

ATTACHMENT J

DUPONT CASE STUDY

This technology evaluation report, *Technology Evaluation: On-site Lead Analysis Using a Field Portable XRF Analyzer*, describes the use of a field-based measurement technology, the portable NITON Model 700 Series X-ray fluorescence (XRF) analyzer, to measure lead contaminant levels in soil on a real-time or quick turnaround basis.



Innovations in Site Characterization

Technology Evaluation: On-site Lead Analysis Using a Field Portable XRF Analyzer



**Innovations in Site Characterization
Technology Evaluation:**

On-site Lead Analysis Using a Field Portable XRF Analyzer

U.S. Environmental Protection Agency
Office of Solid Waste and Emergency Response
Technology Innovation Office
Washington, D.C. 20460

Notice

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Comments or questions about this report may be directed to the United States Environmental Protection Agency, Technology Innovation Office (5102G), 1200 Pennsylvania Avenue, NW, Washington, D.C. 20460; telephone (703) 603-9910.

Foreword

This evaluation of a field portable analytical technology is part of a series of case studies designed to provide cost and performance information for innovative tools that support less costly and more representative site characterization. Based on actual field projects, these case studies include reports on new technologies as well as innovative applications of familiar tools in the context of more efficient work strategies. The ultimate goal of this case study series is to aid practicing site professionals to enhance the cost-effectiveness and defensibility of decisions regarding the disposition of hazardous waste sites.

Acknowledgments

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TECHNOLOGY EVALUATION ABSTRACT

ON-SITE LEAD ANALYSIS USING A FIELD PORTABLE XRF ANALYZER

<p>Site Name and Location: Lake Success Business Park (LSBP) Bridgeport, Connecticut</p>	<p>Sampling & Analytical Technologies: NITON Model 700 Series field portable XRF analyzer (SW-846 Method 6200) for on-site soil characterization by: 1) in-situ (in-place) analysis with minimal sample preparation (e.g., surface leveling and debris removal) 2) bagged-sample analysis with homogenization of collected sample 3) prepared-sample analysis with sample drying, sieving, grinding, and homogenization in on-site laboratory.</p> <p>Off-site laboratory referee analysis on prepared samples by SW-846 Method 3050/6010 [acid digestion/inductively coupled plasma-atomic emission spectrometry (ICP-AES)].</p>	<p>Current Site Activities: RCRA corrective action activities, involving characterization of contaminated areas and removal, storage, and treatment of contaminated media.</p>
<p>Period of Operation: Late 1800s – 1989</p> <p>Operable Unit: Not applicable.</p>		<p>Technology Demonstrator and Project Contact: Scott Northey Assistant Project Scientist The URS Diamond Group The URS Corporation Barley Mill Plaza, Bldg. 27-2369 4417 Lancaster Pike Wilmington, DE 19805 (302) 892-8040</p>
<p>Regulatory Agency Contact: Stephanie Carr RCRA Facility Manager US EPA, Region I One Congress Street, Suite 1100-HBT Boston, MA 02114-2023 (617) 918-1363</p>	<p>Media and Contaminants: Soil contaminated with lead. Other analytes of interest during site clean-up included arsenic, antimony, zinc, copper, and mercury.</p>	
<p>Number of Samples Analyzed during Site Investigation: Thousands of soil samples were characterized for metal contamination at up to 51 areas of environmental concern, including on-site lead level characterization using the field portable NITON Model 700 Series XRF analyzer. As of Fall 1999, as part of an effort to evaluate XRF performance, results from 793 sample pairs had been verified using ICP-AES at an off-site laboratory.</p>		
<p>Estimated Resource Savings: Approximately \$205,000 for analyses covered by this report — Almost 50% savings in lead analysis cost when compared with estimated costs from using only conventional ICP-AES technology at an off-site laboratory. Savings are greater if include benefits of shorter project time frame and less project down time from waiting for off-site laboratory results.</p>		
<p>Description: During remediation activities at the LSBP, a NITON Model 700 Series field-portable XRF instrument was used for the on-site characterization of lead levels in soil. Three different approaches using XRF (in-situ, bagged-sample, and prepared-sample analysis) were used to guide decisions regarding the remediation. The XRF results provided real-time lead analyses to support field decisions regarding site delineation and the identification of lead-contaminated soils. The performance of at least 10% of the XRF analyses (793 samples as of Fall 1999) was evaluated based on a comparison of sample pair results (aliquots taken at time of collection) from the prepared-sample on-site laboratory XRF analyses and off-site laboratory ICP-AES analyses (SW-846 Methods 3050/6010). The U.S. EPA requested the 10% level of referee/verification analyses based on the results of an initial sample pair evaluation using both XRF and ICP-AES. The results were compared against action levels of 500 ppm and 1,000 ppm to evaluate agreement. Analytical disparities of sample pairs were noted.</p>		
<p>Results: This project illustrated the successful use of a cost-effective and quick turn-around sampling and analysis approach involving a field-portable technology (NITON Model 700 Series XRF analyzer) to generate lead-in-soil data effective for guiding real-time decision-making at a remediation site. Comparability of the XRF analysis procedure was established by comparing results from sample pairs analyzed by both prepared-sample on-site laboratory analyses using the XRF analyzer and prepared-sample off-site laboratory analyses using conventional analysis by ICP-AES. An evaluation of 793 sample pairs showed 99.0% agreement with the site's 1,000 ppm action level and 97.4% agreement with the site's 500 ppm action level. The project also illustrated the importance of understanding the effect of sample preparation on the data. The prepared-sample on-site laboratory XRF analyses showed greater agreement with the conventional ICP-AES results than XRF analyses involving less sample preparation (i.e., the in-situ and bagged-sample results). In general, in-situ or bagged-sample XRF results differ from prepared-sample results because sample preparation alters the sample support (e.g., alters the physical properties of the sample to be subjected to analysis by homogenizing the particle size and removing pebbles that might block the X-rays). It is important to consider the project-specific decision goals (i.e., the data quality objectives, DQOs) when determining both the appropriate mix of in-situ or bagged-sample analyses versus prepared-sample testing by XRF, and when determining the appropriate level of referee analyses by an off-site laboratory using a more conventional technology. The use of the field portable XRF analyzer saved approximately 50% in analytical costs over what would have been incurred had ICP-AES been used for all sample analyses. In addition, exclusive use of off-site laboratory analyses instead of on-site XRF analyses would have resulted in higher overall project costs due to a longer project time-frame.</p>		

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TECHNOLOGY QUICK REFERENCE SHEET

NITON Model 700 Series X-ray Fluorescence Analyzer

Technology Evaluation: On-site Lead Analysis Using a Field Portable X-ray Fluorescence (XRF) Analyzer

Technology Name: NITON Model 700 Series Field Portable XRF Analyzer			
Summary of Technology Evaluation's Performance Information			
Project Role: Provide quick turnaround results to support on-site decisions regarding identification and disposition of lead-contaminated soils	Analytical Information Provided: Lead concentrations (ppm) in soil using three different sample preparation and analytical approaches to make project decisions at 500 ppm and 1,000 ppm action levels.		
Total Cost for Sampling and Analysis: Approximately \$219,000 (for analyses evaluated by this study)		Total Cost Per Sample: \$27.61 (includes cost of off-site verification analyses at 10%)	
Project Analytical Cost Breakdown			
XRF Instrument Cost: 9,000 to 10,000	Consumables Cost: \$0.32/sample	Labor Cost: Approx. \$143,000	Waste Disposal Cost: No additional cost.
Site-specific Sensitivity, Accuracy, Precision and Comparability Achieved for Lead Analysis: <u>Sensitivity:</u> The site-specific sample detection limit was calculated to be 100 ppm; the site-specific sample quantitation limit was calculated to be 340 ppm. <u>Analytical Precision:</u> For the LSBP samples, prepared XRF analyses provided precision estimates of 0–103 relative percent difference (RPD) for duplicate sample results (n =71). This compared favorably with the precision estimate of 0–166 relative percent difference (RPD) for duplicate sample results (n =61) produced by the off-site analytical laboratory using ICP-AES analyses. <u>Analytical Accuracy:</u> Accuracy of the XRF analyzer was not evaluated on LSBP site-specific samples, however, concurrent with the LSBP activities, the LSBP XRF laboratory participated in over 10 rounds of testing with the ELPAT Proficiency Program. All NITON XRF results were within the statistically-determined range of acceptable concentrations for all samples. Relative bias calculations ranged between -11 and + 17 for proficiency samples with lead concentrations between 100 ppm and 2000 ppm. <u>Data Comparability:</u> Paired analyses of 793 project soil samples (split in the field after moderate homogenization) demonstrated 99% decision agreement at the 1,000 ppm action level and 97% agreement at the 500 ppm action level. The majority of disagreements (70%) were instances where the XRF results were higher (i.e., more conservative) than the paired ICP-AES referee results. The false negative and false positive decision error rates (across both action levels) for the prepared-sample XRF technique (as judged against the referee ICP method) were 0.9% and 2.1%, respectively. Regression analysis of 40 data pairs from a demonstration study showed a coefficient of determination (r^2) of 90.4%. However, the fit of the regression line for a larger data set (262 data pairs) was notably worse (66.9%) indicating additional variability in the site-wide data compared to the initial demonstration data set.			Throughput Achieved: Varied, but at least 30 samples/day.
<i>(continued)</i>			

General Commercial Information (Information valid as of November 2001)

<p>Vendor Contact: Tel: 1-800-875-1578 Tel: 978-670-7460 Fax: 978-670-7430 xrf@niton.com</p>	<p>Vendor Information: NITON Corporation 900 Middlesex Turnpike, Bld #8 Billerica, MA 01821 http://www.niton.com</p>	<p>Limitations on Performance: Does not distinguish between different isotopes or chemical forms of an element. Accuracy improves with sample preparation (e.g., drying, grinding, sieving).</p>
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Principle of Analytical Operation:
The NITON Model 700 Series XRF analyzer is a hand-held, battery operated instrument that uses X-ray fluorescence (XRF) spectrum analysis to identify and quantify metals. In XRF, a radioactive source, such as Cd-109 (used in this project's analyzer) or Am-241, emits high energy photons (X-ray or gamma-ray) that strike the sample, causing the ejection of electrons from the element atoms. Other electrons drop into the vacancy and release energy in the form of another X-ray, which is received by X-ray detectors, electronics and on-board microprocessors. The intensity (number of electrons) and spectral energy (frequency) of the electrons released are used by the detector to quantify and identify the metal present in the sample. When used according to its instructions, the NITON Model 700 Series XRF analyzer poses minimal radiation exposure to the operator, even with the shutter open.

General Commercial Information (continued)

<p>Instrument Weight and/or Footprint: Dimensions: 8.25" X 3.0" X 1.875" Weight: 2.5 pounds (with the battery pack installed)</p>	<p>Availability and Rates: Commercial purchase cost of a NITON Model 700 Series XRF analyzer ranges from approximately \$21,000 to \$50,000, depending on instrument features. Leasing options are available.</p>
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<p>Power Requirements: Internal battery pack, provides power for eight hours and charges in two hours.</p>	<p>Other Information: The NITON Model 700 Series XRF analyzer can characterize metal levels in about 20 to 30 seconds. The analyzer stores up to 3,000 data points, including sample locations. The data are easily downloaded to a conventional personal computer. The instrument can be shipped without exterior labeling (meets DOT requirements in 49 CFR 173.41).</p>
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General Performance Information

Known or Potential Interferences for Lead Analysis:
Interferences by several elements (including arsenic, rubidium, bromine, and strontium) that have K line X-rays near in energy to the lead L-beta line X-ray at 12.6 keV. Large particles may cause a negative bias in XRF analyses if sample preparation does not involve sufficient grinding.

Analytes Measurable with Expected Detection Limits:
Analytes include the RCRA TCLP metals and several other elements. Estimated detection limits for soil measurements range from <20 ppm to <3,500 ppm (60 second test time), depending on the analyte and matrix. See the appendix for more information. Longer test times lower the detection limits.

Other General Accuracy and Precision Information:
Regarding accuracy, the NITON Corp. User's Guide for the NITON Model 700 Series XRF analyzers [1] states that the NITON XRFs are calibrated to give accurate values for most elements at 10,000 ppm or less. For actual concentrations of 10,000 to 20,000 ppm, the analyzer may overstate the concentration, and may do so even more at concentrations over 20,000 ppm. Regarding precision, the User's Guide states that, for every measurement, the NITON XRF analyzer gives an uncertainty range that represents a 95% confidence limit.

SW-846 Method 6200 contains performance information from the use of field portable XRF, although the data are not from the NITON Model 700 Series XRF analyzer.

