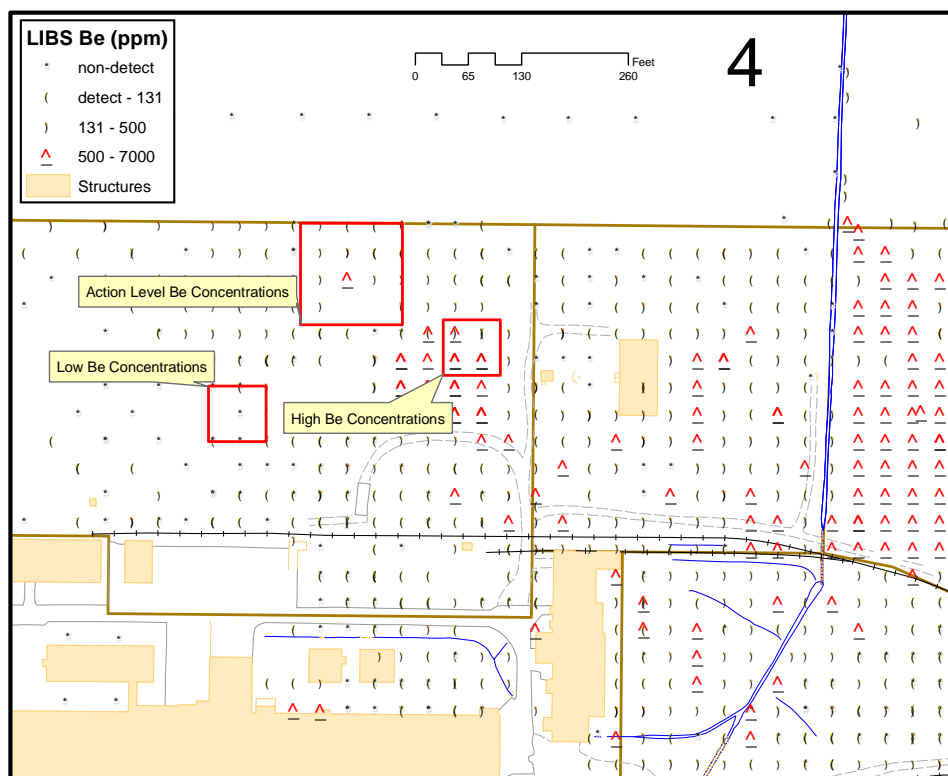


Fig. 1. RI LIBS surface soil Be results and areas targeted for study data collection.

Unfortunately, the prototype systems developed by Los Alamos for Be are no longer available, and there is no commercially-available LIBS system calibrated for detecting Be in soils. Ocean Optics produces LIBS systems designed for other purposes; the current study evaluated their applicability to soil Be characterization. Unlike Berylliant's methods, LIBS requires no extraction step. The primary potential issues with LIBS applied to soil sample analysis include proper matrix preparation, detection limits, and proper calibration. In the case of matrix preparation, loose soil can pose problems for LIBS analysis because the laser used to create plasma can also potentially disperse loose soil particles into the air, complicating the analysis of plasma spectral emissions.

Study Design

Forty surface soil sampling locations were selected at the Luckey site from three general areas (Figure 1). These areas targeted soils that were slightly impacted (low Be values), impacted around the action level (medium Be values), and heavily impacted (high Be values) by beryllium. The areas were also selected to avoid radiological contamination, which is also present at the site and which would have complicated sample handling for Berylliant and Ocean Optics. Confirmatory analysis of samples for radiological constituents occurred prior to shipment to Berylliant and Ocean Optics. Selection of the areas was based on the original LIBS data collected as part of the RI. The areas described by low and high Be concentrations were around 440 square meters (m²), while the area associated with site action-level Be concentrations was approximately 1,420 m².

Ten samples were allocated to the slightly impacted area, 20 to the area impacted around the action level (131 ppm), and 10 for the highly impacted area. To evaluate short-scale heterogeneity effects on Be sample results, samples were paired. Samples comprising a pair were separated by 1 m. The distance between adjacent pairs of samples ranged between 10 and 14 m. The sample pairs were systematically distributed across the targeted areas.

For each sampling location, the surface was cleared of vegetation and a soil sample obtained to a depth of 15.2 centimeters (6 inches) with a 10.2-centimeter (4-inch) diameter tool, yielding approximately 600 g of soil per sampling location. Samples were submitted to an off-site laboratory for preparation and homogenization. Sample locations were adjusted as necessary according to specific field conditions. Preparation included thoroughly drying the samples and homogenizing (but not grinding) them. After preparation and homogenization, all samples were sub-sampled at least three times. The first set was analyzed by the laboratory by using ICP-MS. The second set was sent to Berylliant for analysis by using optical fluorescence. The third set was sent to Ocean Optics for analysis by using LIBS. In addition, the sample with the ICP-MS result closest to 131 ppm was sub-sampled an additional 15 times. Five of these sub-samples were analyzed by ICP-MS, five by Berylliant, and five by Ocean Optics. The purposes of the re-sampling and analysis were to evaluate the efficacy of sample homogenization procedures used by the laboratory when Be concentrations were around the action level and to separate out the effects of within-sample heterogeneity from analytical variability when comparing analytical results from the three methods.