<p>Applicable Media/Matrices: Soil, dust, paint</p>	<p>Wastes Generated Requiring Special Disposal: None</p>	<p>Rate of Throughput for Bagged samples: Sample preparation: Approx. 5–10 min per location. Analysis: At least 20 seconds/test On-site laboratory: Sample preparation: Approx. 2.5 to 4.5 hours per sample (2–4 hrs for drying, 0.5 hrs for other preparation steps) Analysis: At least 60 seconds/test</p>
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EXECUTIVE SUMMARY

This technology evaluation report describes the use of a field-based measurement technology, the portable NITON Model 700 Series X-ray fluorescence (XRF) analyzer, to measure lead contaminant levels in soil on a real-time or quick turnaround basis. The XRF lead data were effective for making field decisions regarding the extent of lead contamination during remediation efforts at Lake Success Business Park (LSBP) in Bridgeport, Connecticut. The real-time and quick-turnaround use of data from the XRF analyzer allowed field decisions at a lower cost than if the analyses were conducted using more conventional technologies with a longer turnaround time for results (i.e., conventional off-site, fixed laboratory analyses).

The LSBP covers a land area of 422 acres, and was owned and operated by the Remington Arms Company, Inc. until 1989 as a small arms and ammunition storage and manufacturing facility. The site is presently owned by Sporting Goods Property, Inc. (SPG, Inc.), a subsidiary of E.I. DuPont de Nemours and Company. SPG, Inc. is developing the site into a business park.

The LSBP is regulated as an interim-status RCRA facility and is undergoing corrective action. Soil contamination with lead and other metals exists throughout the site as a result of the arms storage and manufacturing activities. In the early 1990s, a RCRA Facility Investigation at the site identified 51 areas of environmental concern (AECs), with lead as the primary constituent of concern. In 1997, a remedy (referred to as EPA Remedy I) began for soil remediation at most of the AECs. Remedy I called for excavation and treatment of any soil with lead levels exceeding certain action levels based on soil location at the LSBP site. The EPA assigned two action levels, one of 500 ppm for areas within the boundaries of a buffer zone around the site perimeter, and one of 1,000 ppm for non-buffer zone site areas. The site owners proposed the use of XRF analysis for lead during site characterization to delineate contaminated areas and evaluate the completeness of contaminated soil excavation. The EPA project manager approved the use of XRF, provided its use included referee/verification analysis by a more conventional technology. In addition, EPA requested that the LSBP XRF on-site laboratory participate in the Environmental Lead Proficiency Analytical Testing (ELPAT) Program administered by the American Industrial Hygiene Association (AIHA). In order for a method of lead analysis to comply with the standards of the ELPAT Program, analytical results of blind samples must lie within an acceptable limit range.

Two field portable NITON Model 700 Series XRF analyzers were used for lead analysis at the site. One analyzer was used for in-situ (in-place soil analysis) and bagged-sample analyses on minimally prepared samples (e.g., debris removal and some homogenization); and the other analyzer was used in an on-site laboratory on more fully prepared samples (e.g., dried, ground, sieved, and homogenized samples). As requested by the EPA project manager, at least 10% of the prepared-sample XRF on-site laboratory analyses were verified at an off-site laboratory by comparison with results from using the more conventional SW-846 Method 3050 [2] (acid-soluble digestion) and SW-846 Method 6010 [3] (determinative analysis by inductively coupled plasma-atomic emission spectrometry, or ICP-AES). As of Fall 1999, XRF results from 793 sample pairs had undergone comparison with Methods 3050/6010 analysis.

This technology evaluation addresses the results from the 1999 sample pair verification analyses and from the ELPAT Program participation, and estimates cost savings from use of the NITON Model 700 Series XRF analyzer versus use of a more conventional technology (i.e., Methods 3050/6010) and analytical approach. It also provides information regarding the use of field portable XRF analyses to characterize lead levels in soils.

EXECUTIVE SUMMARY (continued)

Based on the data set evaluated as part of this technology evaluation, the XRF sample results showed sufficient agreement with the Methods 3050/6010 results to justify the use of XRF analyses to promote timely decision-making regarding the delineation of contaminated areas and the completeness of contaminated soil excavation. Agreement between XRF and ICP results with respect to decisions made at a specific action level increased with the degree of XRF sample preparation (e.g., drying, grinding, sieving, and homogenizing). In addition to demonstrating that the data sets were comparable with respect to project decision-making, comparison between results generated by the two methods indicated that the prepared-sample XRF results were usually more conservative (i.e., XRF results were higher) than the Methods 3050/6010 results. The prepared-sample on-site laboratory XRF results also met the ELPAT requirements for proficiency in analyzing lead concentrations in soil.

Based on the cost evaluation for use of the NITON Model 700 Series XRF analyzer in lieu of the use of a more conventional method for all analyses, a significant savings in analytical costs of up to 50% was realized. The cost savings, however, do not compromise the reliability of project decisions, but actually improve it. Since more measurements can be made at the same or lower cost using the field portable technology and since the greatest source of error in project decisions is due to inadequate sampling density, field analysis can produce a higher confidence in the interpretation of analytical results, as long as the relative uncertainties due to sampling and analysis are understood and managed. Besides savings in analytical costs, the use of field analytical technologies such as the XRF analyzer also can include time and labor savings when the ability to make reliable timely decisions minimizes the down-time of costly site remediation services (e.g., soil excavation) and repeated mobilizations back to the field to obtain additional data or fill data gaps after the receipt of results from an off-site laboratory.

Based on these evaluations, field portable XRF analyses can provide effective data in a cost-efficient manner during site characterization and remediation efforts. ("Effective" data are analytical data of a known quality that can be shown to be effective for making specific project decisions because both the sampling and analytical uncertainties are managed to the degree needed to meet the desired overall goals for decision confidence.) Therefore, field portable XRF analyses can be used as part of a dynamic work plan strategy (which allows project teams to make real-time decisions in the field about subsequent activities [4, 5]), as long as project-specific planning and documentation ensures that the sampling and analytical procedures used are compatible with the intended use of the data. Project plans should identify what sampling and analysis uncertainties need to be managed to meet project goals and discuss the strategies that will be used to do so, such as how sampling locations and sample collection procedures will impact sample representativeness [6]. Such considerations are critically important during the sampling and analysis of a heterogeneous matrix such as lead-contaminated soil. Careful planning and implementation of strategies to control both sampling and analytical uncertainties will promote confidence in the data and the decisions made based on the data.

In particular, the effective use of field portable XRF analyses should take into account the necessary level of sample preparation based on the purpose of the analysis. For instance, during the LSBP remediation, prepared-sample XRF analysis results showed greater agreement with conventional technology results than results from less intensively prepared samples. Therefore, the use of prepared-sample results may be preferred when determining regulatory compliance. On the other hand, the use of less sample preparation to obtain in-situ or bagged-sample XRF results may be adequate for guiding the removal of contaminated soil, or the selection of sample collection locations for a more rigorous analytical procedure (e.g., prepared-sample XRF analyses).

Appropriate quality assurance/quality control (QA/QC) procedures should be implemented to fully document the sampling and analysis procedures and the quality of the data. A chemist familiar with lead

EXECUTIVE SUMMARY (continued)

analysis by XRF should be consulted during project planning and implementation. The project plan may also include verification of XRF results using a more conventional referee analytical technology at a frequency determined on a project-specific basis. One goal of referee analysis is to establish comparability between field results and the more traditional analytical results from which the action levels were derived. The compared samples should go through similar sample preparation steps to promote a high quality comparison.

SITE INFORMATION

Identifying Information

Site Name:	Lake Success Business Park
Location:	Bridgeport, Connecticut
Technology:	NITON Model 700 Series field portable X-ray fluorescence (XRF)
Operable Unit:	No operating manufacturing units, site remediation activities are on-going.
ACO Date:	August 21, 1990, modified October 1994 and September 1997

Background [7, 8]

Physical Description: The Lake Success Business Park (LSBP) is located in the State of Connecticut and straddles the Town of Stratford and the City of Bridgeport. The LSBP site covers a total of 422 acres, which consists of approximately 344 acres within the City of Bridgeport and approximately 78 acres within the Town of Stratford. The site includes a large lake currently called Lake Success.

Site Use: From the late 1800s to 1989, the LSBP site was owned and operated by the Remington Arms Company, Inc., and used to manufacture, test, and store small-caliber and other types of ammunition. Site operations were scaled back after the Vietnam War, and ceased completely in 1989. Subsequently, E.I. DuPont de Nemours and Company (DuPont) became the owner of the closed Bridgeport/Stratford facility. The portion of Remington Arms retained by DuPont was renamed Sporting Goods Properties, Inc. (SGP, Inc.) and remains a subsidiary of DuPont. The site, formerly known as Remington Park or Remington Woods, was renamed the Lake Success Business Park (LSBP), which it is called throughout this technology evaluation. The site will be developed into a business park, to consist of developed parcels and open spaces. Light industry, research and development, office complexes, and other commercial activities will be located in the developed parcels.

Release/Investigation History: A Phase I RCRA facility investigation (RFI) was conducted between September 1989 and February 1991 to identify the universe of contaminants present at the site. The RFI included soil, groundwater, surface water, and sediment sampling. Extensive XRF analyses of the soil were conducted to delineate the vertical and aerial extent of contamination by lead, mercury and strontium, the primary metals of concern at 51 areas defined as areas of environmental concern (AECs). Representative soil samples were collected from 36 AECs. Groundwater samples were collected from 14 monitoring wells, while surface water and sediment samples were collected from eight locations. The results of this investigation indicated that lead was the main constituent of concern at the site. Additional constituents of interest were identified on an AEC-specific basis.

Based on the results generated from the Phase I RFI and other investigations, a phased approach to future remediation and investigation activities was planned for the site. Phase I of the approach, also known as EPA Remedy I, was approved in September 1997 and included soil excavation/treatment and debris removal activities for 37 AECs, which consisted primarily of upland soils. Remedy I called for the excavation of contaminated soils, stockpiling of contaminated soils on the Corrective Action Management Unit (CAMU) and treatment or disposal of the soils. Initially, soil washing was identified as the treatment technology to address excavated soil. However, after an economic and technological evaluation of alternative technologies, soil stabilization proved to be a more favorable treatment technology.

Regulatory Context: LSBP is an interim-status RCRA facility. In 1986, a site analysis was performed by EPA. During the Phase I RCRA Facility Investigation, an on-site surface impoundment was closed. Also during this time period, as part of the RCRA Corrective Action process, the process facilities were cleaned, sludges and wastewaters were removed, explosives were deactivated, and explosive residuals were removed. Asbestos was removed from the site and 177 buildings were demolished. In 1993,

SITE INFORMATION (continued)

interim measures were proposed, and in 1994, a Corrective Action Management Unit (CAMU) was approved and constructed. A soil washing pilot study was performed in 1995, and excavation of areas of environmental concern began in 1996.

National Priority Listing (NPL): None

Enforcement Dates: On August 21, 1990, the site owner entered into an Administrative Consent Order (ACO), pursuant to Section 3008(h) of RCRA, with EPA for the performance of corrective action activities at the facility. Corrective actions are presently being conducted at the site in accordance with the ACO, which was modified in October 1994 and September 1997. The September 1997 modification to the ACO approved Remedy I, or Phase I of the remediation activities, which included the soil excavation and treatment and debris removal activities for 38 AECs.

Contacts

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Matrix Identification

Type of Matrix Sampled and Analyzed: Soil

Site Geology/Stratigraphy [7]

The LSBP site is underlain by four metamorphic crystalline bedrock units with formational contacts trending approximately north 30° east. These units are, from southeast to northwest: the Straits Schist, the Trap Falls formation, the Pumpkin Ground Gneiss, and the Beardsley Gneiss. Fracture trace analysis, using aerial photographs, determined that the primary orientation of fracture traces occurs between north 10° west and north 20° west. The secondary fracture trace orientation is between north 20° east and north 30° east. The overburden deposits at the site are interpreted as glacial drift. These deposits consist primarily of sand, silty sand, and occasionally silty clay. These deposits occur in linear channels or closed depressions between bedrock outcrops, possibly beneath Success Lake and its northern extensions, in several buried glacial channels, and along the northeastern side of the site.

Contaminant Characterization [7]

Primary Contaminant Groups at the Site: Lead is the main constituent of concern at the LSBP site and its characterization is addressed by this report. Additional constituents of interest were identified on an AEC-specific basis during Phase I of the RFI and included arsenic, antimony, copper, mercury, zinc, and others. Some samples from the LSBP also were analyzed for arsenic by XRF and some of the results are briefly addressed by this report. If remediation activities show that soils meet the lead media protection standard (action level), then 95% of the time the other metals meet the applicable media protection standards. Therefore, the other metals were not evaluated by XRF procedures during the period covered by this report.

Site and Matrix Characteristics Affecting Characterization Cost or Performance [7]

The lead-in-soil matrix was not homogeneous and contained vegetation and pebbles or rocks. During in-situ analysis, the site selected for analysis was cleared of debris and vegetation (e.g., weeds) and leveled before placement of the analyzer on the soil surface. During bagged-sample collection and collection of samples for prepared-sample on-site XRF analysis and off-site ICP-AES analysis, large rocks or pebbles were removed from the samples. The samples were further prepared at the laboratories through drying, sieving, grinding, and homogenizing to control inaccuracies that may be caused by the inhomogenous lead-in-soil matrix. In addition, sample collection protocols had to consider the probable uneven distribution of contamination throughout areas of environmental concern, and required adequate sample selection and compositing measures to fully address sample support (the physical size, orientation, and shape of a sample) and ensure sample representativeness. These necessary sample collection and sample preparation considerations cause slightly higher sampling and analysis costs than might be incurred for a more homogeneous matrix and, if not done sufficiently well, can adversely affect analytical performance.

SITE CHARACTERIZATION AND REMEDIATION PROCESS

A Phase I RCRA Facility Investigation (RFI) was conducted at the LSBP between September 1989 and 1991. Its objectives were to identify the universe of contaminants and determine the location of each area of environmental concern (AEC) prior to more in-depth site characterization and the start of the remediation process. The RFI results indicated that lead was the primary constituent of concern. Additional constituents of concern were identified on an AEC-specific basis. Data from the RFP Phase I report were used to develop the action levels for each constituent of concern [7].

Based on an evaluation of data generated from the Phase I RFI and other investigations, remediation activities for the LSBP site were scheduled in three phases. Phase 1 of the remedy, also known as EPA Remedy I, began in 1997 and included the excavation and treatment of upland soils at 38 of 51 AECs. Phase 2 included the deactivation of ordnance. Phase 3 included the remediation of water and sediments, and soil at AECs not addressed during Remedy I. In general, Remedy I site remediation involved identification of which AECs required soil excavation and treatment based on comparison of contaminant levels against the action levels, identification of the boundaries for soil excavation, excavation of the soil, and transport of the soil to a Corrective Action Management Unit (CAMU) for storage and treatment by stabilization. The EPA assigned two action levels for lead, one of 500 ppm for areas within the boundaries of a buffer zone around the site perimeter, and one of 1,000 ppm for non-buffer zone site areas.

In 1998, EPA conditionally approved use of field portable XRF procedures during the phased site remediation. The field portable XRF analytical technology was used to provide real-time and rapid turn-around results during characterization of lead contamination in the AEC soils. This efficient approach to site characterization would not have been possible with exclusive use of a conventional analytical technology. The use of field portable XRF analysis also allowed an increase in sampling density from what might have been economically possible with more conventional approaches. The XRF results were used to make decisions regarding the delineation of the extent of lead contamination at the AECs and regarding sampling locations for further analysis.

Remedy I Characterization Process [7]

The "Stratford Corrective Measures Completion Report (CMCR)" [7] documents Remedy I corrective action activities conducted on the Stratford portion of the Lake Success Business Park site, and includes descriptions of the site characterization and remediation process using various sampling and analysis procedures. As noted earlier, the LSBP site straddles both the Town of Stratford and the City of Bridgeport in the State of Connecticut. Ten of the 51 AECs are located within the Stratford portion. This section of this technology evaluation report summarizes the use of field portable XRF during Remedy I AEC characterization and remediation as documented by the Stratford CMCR.

During Remedy I, XRF sampling and analysis was used to aid site characterization and remediation decisions. Decisions were made to confirm: the boundaries of soil excavation, whether soil excavation was not necessary at some AECs, and whether soil excavation was adequate at others. These decisions were made based on a comparison of sample results against the action levels. The AECs at LSBP fell under the following two corrective action categories according to whether or not the soil had to be excavated and treated:

1. At AECs requiring soil excavation/treatment — Pre-excavation site delineation with analysis to confirm the limits of excavation, confirmation-of-compliance sampling and analysis (in areas projected to be outside excavation boundaries), and post-excavation sampling and analysis to confirm removal of all contamination soil during excavation.

SITE CHARACTERIZATION AND REMEDIATION PROCESS (continued)

2. At AECs not requiring soil excavation/treatment — Debris removal and confirmation-of-compliance sampling and analysis to verify that no excavation was necessary.

Confirmation-of-compliance sampling and analysis also was conducted outside the boundaries of all of the AECs to ensure that surrounding soils met the media protection standards for the site.

Therefore, during Remedy I field portable XRF analysis was used for the following purposes:

- Pre-excavation delineation sampling
- Post-excavation sampling
- Confirmation-of-compliance sampling

These sampling purposes are further described below after a general description of XRF sampling procedures, which included in-situ and bagged-sample XRF analysis on minimally prepared samples and on-site laboratory XRF analysis on fully prepared samples. More information regarding these field portable XRF procedures and the off-site laboratory analytical procedures used to verify the XRF results begins on page 12 under "Characterization Technologies."

General Sampling Procedures at the AECs: As noted above, field portable XRF sampling and analysis occurred under several different characterization scenarios during LSBP remediation. In addition, 10% of the confirmation-of-compliance and post excavation samples were analyzed by an off-site laboratory using the more conventional analytical technologies of SW-846 Method 3050 (acid-soluble sample digestion) and Methods 3050/6010 (ICP-AES) to establish the comparability of the XRF data.

In general, the XRF procedures involved in-situ and bagged-sample analysis on minimally prepared samples and on-site XRF laboratory analysis on more fully prepared samples. The in-situ XRF procedure was conducted on the soil surface or surface of an excavation sidewall, sometimes to guide the location of subsequent sample collection for further analysis. For samples to be analyzed by bagged XRF analysis and on more prepared samples at the on-site XRF laboratory, soil samples were collected at the appropriate depth using a boring device, usually a stainless-steel hand auger or stainless steel spoon, and the samples were placed in a labeled plastic bag. Samples were either homogenized in the field in a pan prior to placement in the bag by rotating the pan, or the samples were homogenized within the bag by shaking. These soil samples were subsequently analyzed in the bags by the XRF analyzer and then transported to the on-site XRF laboratory for prepared-sample XRF analysis.

For those samples selected for paired verification analysis by both the prepared-sample XRF at the on-site XRF laboratory and SW-846 Methods 3050 and 6010 at the off-site laboratory, the collected soil sample was placed in a stainless steel pan or plastic bag, and homogenized in the pan or bag (by rotating the pan or shaking the sample in the bag). The sample aliquots were then removed and placed in containers for the respective laboratory analyses. Those samples going to the off-site laboratory were placed on ice in a sample cooler, along with the chain-of-custody documentation and shipped via laboratory courier or overnight service to the laboratory.

Pre-excavation Delineation Sampling for AECs: Delineation sampling was conducted at AECs requiring soil excavation to confirm that the planned boundaries of excavation were adequate. Delineation sample analysis was limited to lead characterization, and the majority of the samples were processed using a tiered approach for in-situ and bagged-sample analysis, followed by selected prepared-

SITE CHARACTERIZATION AND REMEDIATION PROCESS (continued)

sample XRF analysis at the on-site laboratory. Sample collection and analysis was conducted as described above under "General Sampling Procedures at the AECs."

Post-Excavation Sampling for AECs: Post-excavation sampling was conducted at AECs where soil excavation was performed by establishing a grid pattern within the footprint of the excavation. The size of the grid pattern was based on the size of the excavation area and on statistical calculations that determined the proper number of samples necessary to confirm (with a 95% confidence) that remaining soils met site media protection standards.

The post-excavation samples were collected from the excavation interior at each grid node. The samples were collected from a depth of 0 to 6 inches below the bottom of the excavation. Post-excavation samples also were collected laterally (i.e., on the sidewalls) along the perimeter of the excavation at depths of 0 to 6 inches below grade and 0 to 6 inches above the bottom of the excavation. Where excavation depths exceeded four feet below grade, additional post-excavation samples were collected from the sidewalls from a six-inch interval at the mid-depth of the excavation.

All post-excavation samples were analyzed by XRF on prepared samples by the on-site laboratory. Some post-excavation samples also were sent to an off-site laboratory to be analyzed for additional constituents of interest.

Confirmation-of-Compliance Sampling for AECs: Confirmation-of-compliance sampling was conducted in AECs where no excavation activities were required because contaminant levels were below the action level. However, these AECs still contained soils with contaminant levels exceeding the site background levels, and some AECs contained potentially contaminated debris that was to be removed. Gathering more data in these areas increased knowledge about the distribution of lead in retained soils and increased confidence that non-compliant soils would not be left behind. At those locations, a grid pattern was established within the area identified as including debris or soils with concentrations exceeding background levels. The size of the grid pattern was determined based on the size of the sampling area and on statistical calculations that determined the proper number of samples necessary to confirm (with a 95% confidence) that the area did not contain soils exceeding the site media protection standards. Confirmation-of-compliance samples were collected from a depth of 0 to 6 inches below grade within that grid. Sometimes, based on AEC history, samples were collected at depths up to four feet below grade.

Confirmation-of-compliance sampling also was conducted at certain AECs which had required excavation because of elevated contaminant levels. EPA requested that such sampling be conducted in areas located outside the excavation boundaries where soil concentrations were below the action level but exceeded background concentrations. Confirmation-of-compliance samples were collected at 10% of the delineation sample locations which exhibited those properties. Sample collection and analysis was conducted as described above under "General Sampling Procedures at the AECs."

XRF Analysis and Project Planning

During site characterization and remediation at the LSBP, the sampling and analysis procedures were carefully planned and conducted in accordance with a project-specific quality assurance project plan (QAPP). QAPPs should begin by describing the project-specific decision goals (i.e., data quality objectives, DQOs) from which the sampling and analytical measurement quality objectives (MQOs) will be derived [9]. Measurement quality objectives drive selection of the sampling and analytical methods and technologies that will be able to meet the measurement needs in the most cost-effective manner.

SITE CHARACTERIZATION AND REMEDIATION PROCESS (continued)

Evaluation of cost-effectiveness should not be limited to a consideration of per sample costs, but should include an evaluation of whether real-time data results and real-time decision-making can markedly cut overall project costs by minimizing the number of mobilization trips to the field to fill data gaps or complete cleanup activities. After the appropriate sampling and analytical tools are selected, project- and method-specific quality assurance/quality control (QA/QC) procedures are set up that will monitor the integrity of sampling and analysis procedures. The QAPP also should define the acceptance limits for QC checks, and the corrective actions to be taken should the QC acceptance limits be exceeded. In this way, a QAPP documents the reasoning process that leads logically from project decision goals to a project-specific sampling and analysis plan, and then to data of known and documented quality capable of supporting defensible site decisions. A project-specific QAPP thus ensures that all relevant sampling and analytical uncertainties are managed for successful data collection and interpretation, and serves as a vital documentation and implementation link between the outputs of a systematic planning process (a common sense approach to ensure that the level of detail in planning is commensurate with the importance and intended use of the data), and the end product (defensible data effective for making the intended project decisions) [10].

As with any sampling and analysis effort, the use of a field portable XRF technology during site characterization should be planned and implemented as part of a systematic project planning procedure [5] and include use of a QAPP. The sampling and analysis portion of the QAPP should outline exactly how the site will be sampled and analyzed during XRF use. The seven-step "DQO process" is one type of systematic planning process. It defines its DQOs as qualitative and quantitative statements that clarify study objectives and specify tolerable levels of decision errors. This information is used as the basis for the quality and quantity of data needed to support decisions, and thus allows project planners to define the appropriate type of data [11]. The project's decision goals (i.e., the DQOs) should be identified and carefully considered before designing the sampling and analysis portion of the QAPP. Examples of questions that should be answered include: What types of decisions will be made based on data (e.g., are data needed to direct remediation activities in the field)? What are the action levels for analytes of interest? From where should samples be collected? What depth of contamination is to be characterized? All steps should be detailed regarding, for example, mode of XRF analysis (e.g., in-situ or bagged), sample collection locations, sample handling and preparation, and quality control procedures and how the data will be used to evaluate analytical performance.

Development of a QAPP for site characterization and remediation using a field portable technology such as XRF also requires expertise in analytical chemistry and an understanding of instrument operation and limitations. The technology operator should be well-informed regarding the proper operation of the instrument and, if any results appear questionable, take advantage of immediate re-analysis allowed by the field technology.

For those that rely on field portable XRF analyses for project decision-making, the quality of the analytical information should be established and documented through:

- C The identification and management of error that may be introduced based on sampling design and during sampling procedures. This includes consideration of how well sample support is represented, including consideration of the physical characteristics of the sample that influence representativeness, the orientation of the sample and its components relative to the use of the sampling site, and the ability of the sampling tool (such as a coring device) or sample collection process to retrieve a representative sample. Sample support will affect whether the contaminants are correctly sampled and whether the data are representative of the actual site conditions in the

SITE CHARACTERIZATION AND REMEDIATION PROCESS (continued)

context of the decisions that are to be made. Data that are not representative can lead decision-makers to erroneous conclusions about site conditions. Thus, management of sampling error is a concept that must be addressed throughout the effort to optimize selection of both sampling methods and analytical methods.

- C The identification and management of error that may be introduced during sample preparation. This includes consideration of the impact of certain sample preparation steps (e.g., drying, grinding, sieving, and homogenizing) on the representativeness of the resulting prepared samples and the ability to compare and interpret results from samples receiving different sample preparation steps before the determinative step (i.e., sample analysis).
- C The verification of selected data points by a conventional analytical technique. This includes making sure that the referee verification samples are collected with the same sample support considerations and similar sample preparation steps.
- C The identification and management of error that may be introduced during analytical procedures. This includes the use of appropriate analytical QC procedures to document analytical performance.