Berylliant used its standard sample preparation protocol for all samples, which involved a 40-hour extraction. In addition, Berylliant selected four samples (one from the low area, two from the middle area, and one from the high area) and obtained an extract aliquot after 2 hours of extraction to compare to the 40-hour extraction value. The purpose was to determine how much potential bias would be introduced into the Be results if the extraction was shortened to facilitate real-time implementation in the field as part of characterization or remediation efforts.

Ocean Optics experimented with several different methods for “fixing” prepared soil samples prior to LIBS analysis. The purpose was to determine what method could be readily implemented in the field and result in a soil sub-sample suitable for LIBS analysis.

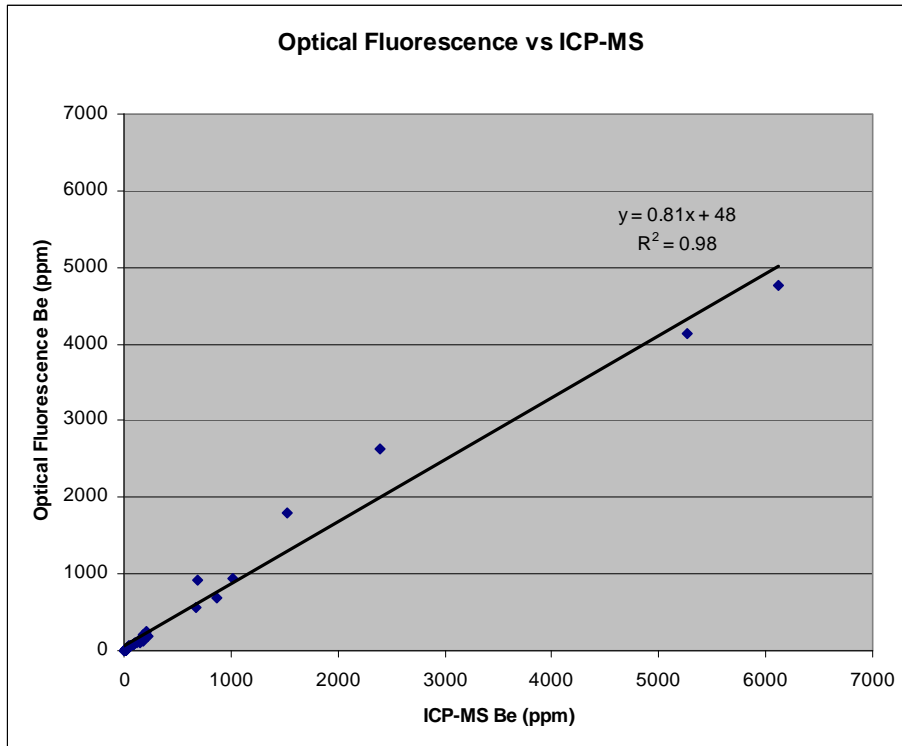
STUDY RESULTS

The original LIBS data proved highly effective in predicting the concentrations for the study target areas. The minimum ICP-MS Be result for the low area was 6 ppm, the maximum was 88 ppm, and the average was 35 ppm. The corresponding results for the medium area were 8 ppm, 221 ppm, and 110 ppm, respectively. For the high area, the results were 178 ppm, 6,120 ppm, and 1,978 ppm, respectively. In comparison, the RI [7] reported a 95% upper tolerance limit (UTL) background value of 1.13 ppm for beryllium in area soils.

Sample M5 was selected for repeated sub-sampling and re-analysis. After the initial set of ICP-MS analyses were complete, M5 was sub-sampled five times and the sub-samples analyzed, resulting in a total of six ICP-MS results. The replicate results ranged from 110 ppm to 126 ppm, with an average of 119 ppm and a standard deviation of 6 ppm. This result corresponded to a coefficient of variation equal to only 5%, which captured both the residual within-sample heterogeneity remaining after sample preparation and analytical error for a sample with Be concentrations around the action level.

The minimum Berylliant optical fluorescence results for the low area was 8 ppm, the maximum was 86 ppm, and the average was 36 ppm, which compared very favorably with the 35 ppm average observed in the ICP-MS data set for the low area. The corresponding results for the medium area were 8 ppm, 247

ppm, and 106 ppm. The 106 ppm average again compared favorably with the 110 ppm Be ICP-MS result observed for the medium area. For the high area, the optical fluorescence results were 215 ppm, 4,773 ppm, and 1,853 ppm, respectively. Figure 2 shows two scatter plots. The top compares the laboratory's ICP-MS Be results with Berylliant's optical fluorescence results over the whole range of values encountered. It also includes a best fit linear regression line through these data. The linear regression indicates a high degree of correlation as evidenced by the adjusted R^2 value almost equaling one; however, the optical fluorescence appeared to be under-reporting the Be present as indicated by the slope of the line. By visually inspecting this scatter plot, the "under-reporting" appeared to occur primarily at higher values (Be > 3,000 ppm).



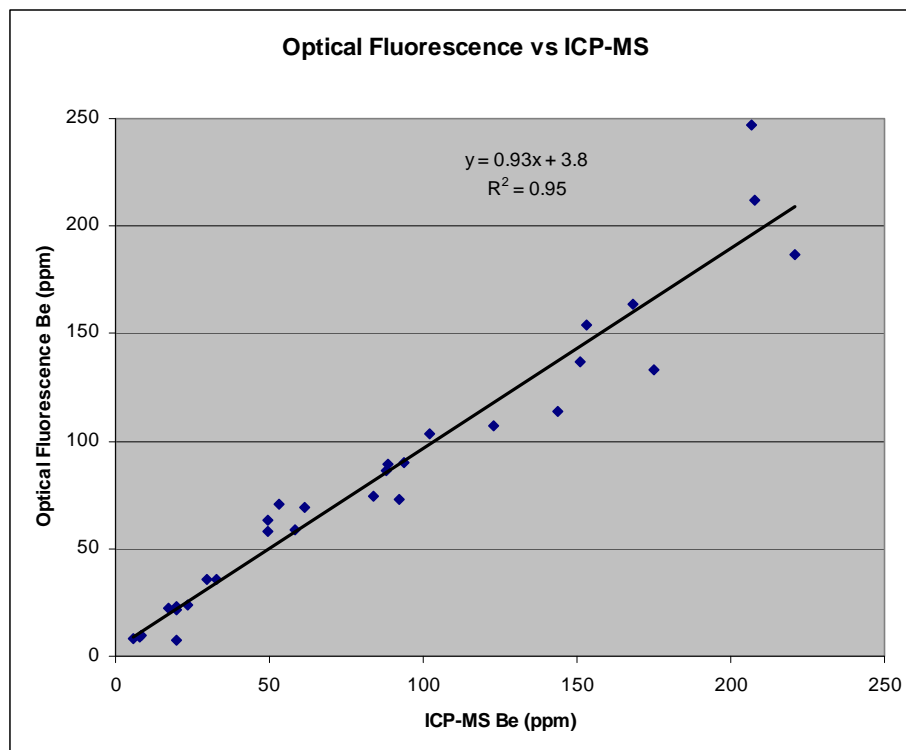


Fig. 2. Scatter plots and regression lines for optical fluorescence Be results as compared to ICP-MS Be values.

The bottom plot shows data only for the low and medium areas, with concentrations that bracket the action level for the site (131 ppm Be). In this instance, there remains a high degree of co-linearity between the two methods, but the rate of under-reporting is not as marked, with the slope rising to 0.93.

Five replicate sub-samples from sample M5 were also submitted for optical fluorescence analysis, resulting in six analytical results for that sample. The replicate results ranged from 100 ppm to 109 ppm for Be, with an average of 106 ppm and a standard deviation of 3 ppm. This result corresponded to a coefficient of variation of 3%, suggesting that the analytical variability for the optical fluorescence method was less than that for the ICP-MS for Be concentrations in the range of the site action level.

Extracts were obtained from four samples after only two hours into the extraction process (as compared to the standard 40 hours). The ICP-MS results for these four samples were 17 ppm, 33 ppm, and 873 ppm. Optical fluorescence results for the 2-hour extraction were compared to the corresponding results for these samples after the standard 40-hour extraction. The 2-hour results ranged from 81% to 94% of the 40-hour results, with an average recovery of 89%. The recovery efficiency for the 2-hour extraction as compared to the 40-hour extraction did not appear to be a function of concentration, although with only four pairs of results it was difficult to draw absolute conclusions. The primary conclusion was that extraction times could be dramatically shortened without significantly compromising data quality. In the case of LIBS, Ocean Optics experimented with several different sample preparation methods before determining that a simple press produced soil sub-sample "hockey pucks" with sufficient cohesion to allow LIBS analysis to take place (Figure 3). After forming sub-sample soil pucks, the LIBS analysis is virtually real-time. The laser was a 200-millijoule (mJ) neodymium-doped yttrium aluminum garnet

(Nd:YAG) operating at 1,064 nanometers (nm) and used in conjunction with the Ocean Optics sample chamber, imaging module, LIBS2500+ spectrometers, and OOILIBS software application for data acquisition. Five LIBS spectra were acquired for each sub-sample puck for a total of $45 \times 5 = 225$ scans (40 original samples plus the 5 sub-sample replicates from M5). Post processing of the data for Be detection utilized the SpecLine software package.