Such considerations are critical to establishing confidence that correct decisions will be made based on the XRF data. Recognizing that all decisions are based on data and all data have some degree of uncertainty, the goal should be to identify factors causing the uncertainties and have a plan for managing them to minimize the impact of total measurement error (combination of sampling and analytical errors) on the decision-maker's ability to arrive at the correct conclusion. Total measurement error can be effected by sample representation, sample collection, sample handling, sample preparation, and analysis procedures. As noted by NITON, analytical errors are usually well-characterized and controlled [12]. However, every sample handling and preparation step introduces some error, and both those and potential analytical errors should be understood and managed to the degree needed to meet the desired decision confidence.

Field Analytical Technology: SW-846 Method 6200 Field Portable XRF [1, 12, 13]

The NITON Model 700 Series XRF analyzer is a hand-held, battery operated instrument that uses X-ray fluorescence (XRF) spectrum analysis to identify and quantify metals. The XRF analysis technology is well-established and has been applied with increasing frequency to environmental characterization and remediation efforts.

In XRF spectrum analysis, a radioactive source, such as Cd-109 (used in the NITON Model 700 Series XRF analyzer), emits high energy photons (X-ray or gamma-ray) that strike the sample, causing the ejection of electrons from the element atoms. Other electrons drop into the vacancy and release energy in the form of another X-ray, which is received by X-ray detectors, electronics and on-board microprocessors. The intensity (number of electrons) and spectral energy (frequency) of the electrons released are used by the detector to identify and quantify the metal present in the sample. A Cd-109 source is useful for a list of about 17 target analytes. Other radioactive sources must be used for other target analytes.

All NITON XRF analyzers are equipped with at least a Cd-109 source, and they also may be equipped with an Am-241 or Fe-55 source to increase the number of possible analytes. Standard features also include battery packs, battery charger, and reporting software. The XRF analyzer itself consists of a source that provides the X-rays, a probe window for sample presentation to the instrument, a detector that converts the X-ray-generated photons emitted from the sample into measurable electronic signals, a data processing unit that processes the signals into an X-ray energy spectrum from which elemental concentrations are calculated, and a data display and storage system. When used according to its instructions, the NITON Model 700 Series XRF analyzer poses minimal radiation exposure to the operator, even with the shutter open. When operated in the in-situ or bagged-sample mode, the probe window is placed in direct contact with the soil surface or plastic bag containing the soil. When operated in the prepared-sample and laboratory modes, the sample is prepared and placed in a sample cup and covered with a mylar film window before placement of the probe window on the sample. Test times can be as low as 20 seconds and as high as 120 seconds, and NITON notes that longer test times can lower detection limits. The results are read from the screen facing the user on the instrument. The data can be downloaded from the instrument.

NITON publishes a user's guide for its XRF analyzers, which is available on-line at: <http://www.niton.com/support.html>. The user's guide provides a large amount of useful information regarding the instruments. In addition, EPA's Clean-Up Information (CLU-IN) website has comprehensive information regarding the use of field XRF analyzers, with links to many information resources including other vendors, at: http://fate.clu-in.org/xrf_main.asp.

Controlling Sampling-related Error during XRF Analysis: NITON has published on-line (<http://www.niton.com>) many useful recommendations for minimizing error and improving decision quality based on analysis by its field portable XRF analyzer. These sampling- and preparation-related considerations are important, since their impact on total error is usually much larger than the impact of analytical error. In other words, even if the analytical QC shows good accuracy and precision, the data still may lead to an incorrect decision if the sampling errors were not actively managed.

In typical lead-in-soil measurements, the impact of particle size related errors from sampling and sample handling often exceed the impact of other sources of error (e.g., analytical) on the results [12]. Particle effects can generate substantial sampling variation, depending on the form of the contaminant. Also, the contaminant is likely to be distributed unevenly throughout the area of concern. Obviously, project planners must pay close attention to sampling design during the sampling of soil expected to exhibit

CHARACTERIZATION TECHNOLOGIES (continued)

spatial variability in analyte distribution. One advantage of the field portable XRF technology over more conventional technologies is that it can address spatial variability through an economical increase in sampling density.

Moisture and particle size may affect XRF analysis results to greater or lesser degrees, depending on a number of variables. Sample preparation (drying, sieving, grinding, homogenizing) will minimize the potential for effects from moisture, large particle size, and variations in particle size. Moisture alters the soil matrix from what the instrument is calibrated to characterize and also may have a diluting influence. NITON recommends that water content should be no more than around 2 or 3% of the sample mass [12]. Air drying of a surface area or the sample can remove the diluting influence of soil moisture, and facilitate any further sample preparation such as grinding and sieving. According to NITON [12], large contaminant particles cause negative bias in lead-in-soil analysis. Additional particle-related bias occurs when the particle size is larger than the attenuation length for the fluorescence X-ray. Grinding and screening steps facilitate thorough homogenization of the sample, reducing the effects of particle error and XRF particle-related bias. Sieving with a grinding step assures complete particle size reduction. Homogenization after sample collection promotes accurate and unbiased subsampling.

Subsampling is typically conducted to reduce sample size or to split a sample for replicate analysis. (A sample is often subsampled before sample digestion and analyses by conventional methods because using a larger quantity of sample material requires larger amounts of acid and increases cost.) Subsampling can contribute bias to any analytical results, including XRF results. If subsampling or sample splitting occurs, every particle in the sample should have an equal probability of being included in the portion submitted for analysis. To approach this probability, the sample should be ground to a smaller particle size. NITON recommends grinding and subsampling in stages [12]. The sample also should be properly homogenized (mixed), without causing stratification. Agitating or shaking a sample with particles of different size can cause stratification.

As done in the LSBP project, referee analysis using a more conventional analytical technology is one means of checking the comparability of the XRF field analyses for decision-making purposes. However, error introduction from differences in sample support and sample preparation measures must be controlled to avoid misinterpretation of a low correlation as the fault of the field XRF analyses. NITON recommends that in-situ test results never be compared to laboratory results as part of a performance evaluation to establish comparability of the XRF data; that such an evaluation should always be done on prepared samples [1]. If sample results from unprepared samples are compared to laboratory analyses on prepared samples, NITON recommends comparing the same samples. For best results, a large sample should be collected in a zipper-locking storage bag, the bag shaken or kneaded to thoroughly mix the sample before the bagged-sample is tested several times at a number of points on the bag and the readings averaged. The average reading can be compared with the laboratory results. If in-situ results must be used to establish data comparability, then the operator should take several readings bracketing a location, according to the NITON User Guide for its XRF analyzer [1]. The sample for laboratory testing should be taken from that location, concentrating on the soil surface layer (the upper 1-2 mm) from which the XRF device takes its readings.

EPA Approval for Use of XRF at LSBP [7, 8]

Based on initial data collected at LSBP, DuPont/SPG, Inc. submitted a proposal to EPA requesting the use of XRF lead analysis of soil samples. The proposal documented the QA/QC procedures implemented at the site and results from the Environmental Lead Proficiency Analytical Testing (ELPAT) Program administered by the American Industrial Hygiene Association (AIHA). The proposal also included a

CHARACTERIZATION TECHNOLOGIES (continued)

statistical evaluation that focused on the reliability of the field portable XRF instrument to replicate laboratory results from a more conventional analytical approach.

After a review of the proposal, EPA requested that further evaluation be conducted by comparing analytical results of sample pairs to site action levels. In this instance, a sample pair is identified as two aliquots from one sample with one aliquot analyzed for lead by conventional laboratory procedures and the other aliquot analyzed for lead by prepared-sample XRF procedures. Evaluation of sample pairs monitors the occurrence of sample pair disparities.

LSBP re-submitted their XRF proposal, after documenting sample pair disparity frequency on some samples. Of the initial 206 sample pairs evaluated, there was a sample pair disparity frequency of 1.5%, or a 98.5% agreement between the lead concentrations in the sample pairs when compared against the 500 ppm action level. Comparison against the 1,000 ppm action level resulted in a sample pair disparity frequency of 0.0%, or a 100% agreement between the lead concentrations in the sample pairs.

Based on information provided in the proposal and the results of sample pair evaluations, the EPA project manager approved the use of XRF procedures for lead analysis, contingent on adherence to the following steps:

- C Evaluation of lead sample pairs on a routine basis and documentation of sample pair disparities and associated corrective actions, and a reporting of these results to EPA every six months.
- C Participation in the ELPAT program to show that the XRF instruments, the operators, and the procedures used are proficient in measuring lead concentrations in soil.
- C Adherence to and implementation of the QA/QC procedures documented in the site QAPP.
- C Verification of 10% of prepared XRF lead analysis by laboratory lead analysis using a conventional technology to establish on-going comparability of the XRF data.

Procedures of XRF Analyses at LSBP [1, 7]

In accordance with the Lake Success Business Park project plan, two NITON Model 700 Series XRF instruments were utilized at the site for the detection of lead in soils. The average detection limit (not site-specific) for lead analysis achieved by these instruments is approximately 50 ppm [13]. The instruments were used during in-place or in-situ soil analysis and on bagged and homogenized (mixed) soil samples and on prepared samples in the on-site XRF laboratory. The XRF procedures were used to delineate areas of environmental concern, direct excavation activities, and confirm adequate soil excavation, as described above on pages 7 through 9 in the "Site Characterization and Remediation Process" section. In general, in-situ XRF and bagged-sample XRF procedures were utilized to obtain real-time and rapid turn-around lead concentrations in the soil. XRF analysis was performed on prepared samples at the on-site lab to confirm the appropriateness of decisions which were based on the in-situ and bagged-sample analyses and to further direct remedial activities.

The XRF procedures used at the LSBP site and the recommended sample preparation methodologies associated with them are described below. In addition, for further guidance, see Method 6200, "Field Portable X-ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment," found in EPA's SW-846 (Test Methods for Evaluating Solid Waste, Physical/Chemical Methods) [14]. This analytical protocol provides guidance for implementing XRF in the RCRA testing environment. It contains guidelines regarding the use of field portable XRF technologies and recommendations regarding QA/QC procedures.

CHARACTERIZATION TECHNOLOGIES (continued)

In-situ XRF Analysis: This procedure analyzes the soil in-situ (in place on the ground). The procedure is most practical for surface samples but also can be used on the bottom and sidewalls of test pits and excavations. The use of field portable in-situ XRF analysis allows for real-time analyses of heavy metal levels in soils and can be used to delineate contaminated areas and guide remediation activities, or gather data that will be used to design a sampling and analysis plan for more in-depth characterization. Accordingly, in-situ measurements were used at the LSBP site to delineate sampling locations and to guide on-going excavation activities. The in-situ XRF analysis was performed on surface and sidewall areas of each AEC. Soil surface was cleared of vegetation and smoothed to a flat surface using a shovel or trowel before taking measurements.

The in-situ measurements require little or no sample preparation. However, NITON recommends a minimal preparation protocol [12] to improve the representativeness of the reading. This includes removing any large or nonrepresentative debris from the soil surface, loosening the soil to a depth of 1.5 to 2.5 cm over an area of at least a 10-cm diameter, and stirring the loosened soil to achieve some homogenization. The operator may screen or comb the loose soil with a 2-mm mesh to remove stones, roots, broken glass, or other such objects. The loosened soil may be dried in the sun for a few hours before the measurement. Just before analysis, the operator should level the loosened soil and pack it down gently. During analysis, the NITON Model 700 XRF analyzing window is placed directly on the surface of the soil. Short measurement times (20 to 30 seconds) are generally used with this procedure for initial media characterization and hot spot detection and boundary estimation.

NITON considers in-situ XRF analysis results to be only approximate because the sample matrix is not typically homogeneous, and that can introduce considerable uncertainty into the results. Although in-situ results may correlate well with other methods if the matrix is very homogeneous, they probably will correlate poorly when the matrix is heterogeneous [1]. Items such as small pebbles in the soil surface can shield the X-rays from reaching the XRF detector during in-situ analysis. These pebbles would be removed during more intensive preparation of a sample.

Quality assurance procedures for in-situ analysis can include daily calibration checks using known standards, analysis of blanks to check for instrument contamination, and routine checks of instrument performance. Side-by-side duplicate readings can help detect excessive fluctuations caused by shielding by pebbles. Duplicate readings also may provide an indication of the degree and scale of variation in contaminant concentrations across the matrix—this provides a measure of sampling variability.

Bagged-sample XRF Analysis: Bagged-sample XRF analysis encompasses a variety of sample preparation strategies that progress in the amount of effort put into sample preparation. It can be used to analyze soil in the field after the soil sample has been collected and homogenized by kneading inside the bag without additional manipulation, as was done at LSBP. The level of effort should be commensurate with site-specific matrix characteristics and the intended use of that data. Bagged-sample XRF analysis was used at LSBP to measure lead concentrations in subsurface samples during both the delineation and excavation sampling process at the AECs (see pages 7 through 9). Soil samples were collected at the appropriate depth using a clean core boring device, usually a stainless-steel hand auger or stainless steel spoon. The soil samples were then placed in a clean self-sealing plastic bag and homogenized by shaking the bag [7]. The homogenized samples were analyzed by placing the XRF analyzing window, which is roughly 1 cm x 2 cm [1], directly on the bag.

Alternatively, the NITON User's Manual [1] notes that more thorough homogenization of the sample may be achieved by mixing it in a clean pail prior to bagging. The sample should be mixed thoroughly by stirring and rotating the pail at a 45 degree angle, with no shaking to avoid sample stratification. If the

CHARACTERIZATION TECHNOLOGIES (continued)

sample in the pail is too large, it should be reduced by taking a vertical slice that is representative of the whole sample (e.g., a slice about one inch wide if a spade or trowel was used for collection).

NITON also observes that the sample may be dried after mixing by spreading it out on paper and exposing it to air, or by using a field oven. Note however, that oven drying would be inappropriate when volatile compounds may be of concern, for example, if lead is suspected as being present in the form of tetraethyl lead. Air drying will preserve more of such substances. A dried sample can be screened with a 2-mm mesh to remove large objects. The ultimate sample preparation before bagged-sample XRF analysis would involve grinding and sieving the soil to reduce particle size to less than 0.250 (or to less than 0.125) mm and then further homogenizing the soil. Before analysis with the XRF instrument, the bag of soil should be shaped to form a continuous uniform layer of at least 1 cm (0.4 inch) thickness and placed on a firm surface (not held in the operator's hand).

On-site Laboratory XRF Analysis: The LSBP prepared-sample XRF analysis was conducted in an on-site laboratory. Prepared-sample XRF analysis was used at the on-site XRF laboratory for all confirmation-of-compliance and post-excavation samples. Samples were dried, sieved through a 10 mesh (2-mm) sieve to remove organics, gravel, rock and other materials, and ground with an electric mixer. The ground samples were placed in plastic XRF sample cups and analyzed for approximately 60 seconds.

This procedure involves more sample preparation steps than in-situ and bagged-sample XRF analysis and therefore more effectively limits the effects of moisture, particle size, and particle distribution on XRF lead results. Longer measurement times than those used during in-situ or bagged-sample XRF analyses are typically used with this procedure to meet precision and accuracy requirements. According to NITON, prepared-sample laboratory XRF analysis is the most accurate method for determining the concentration of an element in a bulk medium using its XRF instruments [1].

The NITON Model 700 Series XRF analytical kit includes the equipment needed for preparing samples. If a sample needs to be divided during preparation, NITON recommends the cone and quartering method of splitting the sample into homogenous quarters. The entire sample should be dried to a constant weight, sieved to remove debris (2-mm mesh), and ground or milled to a fine powder using an electrically powered grinding mill or a mortar and pestle. A sample can be dried by oven or air. (As noted earlier, oven drying may be inappropriate if volatile compounds of concern are of interest.) After grinding, NITON recommends sieving the sample again through a 250- μ m and 125- μ m mesh. Unpassable material can be ground again until it will pass through the mesh (be aware that indiscriminate discarding of certain fractions of the matrix may render the resulting sample nonrepresentative). The resulting sample should be mixed. Regarding the XRF sample cups, NITON recommends using the same kind of container and window (e.g., mylar film on top of the cup) for each sample [1].

Quality assurance procedures for prepared XRF analysis include calibration verification procedures, precision measurements, and generation of site-specific method detection and quantitation limits. (SW-846 Method 6200 provides guidance on XRF prepared-sample quality control measures [14].)

Off-site Laboratory Analytical Protocols on Prepared Samples by SW-846 Methods 3050/6010

During the LSBP project, referee sample analyses for lead were performed on prepared samples at an off-site laboratory using standard method protocols. SW-846 Method 3050 [2] and Method 6010 [3] were used for referee testing in the LSBP effort. Method 6010 utilizes inductively coupled plasma-atomic emission spectrometry (ICP-AES) to determine trace elements, including metals, in solution. Method 6010 requires that the soil sample be introduced into the instrument as a solution, therefore, the samples first were solubilized or digested by Method 3050. This procedure is not a total digestion procedure; its

CHARACTERIZATION TECHNOLOGIES (continued)

digestion process only extracts the most acid-soluble portion of the sample. Acid-based extractions such as performed by Method 3050 do not recover analytes that are locked within an insoluble silicate mineral structure. In contrast, with optimal sample presentation, XRF analysis will read total analyte content. Therefore, according to NITON, the most appropriate comparison method sequence for XRF use would involve the complete digestion of siliceous materials [16].

During the LSBP project, project planners ensured that the sample support was similar for both the prepared-sample XRF analyses and the prepared-sample Methods 3050/6010 analyses. Aliquots were taken from the same moderately homogenized sample at the time of collection, and similar sample preparation steps (drying, sieving, grinding, and homogenizing) were performed on the aliquots at each laboratory before analysis. Utilizing different sampling locations and sample preparation procedures could have resulted in very different results, which would have prevented an accurate assessment of analytical equivalency and technology performance. The most accurate assessment of the equivalency of two different analytical methods involves the analysis of identical sample material, as noted by NITON [16]. Ideally, the material should be split as late as possible in the process (e.g., after all sample preparation steps) to assure that the methods analyze identical material. In lieu of splitting a soil sample immediately after collection from the field, the prepared-sample XRF cup containing analyzed sample could be later sent to the off-site laboratory, thereby assuring that the sample being presented to the two different methods is truly identical. This approach is possible because XRF technology does not destroy or alter the sample during the analysis. Any difference between results can then be attributed to the sample digestion and analysis stage, and not to variations in sample collection or handling.

PERFORMANCE EVALUATION

At the LSBP, thousands of samples were analyzed to characterize the extent of metal contamination at up to 51 areas of environmental concern (AECs) and to guide decisions regarding remediation. Soil lead levels were characterized using the NITON Model 700 Series XRF analyzer by in-situ and bagged-sample analyses in the field at an AEC, and by prepared-sample XRF analyses at an on-site laboratory. Several performance checks were used to evaluate performance of the XRF technology:

- Analyses in support of the LSBP remedial effort followed certain quality assurance/quality control (QA/QC) procedures, as specified in the project-specific Quality Assurance Project Plan (QAPP).
- The on-site XRF laboratory participated in the Environmental Lead Proficiency Analytical Testing (ELPAT) Program.
- The comparability of up to 10% of the XRF prepared-sample analyses was established based on a comparison of sample pair (aliquots from the same sample) analyses using a more conventional technology as the referee method, SW-846 Methods 3050/6010 (ICP-AES), at an off-site, fixed laboratory.

Each of the above performance checks were part of the EPA conditions for use of XRF at the site. The following technology performance evaluation reviews the results of the performance checks and answers the following questions:

- C To what extent were the XRF data comparable to ICP-AES data for the purposes of this project?
- C Were the sample preparation and XRF techniques sufficiently sensitive?
- C Were they sufficiently accurate?
- C Were they sufficiently precise?
- C Can the XRF instrument be a useful tool in site characterization and clean-up operations?

Technology Performance Based on Referee/Verification Analysis of Sample Pairs [8]

One of EPA's conditions for use of field portable XRF analyses during LSBP remediation included the verification of 10% of prepared-sample XRF analysis results by analysis using a conventional technology to establish data comparability for the purpose of project decision-making. As of Fall 1999, results from up to 793 samples pairs using both the NITON Model 700 Series XRF analyzer and Methods 3050/6010 were compared with the site media protection levels (action levels) for lead. As illustrated by the first row of Table 1, results of an evaluation of the 793 sample pairs show 99.0% agreement with respect to the site's 1,000 ppm action level and 97.4% agreement with respect to the site's 500 ppm action level. Stated another way, 97.4% of samples that had a lead concentration greater (or less) than 500 ppm by ICP-AES also had a concentration reported as greater (or less) than 500 ppm by XRF. As shown by the other rows in Table 1, the percent agreement decreased slightly during a comparison of in-situ and bagged-sample XRF analyses against laboratory analyses involving more sample preparation. This is to be expected since the more soil samples are prepared (e.g., drying and homogenization), the better the agreement will be between sample pairs. The experience at LSBP is consistent with NITON's recommendation that data comparability studies always be done using prepared samples [1].

Table 1.
Percent Agreement between XRF and Laboratory Results for Lead [8]

Sample Pair	Number of Sample Pairs	Percent Agreement of Sample Pairs at 500 ppm	Percent Agreement of Sample Pairs at 1,000 ppm
Prepared-sample on-site laboratory XRF vs. off-site laboratory Methods 3050/6010	793	97.4	99.0
Bagged-sample XRF vs. off-site laboratory Methods 3050/6010	652	95.7	99.0
Bagged-sample XRF vs. prepared-sample on-site laboratory XRF	3,153	96.4	99.2
In-situ XRF vs. off-site laboratory Methods 3050/6010	521	93.1	98.5
In-situ XRF vs. prepared-sample on-site laboratory XRF	1,864	91.4	97.5

Technology Performance Based on Quality Assurance/Quality Control Procedures

Quality assurance (QA) is a system of management activities designed to ensure that a product meets required levels of quality. Quality control (QC) is a system of technical activities that measures the performance of a process against defined standards to ensure that project requirements are met. QA/QC procedures are often written together because they comprise interrelated processes that ensure that the data collected will meet the decision-making needs of the project.

All quantitative analyses, whether conducted in a fixed laboratory or in the field with portable instrumentation, require quality control (QC) measurements that document the quality of the analytical results. Quality control results are evaluated against acceptance criteria determined both by the method (to ensure that the method is implemented properly) and by the project's data quality needs (to ensure that the analytical results are adequate for their intended purpose). Dynamic field activities, such as those involving use of a field portable XRF analyzer, must have well-planned QA/QC procedures to be successful because real-time fieldwork depends on the rapid turnaround of data. A site-specific demonstration of method applicability may be performed prior to field mobilization to verify that the instrumentation, operators, QA/QC procedures and corrective actions will perform as expected during actual field work [17].

Before data collection begins, the project team must establish the quality of data needed to make decisions and the necessary QC checks to ensure the required level of certainty. It is important to draw upon the expertise of an analytical chemist so that selection and use of the technology will be appropriate to the project goals. The chemist will help design a QC/corrective action protocol that is sufficient to ensure that the resulting data are of known quality commensurate with their intended use. If needed to meet project goals, the same types of QC activities used in a conventional fixed laboratory can be applied to field analyses.

PERFORMANCE EVALUATION (continued)

The generation of analytical data can be most cost-effective if the QC acceptance criteria specifically accommodate the sensitivity, precision, and bias needed to meet decision-making goals. Depending on the rigor of data needed for a particular project, acceptance criteria might be chosen that are "tighter" or "looser" than those used for the LSBP project. This is in accordance with the guidance provided in the SW-846 methods manual, Third Edition (see section 2.0 of Chapter Two, page TWO-1) [17].

The LSBP sampling and analysis plan implemented project-specific quality assurance/quality control (QA/QC) procedures in accordance with the project-specific QAPP. Procedures in the plan included:

- C daily calibration and routine calibration checks,
- C duplicates, and
- C blank samples.

The LSBP field QC analyses are discussed below for each QC activity.

Calibration: Calibration procedures are used to check the measurement of an instrument's response against a known quantity. Analytical instruments, particularly field instruments that are subject to frequent disturbance (e.g., relocations) require both an initial (e.g., daily) calibration and routine periodic calibration checks. Calibration of the NITON Model 700 Series XRF instrument for lead and other metals comes pre-programmed from the manufacturer. Prior to use each day, the instrument operator conducted a baseline check of the factory calibration against a tungsten shield located within the instrument. Analyte-specific checks of the factory calibration were performed by analyzing three National Institute of Standards and Technology (NIST) standards at least once a day. The project-specific QAPP specified that the XRF result must fall within $\pm 10\%$ of the NIST certified lead value for each standard. The ranges for the NIST standards used for daily calibration and the acceptable XRF results are listed in Table 2.

Table 2.
Ranges of NIST Standards Used for Daily XRF Calibration and Acceptance Criteria [8]

NIST Standard	Certified Lead Value (mg/kg)	90% Lower Limit (mg/kg)	110% Upper Limit (mg/kg)
2704	161	145	177
2711	1,162	1,046	1,278
2710	5,532	4,979	6,085

During the course of sampling and analysis, routine checks of the instrument calibration were performed. The XRF project-specific QAPP called for the analysis of the NIST 2711 standard at a frequency of 5% (once after every 20 samples analyzed) or at the end of an analytical sequence if less than 20 samples were analyzed. The NIST standard result had to be within the upper and lower acceptance limits shown above in Table 2.

Duplicate Analyses: Duplicate analyses are used to evaluate the precision, or reproducibility, of a measurement system. Duplicate analyses involve the measurement of the same analyte in two samples and a mathematical assessment to determine how close the results are to each other. The degree of agreement is expressed as either relative percent difference (RPD) or percent difference (%D). Usually two repeat measurements are compared (duplicates), although more than two repeat analyses are sometimes compared (referred to as replicates). The results of duplicate analyses, especially on

PERFORMANCE EVALUATION (continued)

heterogenous materials such as soils, can sometimes be difficult to evaluate because many variables stemming from both the sample collection and the sample analysis procedures can be involved. The project planning team should carefully consider which analytical or sampling variables they want to evaluate for precision before deciding on the number and exact nature of duplicate analyses to be performed [18]. Meticulous records of sampling and subsampling procedures have to be kept to allow proper interpretation and use of the results [19].