Fig. 3. Sub-sample soil “pucks” submitted for LIBS analysis.

On the basis of these spectra, Ocean Optics identified four wavelengths that were characteristic of Be and that consistently appeared in all LIBS sample analyses. Figure 4 shows one example spectra with the Be peaks identified. The fact that all samples yielded these four peaks suggests that the LIBS detection limits were sufficient to identify Be across the range of concentrations represented by these samples. At this time, additional analyses are being performed to determine whether the LIBS spectra can be used to reliably quantify the concentrations of Be present in the samples. Preliminary results in this regard are promising.

It is interesting to note the fact that one of the high area samples was initially reported by the laboratory (ICP-MS) as having only 1.53 ppm of Be, a value that was inconsistent with the neighboring sample results. When the laboratory was questioned and checked its quality control (QC), there was no evidence of analytical problems. Berylliant returned a result for this sample that was almost 2,000 ppm. When this information was passed to the laboratory, the laboratory more closely scrutinized the data sets and found a transcription error that resulted in a misplaced decimal for that sample; the actual ICP-MS result was 1,530 ppm. This underscores one of the significant benefits of on-site analytics; having results available in “real-time” allows anomalous data to be pursued and clarified. In a field setting, the worst case scenario would have been to re-sample and re-analyze a sample from that location.

This information can also be used to understand the performance of individual samples for predicting the general Be concentrations present in specific areas. For the low Be area, none of the 10 samples collected exceeded the action level. Likewise, for the high Be area, all of the 10 samples exceeded the action level. However, for the medium Be area, where the observed average concentration was 110 ppm based on ICP-MS results, 8 of the 20 samples collected exceeded the action level of 131 ppm. Looking at the 10 pairs individually, 8 of the 10 pairs yielded results either consistently above or below the action level, while two of the pairs yielded conflicting results (i.e., one member of the pair was above 131 ppm while the other was below).

CONCLUSIONS

The EPA's Triad approach (incorporating systematic project planning, dynamic work strategies, and real-time measurement systems) has great potential at sites like the Luckey site for cost-savings and remedial performance improvement. The key to implementing the Triad approach is the availability of real-time measurement systems appropriate for detecting the contaminants of concern. In the case of beryllium, until recently there was no good field alternative to conducting off-site analyses with detection limits sufficient to meet remediation action level requirements.

For Luckey, two promising technologies were identified: optical fluorescence and LIBS. A field study was conducted to establish the performance one might expect from these systems and to explore the comparability of data produced by LIBS and optical fluorescence with that from standard laboratory methods, such as ICP-MS. Forty samples were collected from the site and analyzed by all three methods. The optical fluorescence method produced data with a high level of correlation with ICP-MS for Be, detection limits that were below Be background levels, and analytical precision that appeared to be better than ICP-MS. There was a slight bias that appeared to be present in the optical fluorescence data sets that became more marked as concentrations increased. Current standard sample preparation procedures for optical fluorescence (i.e., 40-hour extractions) do not lend themselves to "real-time" decision-making in the field. Shortening the extraction time to only 2 hours appears to provide results that are close to those yielded by the full extraction period.

The LIBS system is truly "real-time," and prototype LIBS systems have shown significant promise at the Luckey site in the past. There currently is no commercially available LIBS system designed for conducting Be analysis in soils. However, an evaluation of a bench-top commercial system from Ocean Optics as part of this study suggested that the LIBS can identify the presence of Be in soils at levels that approach background. Work is currently underway to determine whether this system can be calibrated to provide reliably accurate estimates of Be concentrations in soil matrices.

Finally, a review of the variability present in the sample results suggests that relatively few samples are required to demonstrate that Be concentrations are well above or well below the site-specific action level. Conversely, in areas where Be concentrations are close to the action level, as many as 20 samples might be required to reliably determine whether true concentrations were above or below the action level. Sampling programs that rely on off-site laboratory analyses and on obtaining a pre-selected number of samples seldom achieve an optimum number of samples; some areas are over-sampled and some under-sampled. The advantage of a real-time technique, such as a LIBS or optical fluorescence for Be, is that sample numbers can be adjusted for specific areas depending on the timely results of field screening. Sample numbers can be reduced for areas well below and well above the site-specific action level concentrations. This capability allows more resources to be focused on areas where contaminants are closer to action-level concentrations.

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