As called for in the LSBP project-specific QAPP, duplicate XRF analysis was performed on prepared soil samples at a frequency of 5% or one for every 20 samples analyzed. XRF duplicate sample results were evaluated in the same manner that laboratory analytical duplicates are evaluated.

Table 3 illustrates data from 71 duplicate sample pairs analyzed by prepared-sample XRF between the November of 1997 and October of 1999. The RPDs calculated from these data range from 0% to 103%. In the absence of project-specific performance criteria for precision, 25% RPD is a generally accepted acceptance criterion for inorganic analyses. Twenty three of the XRF sample pairs, 32% of the total number of sample pairs analyzed by XRF, resulted in an RPD greater than 25%.

Table 3.
Prepared-sample XRF Analysis Duplicate Results, November 1997 - October 1999
[21, 22, 24]

XRF Primary Lead Concentration (mg/kg)	XRF Duplicate Lead Concentration (mg/kg)	Relative Percent Difference (%)
49	49	0.00
97	97.3	0.31
218	216	0.92
99	100	1.01
90	91	1.10
91	90	1.10
86	87	1.16
65	66	1.53
61	62	1.63
114	116	1.74
48	47	2.11
277	283	2.14
91	89	2.2
86	84	2.35
106	103	2.87
65	67	3.03
99	96	3.08
153	158	3.22
90	93	3.3
59	61	3.33
88	91	3.35
91	88	3.35
97	101	4.04
156	148	5.26
568	601	5.65
154	144	6.71
84	90	6.90
124	133	7.00

PERFORMANCE EVALUATION (continued)

Table 3. (Continued)

XRF Primary Lead Concentration (mg/kg)	XRF Duplicate Lead Concentration (mg/kg)	Relative Percent Difference (%)
102	95	7.11
68.6	63.5	7.72
320	296	7.79
90	97.5	8.00
129	119	8.06
138	127	8.30
86	95	9.9
82.5	91.5	10.3
108	97	10.7
157	140	11.4
111	125	11.9
92	106	14.1
98	114	15.1
112	135	18.6
97	117	18.7
387	478	21.0
105	84.9	21.2
45	36	22.2
174	137	23.8
74	94	23.8
62	48	25.5
93.4	71.7	26.3
132	173	26.9
22.0	29.0	27.5
124	92.4	29.2
255	344	29.7
84	61	31.7
194	140	32.3
94	131	32.9
131	94	32.9
89	127	35.2
88	128	37.0
110	75	37.8
50	76	41.3
159	255	46.4
216	132	48.3
135	79	52.3
182	104	54.5
105	59	56.1
419	801	62.6
78	152	64.3
50	98.7	65.5
506	243	70.2
58	182	103.3

For samples with non-detect concentrations, the detection limit was used to calculate RPD.

PERFORMANCE EVALUATION (continued)

These XRF precision data compare very favorably with the ICP precision data generated on this project. Over roughly the same time period (January 1997 to September 1999) 61 unspiked sample pairs were analyzed by ICP. The RPDs calculated from these data, shown in Table 4, range from 0% -166%. Twenty of the ICP sample pairs, 33 % of the total number of sample pairs analyzed by ICP, resulted in an RPD greater than 25%.

**Table 4.
ICP-AES Analysis Duplicate Results, January 1997 - September 1999 [21, 21, 24]**

Sample Duplicate			Matrix Spike				Matrix Spike Duplicate				MSD RPDs (%)
Sample Result mg/kg	Replicate Result mg/kg	RPD %	Spike mg/kg	Theoretical Spike mg/kg	Sample Result mg/kg	Recovery %	Spike mg/kg	Theoretical Spike mg/kg	Sample Result mg/kg	Recovery %	
4.0	3.8	5	49	53	50.3	95	49	53	49.6	94	1
4.7	4.4	7	50	54.7	51.1	93	50	54.7	51.1	93	0
5.1	4.4	15	49	54.1	49.7	92	49	54.1	49.4	91	1
5.3	4.9	8	50	55.3	54.9	99	50	55.3	48.5	88	12
5.4	4.4	20	50	55.4	52.3	94	50	55.4	52.4	95	0
6.0	4.3	33	50	56	51.7	92	50	56	51.7	92	0
8.1	7.1	13	50	58.1	53.4	92	50	58.1	54.1	93	1
8.1	8.4	4	50	58.1	53.8	93	50	58.1	53.9	93	0
8.2	6.5	23	49	57.2	55.1	96	49	57.2	53	93	4
9.2	8.6	7	50	59.2	55.6	94	50	59.2	54.6	92	2
9.5	10	5	50	59.5	52.6	88	50	59.5	53.4	90	2
10.3	8.2	23	50	60.3	56.3	93	50	60.3	55.3	92	2
10.9	8.3	27	50	60.9	56.1	92	50	60.9	57.1	94	2
11.2	9.2	20	50	61.2	53.6	88	50	61.2	54.6	89	2
12.8	11.3	12	50	62.8	57.4	91	50	62.8	57.6	92	0
16.0	14.9	7	50	66	63.3	96	50	66	60.3	91	5
16.5	27.8	51	50	66.5	74.2	112	50	66.5	70.3	106	5
17.1	13.4	24	50	67.1	58.2	87	50	67.1	58.9	88	1
19	15.1	23	49.5	68.5	60.1	88	49.5	68.5	59.3	87	1
20	14.8	30	50	70	63.1	90	50	70	61.8	88	2
20	16.5	19	50	70	68.4	98	50	70	62.3	89	9
22.4	15.5	36	50	72.4	82.2	114	50	72.4	64.8	90	24
22.6	27.3	19	50	72.6	74	102	50	72.6	72	99	3
30.6	72.6	81	50	80.6	73.6	91	50	80.6	25.9	32	96
31.1	25.1	21	49	80.1	79.5	99	50	81.1	68.3	84	15
31.7	23.9	28	50	81.7	79.7	98	50	81.7	80.3	98	1
35.0	27.4	24	50	85	73.1	86	50	85	74.7	88	2
40	35.7	11	50	90	78.8	88	49	89	81.3	91	3
42.5	14.9	96	50	92.5	74.8	81	50	92.5	67.2	73	11
46	56.9	21	49.5	95.5	72.7	76	50	96	76.4	80	5
46.0	42.4	8	50	96	93.8	98	50	96	82.4	86	13
53.4	26	69	49	102.4	71.2	70	50	103.4	69.4	67	3
54.5	5.1	166	50	104.5	53.3	51	50	104.5	52.5	50	2
54.7	43.6	23	50	104.7	120	115	50	104.7	94.7	90	24
55.2	49.5	11	50	105.2	96.2	91	50	105.2	98.2	93	2
66.9	56	18	50	116.9	110	94	50	116.9	110	94	0
68	70.7	4	50	118	110	93	50	118	110	93	0
69	48.6	35	50	119	98.5	83	49	118	97.5	83	1

PERFORMANCE EVALUATION (continued)

Table 4. (Continued)

Sample Duplicate			Matrix Spike				Matrix Spike Duplicate				MSD RPDs (%)
Sample Result mg/kg	Replicate Result mg/kg	RPD %	Spike mg/kg	Theoretic al Spike mg/kg	Sample Result mg/kg	Recovery %	Spike mg/kg	Theoretica l Spike mg/kg	Sample Result mg/kg	Recovery %	
75.7	38.2	66	50	125.7	85	68	50	125.7	85.1	68	0
76	63.4	18	50	126	110	87	50	126	100	79	10
81.1	78	4	50	131.1	120	92	50	131.1	140	107	15
86.1	78.8	9	50	136.1	110	81	49	135.1	120	89	9
90.3	90.7	0	50	140.3	140	100	50	140.3	130	93	7
106	100	6	50	156	150	96	50	156	150	96	0
112	81.2	32	49	161	150	93	49	161	130	81	14
142	120	17	50	192	160	83	50	192	150	78	6
154	87.5	55	50	204	140	69	50	204	140	69	0
173	270	44	48.5	221.5	240	108	48.5	221.5	230	104	4
179	160	11	49	228	220	96	49	228	210	92	5
227	200	13	49.5	276.5	260	94	50	277	260	94	0
227	220	3	48.5	275.5	260	94	50	277	230	83	12
246	220	11	50	296	270	91	50	296	290	98	7
253	230	10	50	303	270	89	49	302	260	86	4
253	220	14	50	303	260	86	49	302	270	89	4
425	310	31	50	475	340	72	50	475	360	76	6
553	140	119	50	603	250	41	50	603	240	40	4
555	430	25	50	605	1800	298	50	605	490	81	114
613	410	40	50	663	460	69	50	663	400	60	14
5000	2800	56	50	5050	3900	77	50	5050	4400	87	12
51500	28000	59	100	51600	32000	62	100	51600	32000	62	0
95200	61000	44	49.5	95249.5	5900	6	48.5	95248.5	6400	7	8

Additional discussion of precision determinations as a data quality indicator appear on page 35 of this report.

The degree of precision in the performance of the XRF instrument itself can be estimated from repeated readings on the exact same sample. Additionally, the XRF instrument displays results with an uncertainty estimate expressed as a 95% (or 2-sigma) confidence interval around the point estimate for the analytical result. Analytical data with accompanying uncertainty estimates are much more meaningful and interpretable than data that provides only point estimates with no indication of the uncertainty (and sources of that uncertainty) in that single value. Overlapping confidence intervals for two analytical results indicates there is some probability that the two values may actually represent the same concentration, with differing point estimates simply reflecting the random variability (“noise”) in the measurement process.

Blank Samples: Blank samples are QC samples used to detect contamination that may be introduced during sample collection, preparation or analysis, and to establish the zero baseline, or background, condition of an instrument. The possibility of extraneous contamination, through improper sample handling for example, must be evaluated to ensure that the concentrations reported are those actually occurring in the matrix of concern. Blank sample analysis was important during use of the field portable XRF analyzer because lead-containing soil residue can contaminate the analyzing window. This contamination may cause the sample lead measurements to be biased high. Routine instrument operation

should include precautions against contamination, such as periodic instrument maintenance and regular checks of the window's condition. As called for by the project-specific QAPP, documentation that the analyzing window was clean was established by analyzing a blank sample at a frequency of 5% (once after every 20 samples analyzed) or at the end of an analytical sequence if less than 20 samples were analyzed. The blank sample was a silica-based sample that contained no lead.

Blank sample data provide valuable information on the source of any contamination, which is needed in order to identify the appropriate corrective action. During the use of field portable technologies such as XRF, the source of contamination can be rapidly identified (e.g., a dirty analyzing window) and corrective action quickly taken (e.g., clean the window and re-analyze as necessary).

Detection Limits: A detection limit is calculated to estimate the lowest concentration level measurable by a method or instrument. The November 1997 initial evaluation of LSBP XRF lead results [21] defined the MDL as "the lowest concentration of an analyte in a sample that can be readily distinguished from zero concentration" and defined the MQL as "the lowest analyte concentration that can be reliably measured at high enough precision to allow comparisons of measurements." The 1997 report also stated that the sample method detection limits (MDLs) and sample method quantitation limits (MQLs) are calculated by multiplying the uncertainty factor by 1.5 and 5.0, respectively. Using these definitions, an average site-specific MDL of approximately 100 ppm concentration and an average site-specific MQL of approximately 340 ppm were calculated for the XRF lead analyses based on the first samples analyzed. These detection limits are below both of the action levels for lead (500 ppm for within the buffer zone boundaries and 1000 ppm for outside of the buffer zone boundaries).

Technology Performance Based on ELPAT Program

As directed by the EPA project manager as a condition for use of XRF analysis, the LSBP XRF laboratory participated in the ELPAT Program administered by the AIHA. This program is recognized by the EPA's National Lead Laboratory Accreditation Program (NLLAP) as an approved lead accrediting organization.

The ELPAT Program evaluates the proficiency of analytical procedures (XRF, ICP, AA, etc.) in determining lead concentrations in soil. Blind samples are sent out to program participants by AIHA on a quarterly basis, analyzed by the participant and the results returned to the AIHA. AIHA publishes upper and lower acceptable limits for lead results and evaluates the performance of the analytical lead results. In order for a lead analysis method to comply with the standards of the ELPAT program, analytical results of the blind samples must lie within the acceptable limit range established by the AIHA. The ELPAT program acceptable limits are determined without regard for the analytical method used for analysis. Table 5 presents results from ten quarterly rounds of the ELPAT program. Results from these rounds show that the LSBP XRF laboratory met the ELPAT requirements for proficiency in analyzing lead concentrations in soil. A regression analysis of XRF results and ELPAT reference lead concentrations showed very good correlation between the lead concentrations (coefficient of determination, $r^2 = 0.995$) [8].

PERFORMANCE EVALUATION (continued)

Table 5. ELPAT Proficiency Analyses
[7, 20, 21, 22]

ELPAT Sample No.	XRF Reading (ppm)	ELPAT Reference Concentration (ppm)	ELPAT Acceptable Range (ppm)	Relative Bias of XRF Results (%)
Round 17				
01	2,443	2,788	2,333 - 3,243	-12
02	2,446	2,785	2,330 - 3,240	-12
03	93.9	88.0	53.3 - 123	+7
04	537	523	417 - 629	+3
Round 18				
01	217	212	165 - 258	-2.4
02	72.6	70.8	45.7 - 95.8	-2.5
03	2,444	2,452	2,083 - 2,821	+0.3
04	1,050	1,050	873 - 1,228	0
Round 19				
01	696	678	569 - 789	+3
02	1,784	1,783	1,481 - 2,085	0
03	60.5	58.3	37.3 - 79.2	+4
04	1,583	1,614	1,369 - 1,859	-2
Round 21				
01	475	464	387 - 540	+2.4
02	841	831	676 - 986	+1
03	90.9	69.2	46.5 - 91.8	+31
04	310	347	262 - 432	-11
Round 22				
01	338	361	292 - 429	-6
02	85.2	73.2	49.7 - 96.7	+16
03	844	835	683 - 987	+1
04	721	683	560 - 806	+6
Round 23				
01	1,343	1,422	1,188 - 1,656	-6
02	48.6	57.4	36.9 - 77.9	-15
03	257	219	168 - 270	+17
04	443	460	388 - 532	-4
Round 24				
01	433	441	354 - 527	-2
02	711	686	545 - 827	+4
03	790	821	651 - 991	-4
04	31.9	34.2	13.1 - 55.3	-7
Round 25				
01	572	532	426 - 639	+8
02	70.0	69.4	33.8 - 105	+1
03	254	278	202 - 354	-9
04	1,616	1,714	1,382 - 2,045	-6
Round 26				
01	155	141	106 - 175	+10
02	552	533	446 - 620	+4
03	422	408	340 - 476	+3
04	75.4	67.6	48.5 - 86.6	+12
Round 27				
01	399	413	335 - 492	-3
02	76.8	87.9	55.8 - 120	-13
03	3,107	3,217	2,738 - 3,695	-3
04	750	712	589 - 835	+5

Relative bias is a common data quality indicator (DQI) which indicates both the magnitude and direction (positive or negative) of the bias. It is calculated as the measured result minus the expected result, divided by the expected result, and can be expressed as a percentage by multiplying by 100. In this form, relative bias is analogous to the relative percent difference (RPD) calculation used as an indicator of precision [23]. The expected results are based on the known properties of the QC sample, in this case, the reference concentration for each ELPAT proficiency sample. Table 5 provides the relative bias values for the ELPAT samples, which range from a positive bias extreme of +31% to a negative bias extreme of -13%. Lower lead concentrations typically have the greater bias values. In part, this is no doubt due to the higher quantitation limit of the XRF compared with conventional lead methods. For ELPAT proficiency samples with concentrations between 100 ppm (approximately the XRF method detection limit) and 2000 ppm (bracketing the project-specific action levels), relative bias calculations range between -11 and +17, with most values between near 0 (no bias).

Answers to the Technology Performance Questions

To what extent were the XRF data comparable to ICP-AES data for the purposes of this project?

The data quality attribute of comparability refers to the confidence that two data sets can contribute to common interpretation and analysis [23], or how well one data set can be compared to another with regard to a common reference point, such as a decision point or action level. SW-846 Methods 3050/6010 (acid digestion/ICP-AES) were used as the referee analytical methods with which to compare the results from SW-846 Method 6200 (XRF analysis for soil) in this study. ICP is the most commonly used determinative method for the analysis of lead in soil. The degree of comparability is strongly influenced by consistency in sample support and handling and preparation steps (to make sure that the analyses are looking at the same thing), and the technology basis of the chemical measurement (to make sure that the analyses are looking for the same thing). In this case, besides any inherent differences in analytical technology, both the process of sample splitting for dual analysis and the subsequent sample preparation procedures can strongly impact the comparability of the data generated by two different methods.

In the case of the LSBP samples, the split sample aliquots were taken after moderate homogenization of the field sample, and sent to the respective laboratories for analysis where they underwent additional sample preparation. Ideally, to ensure that the two analyses being compared are looking at the same thing (i.e., to control for pre-analytical variables that could introduce sample matrix-related variability), the sample should be split as late as possible in the measurement process [16], such as after the physical preparation steps (i.e., drying, grinding, sieving, and homogenizing), so that the compared sample aliquots are more similar. This allows isolation of the determinative method (i.e., XRF vs. ICP-AES) as the only variable being compared.

XRF and ICP-AES are similar in that both are atomic emission techniques that measure energy released from the target atoms in the sample after the atoms are energized. Therefore, both techniques measure lead as an element. However, the sample preparation method (beyond physical homogenization of the sample matrix) used for each technique is necessarily different. The XRF analysis requires only physical preparation of the sample prior to instrumental analysis, while ICP-AES analysis requires the additional step of sample digestion to create a liquid capable of being nebulized into the plasma. Therefore, a sample digestion method involving the use of acid, such as SW-846 Method 3050, is needed prior to ICP (such as Method 6010) analysis. Only the acid-soluble portion of the sample is submitted to the ICP-

AES instrument for analyte quantitation, whereas all original target analyte in the sample matrix is potentially quantified by XRF analysis.

Despite the above sample processing differences, the results from each technology were generally comparable, and comparability improved as sample preparation procedures became more similar, as was shown in Table 1 on page 19 of this report.

How well the field XRF sample analysis results compare to, and are reliable predictors of, corresponding ICP sample analysis results can be measured by means of simple linear regression. To demonstrate the applicability of the XRF technology at the LSBP, an initial study was conducted [21] using duplicate XRF and SW-846 Methods 3050/6010 ICP-AES analyses on 206 post-excavation samples collected mostly from one AEC. The study found a good linear relationship between concentrations in prepared XRF samples and corresponding laboratory ICP analyses in 40 samples with concentrations above the average XRF quantitation limit of 341 ppm. A poor regression fit was found for the remaining 166 sample pairs in which the XRF result was less than the MDL or the detected XRF result was less than the average MQL of 341 ppm. For these low concentration samples, XRF concentrations were positively biased (i.e., higher than the corresponding ICP results). Based on the results of the initial demonstration study [21] and additional information supplied to EPA on level of agreement between XRF and ICP methods, the XRF was approved for use in connection with the remediation of AECs at the site. Between the Fall of 1997 and the Fall of 1999, referee/verification analyses of 10% of the prepared-sample XRF measurements yielded a total of 793 sample pairs.

Simple linear regression models (least squares estimation) were used to estimate the relationship of prepared XRF analysis results to corresponding laboratory ICP analysis results near the action levels of 500 ppm and 1,000 ppm. Project managers can use regression analyses to obtain information on which points are least likely to give a false negative decision, and use that information to help set action levels. Typically, in linear regression, the independent variable (X) is used to predict a value of the dependent variable (Y); however, for the evaluation of the XRF technology, it was desirable to predict the value of the independent variable (ICP value) corresponding to a measured value of the dependent variable (XRF). This is known as the calibration problem, or inverse regression.

Two sets of paired XRF/ICP data were evaluated using statistical calibration to calculate point estimates and prediction intervals for ICP values for given XRF values of 500 and 1,000 ppm. The first data set consists of the 40 pairs used in the initial demonstration study [21], and the second data set is almost 7 times larger, and includes 262 pairs from the set of the total 793 pairs with XRF values above the site-wide average reporting limit of 101 ppm.

Statistical and graphical outputs for the assessment of the two data sets are given below. For each, inverse regression plots are given along with 95% prediction bands. The estimated laboratory ICP analysis result (\hat{x}) and 95% prediction interval are given for XRF values of 500 and 1,000 ppm. Prediction intervals are used because we are interested in what ICP value is predicted from given XRF measurements of 500 and 1,000 ppm. The quality of the fit of the regression line to the sample data is measured by the R^2 value, and the precision of the prediction is measured by the width of the prediction interval.

Analysis of Initial Demonstration Data (40 Data Pairs)

Using 40 data pairs from the initial demonstration study [21], a statistical analysis was performed to estimate the relationship of prepared XRF analysis results to corresponding laboratory ICP analysis results near the action levels of 500 ppm and 1,000 ppm. The data were first examined to determine the appropriate distributional model to use. Normal probability plots suggest the data exhibit an approximately natural lognormal (ln) distribution in which a relatively small proportion of the data exhibit relatively large values. The regression analysis was performed using log-transformed data to remove heterogeneity of variance.

Figure 1 presents the regression fit. The coefficient of determination, R^2 , is 90.4%, and the adjusted R^2 is 90.1%. The R^2 and adjusted R^2 provide a good overall measure of the fit of the regression line to the sample data and to the population, respectively. The R^2 values indicated a reasonably good fit of the regression line to the sample data.

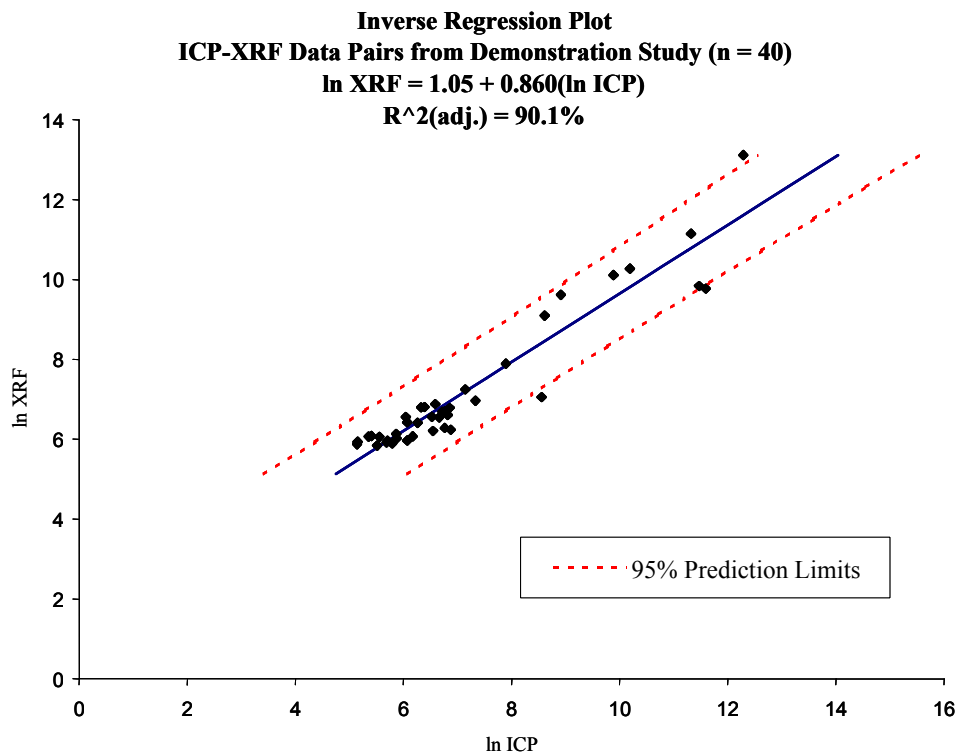


Figure 1.
Inverse Regression Plot of 40 XRF
and ICP-AES Data Pairs from the Initial Demonstration Study

Outputs of the inverse regression are given in Table 6, expressed using the original scale. The ICP values predicted by XRF measurements of 500 and 1,000 ppm were conservative; that is, based on the sample data an XRF reading of 500 ppm would be reported when the "true" value is approximately 402 ppm, and an XRF reading of 1,000 ppm would be reported when the "true" value is approximately 901 ppm. The width of the prediction intervals, however, are remarkably wide and therefore do not provide a very

PERFORMANCE EVALUATION (continued)

precise prediction of an individual ICP value from an individual XRF measurement. The width of the interval is in part related to the relatively small number of sample pairs used in the analysis.

Table 6.
ICP-AES Point Estimates and 95% Prediction Intervals from 40 Data Pairs
of the Initial Demonstration Study

$Y = \text{XRF Value (ppm)}$	$\hat{X} = \text{ICP Point Estimate (ppm)}$	95% Prediction Interval
500	402	LL = 109, UL = 1,491
1,000	901	LL = 245, UL = 3,320

Analysis of "Remedy I" Data Set (262 Data Pairs)

Using 262 data pairs from analysis of soil as part of the "Remedy I" remedial action, a statistical analysis was performed to estimate the relationship of prepared XRF analysis results to corresponding laboratory ICP analysis results near the action levels of 500 ppm and 1,000 ppm. The data were first examined to determine the appropriate distributional model to use. Normal probability plots suggest the data exhibit an approximately natural lognormal distribution in which a relatively small proportion of the data exhibit relatively large values. The regression analysis was performed using natural log-transformed data.

Figure 2 presents the regression fit. The coefficient of determination, R^2 , is 67%, and the adjusted R^2 is 66.9%. The R^2 and adjusted R^2 provide a measure of the overall adequacy of the fit of the regression line to the sample data and to the population, respectively. The fit of the regression line for the larger data set was notably worse than that found in the initial demonstration study indicating additional variability in the site-wide data compared to the initial demonstration data set. The exact sources and magnitudes of the additional variability are not known, however, several possible sources include the following:

- Field sampling (e.g., variability due to pair-wise differences in sample mass and particle sizes, different sampling personnel, different sampling tools and methods, etc.)
- Sample handling,
- Sample splitting,
- Subsampling,
- Homogenization,
- Preparation and digestion,
- Instrument response, and
- Operator error.

Possible sources of variability might be identified by splitting the sample for analysis at varying stages of sample processing and analysis. Each split might be analyzed multiple times by both XRF and ICP-AES and the data examined for variability between stages.

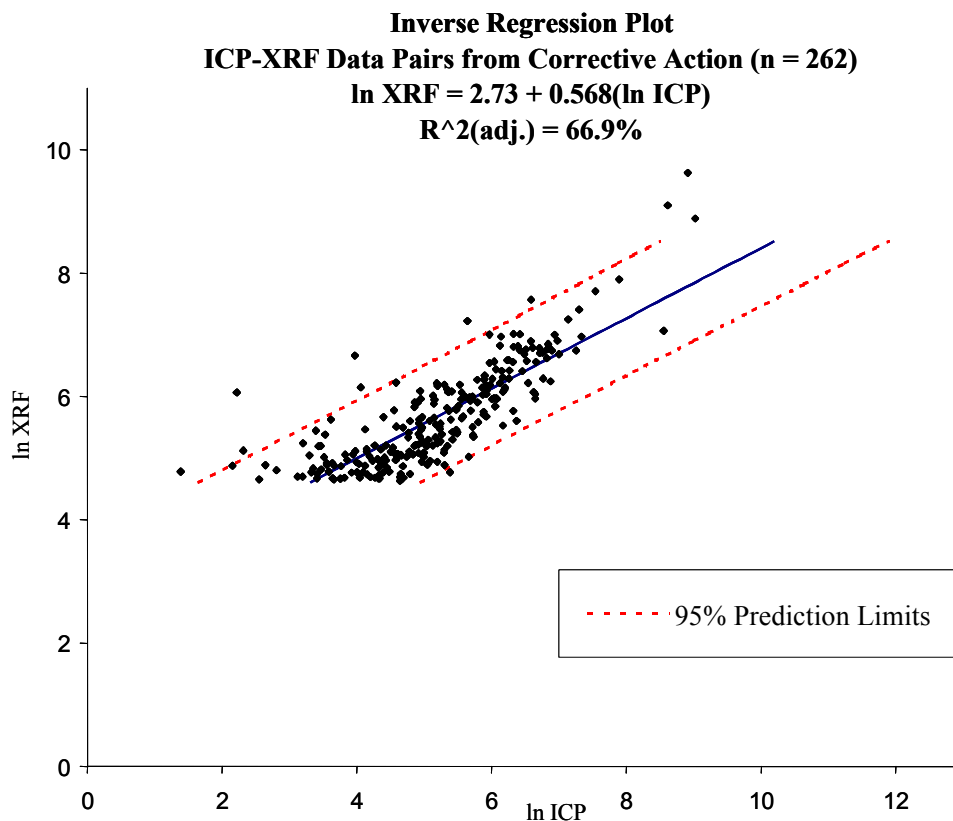


Figure 2.
Inverse Regression Plot of 262 XRF and ICP-AES Data Pairs
from the Remedial Action.

Outputs of the inverse regression are given in Table 7, expressed using the original scale. The XRF yielded a conservative prediction of the ICP value at 500 ppm but underestimated the true concentration when it returned a sample analysis results of 1,000 ppm. An XRF reading of 500 ppm would be reported when the "true" value is approximately 464 ppm, and an XRF reading of 1,000 ppm would be reported when the "true" value is approximately 901 ppm. As with the demonstration data set, the widths of the prediction intervals are remarkably wide and therefore are not particularly useful for predicting an individual ICP value from an individual XRF measurement.

Table 7.
ICP-AES Point Estimates and 95% Prediction Intervals
from 262 Data Pairs of the Remedial Action

$Y = \text{XRF Value (ppm)}$	$\hat{X} = \text{ICP Point Estimate (ppm)}$	95% Prediction Interval
500	464	LL = 90, UL = 2,400
1,000	1,572	LL = 301, UL = 8,202

In spite of the relatively poor fit of the regression line for the larger data set, the "effectiveness" of the XRF technology as a tool for correctly classifying soil samples as either above or below the action level was not compromised. For example, another way to evaluate the comparability of data with respect to decision-making is to show the data from one technique will lead to the same decision as data produced from the other technique. This kind of analysis was presented in Table 1 on page 19, where the XRF data were compared against the ICP data, with the ICP technique given the referee role. The conclusions from this comparison will be discussed in greater detail below. As an evaluation of comparability, agreement between the XRF and ICP data sets with respect to both action levels was very good. Evaluation of instances of disagreement show decisions based on the XRF results to be slightly more conservative (i.e., more protective) than decisions based on Methods 3050/6010 results (see below in the accuracy discussion).

As noted on page 19, agreement between the analytical XRF results and the ICP results occurs when sample preparation steps are most comparable. Therefore, best agreement is found when sample preparation is according to the prepared-sample protocol (drying, sieving, grinding, and homogenizing) in the on-site laboratory. The next best agreement is with the bagged-sample XRF analyses, where the sample is collected and moderately homogenized before the XRF test window is placed in contact with the plastic bag. The least agreement is with in-situ analysis, where there is less preparation of the sample matrix. The in-situ technique places the XRF sample window against the sample (soil) with little disturbance to the matrix, and a reading is taken. Of course, sample support and homogeneity are very different from the collected, dried, screened, ground, homogenized and chemically digested samples analyzed by ICP-AES. Even so, Table 1 showed that there was 93% and 98% agreement between the in-situ XRF and ICP results at the 500 ppm and 1000 ppm action levels, respectively.

Were the sample preparation and XRF techniques sufficiently sensitive?

Sensitivity is the ability of a procedure to detect a change in response to a particular analyte at a particular concentration, and is of special interest at the low concentration range, since this establishes the lowest concentrations that can be reported as either detected (but with considerable uncertainty as to the exact concentration) or quantitated (with greater confidence in the accuracy of the reported concentration). An analytical procedure must be sensitive enough to report analytical results at concentrations that provide some confidence that decisions being made around an action level are likely to be correct. An average matrix-specific sample MDL of approximately 100 ppm and an average sample MQL of approximately 340 ppm were calculated for the prepared-sample on-site NITON Model 700 Series XRF lead analyses based on the first 234 samples analyzed. Both of these reporting limits are below the two action levels relevant to this project (500 ppm and 1000 ppm lead), and therefore meet the sensitivity goals of this project.

Were the sample preparation and XRF techniques sufficiently accurate?

The data quality attribute of accuracy evaluates the closeness of measurements to a true value. The accuracy of a method can be quantitatively determined by analysis of a reference material of known concentration, such as ELPAT proficiency samples. The performance of the on-site XRF laboratory for more than 10 ELPAT rounds and a total of 52 samples showed all analyses within the ELPAT acceptance limits for lead. One measure of correlation between the XRF data and the ELPAT reference concentrations is to perform linear regression analysis. As noted on page 24, the coefficient of determination (r^2) was 0.995, and calculations of relative bias (Table 5) shows little overall bias.

The accuracy of the XRF technology also was evaluated by comparing XRF results with the paired Methods 3050/6010 results. In this evaluation, the referee ICP results were assumed to be accurate for making decisions regarding whether samples exceeded actions levels. Sample pairs analyzed by both prepared XRF and laboratory ICP procedures provide a means for estimating the extent to which the XRF procedure correctly classifies a sample relative to the site media protection standards (500 ppm and 1,000 ppm) even where there is lack of agreement between the measured values. For example, if the XRF sample analysis result is 750 ppm and the ICP result is 550 ppm, then the XRF will correctly identify the soil as exceeding the action level of 500 ppm (assuming the ICP result is the true value). Similarly, if the XRF sample analysis result is 400 ppm and the ICP result is 100 ppm, then the XRF will correctly identify the soil as being less than the action level of 500 ppm. When the estimated (XRF) and the true (ICP) values are either both above or both below the action level, a correct classification or decision can be made in spite of the lack of agreement between the paired values.

Misclassification, however, can occur and lead to decision errors. Consider, for example, a situation in which the XRF sample analysis result is 600 ppm, the true (but unknown) concentration is 400 ppm, and the action level is 500 ppm. The soil represented by the sample would be subjected to unnecessary and costly remedial action due to this *overestimation error* or analytical *false positive*. Now consider the reverse situation in which the XRF sample analysis results is 400 ppm and the true (but unknown) concentration is 600 ppm. The soil represented by the sample would not be subject to remedial response posing potential risks to human health and the environment. This type of misclassification is an *underestimation error* or analytical *false negative*.¹

As demonstrated in Table 1, 793 sample pairs were analyzed and the results compared. There is a 97.4% agreement (correct classification) between the Methods 3050/6010 and the prepared-sample XRF analysis at the 500 ppm action level. At the 1,000 ppm action level the percent agreement increases to 99.0%. Table 8 displays a summary of the 24 pairs of data that disagreed, representing instances where the XRF results reflect either an analytical false positive or analytical false negative that could have resulted in a classification error.

A review of Table 8 shows that sometimes the actual difference between the paired results is relatively small [as expressed by the smaller values for the calculated relative percent difference (RPD)], but just happened to fall across an action level. These 24 sample pairs represent only 3% of the total number of pairs analyzed. Seven of the 24 pair disagreements were analytical false negatives. Five of the false negative decision errors occurred around the 500 ppm action, with only two occurrences at the 1000 ppm action level. Thus the overall false negative decision error rate based on XRF results for this project was less than 1% (0.9%, to be exact), with a rate of 0.3% for false negatives at the highest action level. When decision errors at an action level occurred, they tended to be false positive errors, with an overall positive decision error rate of 2.1%. If more intensive sample preparation and homogenization were performed prior to splitting samples for verification testing by a referee method, an even tighter agreement between the two data sets could be expected.

The slightly higher level of decision errors encountered when using much less intensive sample preparation methods (i.e., in-situ and bagged samples) is to be expected and is easily accommodated by re-analyzing critical soil areas discovered by these procedures by the prepared-sample XRF technique.

¹The terms *false positive* and *false negative*, as used here, are not necessarily the same as used by statisticians to refer to a false rejection of the null hypothesis (a false positive) or a false acceptance of the null hypothesis (a false negative).

PERFORMANCE EVALUATION (continued)

Even so, as reported in Table 1 (page 19), good correlation (always greater than 90%) between the prepared-sample XRF technique and the less intensive on-site XRF techniques was clearly demonstrated. This helps to establish that the data produced by less intensive techniques is of known quality suitable to making the intended decisions, while being a highly cost-effective way to vastly increase sampling density.

Table 8.
False Positive/False Negative Decision Errors
[18, 21, 22]

Action Level (ppm)	Prepared-sample On-site Laboratory, XRF (ppm)	Off-site Laboratory, ICP by Methods 3050/ 6010 (ppm)	RPD (%)	Error Type (F+ = false positive, F- = false negative)
500	532	361	38.3	F+
500	696	391	56.1	F+
500	1,065	463	78.8	F+
1000	1,116	559	66.5	F+
1000	1,370	281	132	F+
1000	1,105	614	57.1	F+
500	391*	772	65.5	F-
1000	802*	1,100	31.3	F-
1000	851*	1,410	49.4	F-
1000	1,100	390	95.3	F+
500	551	476	14.6	F+
1000	1,940	725	91.2	F+
500	500	179	94.6	F+
500	782	53	175	F+
500	506	97.8	135	F+
500	528	326	47.3	F+
500	568	365	43.5	F+
500	536	409	26.9	F+
500	920	457	67.2	F+
500	612	469	26.5	F+
500	318*	555	54.3	F-
500	272*	584	72.9	F-
500	433*	752	53.8	F-
500	419*	772	59.3	F-

The accuracy of the XRF techniques are of a suitably high level to encourage their use in similar projects. However, potential users of the technology should keep in mind that as the concentration of soil lead decreases toward the matrix-specific quantitation limit, accuracy also decreases somewhat.

Depending on the nature of the project and the type of decisions, this loss of accuracy at lower concentration ranges may or may not be important. If accuracy at low concentrations is important, project-specific protocols should specify verification testing of samples as falling in critical concentration ranges.

Were the sample preparation and XRF techniques sufficiently precise?

Precision is the data quality attribute that expresses the degree of agreement among replicate (commonly understood to mean more than two repeated measures of the same property of the same group of properties) or duplicate (commonly understood to imply only two repeated measurements) under prescribed similar conditions. Depending on how duplicates or replicates are selected for collection, the precision estimate includes a fewer or greater number of the components of the sampling and analytical process that introduce variability into environmental data results [23]. Common data quality indicators (DQIs) of precision when two values are involved (i.e., duplicates) are the relative percent difference (RPD) or percent difference (%D) calculations. In this XRF project, RPD was used as the precision indicator, calculated by dividing the mathematical difference between the two results by the average of the two results, then multiplying by 100 to get the percent.

The duplicate XRF samples and the unspiked duplicate ICP samples were split in the field before laboratory-related sample processing, and so the precision estimate contains all components of sample preparation and analysis. <here put something about possible influences?>

The estimates of precision presented in Tables 3 and 4 on pages 21 and 23 show that XRF can be more precise than ICP: the RPD ranges for XRF (0-103%, n=71) are more narrow than the RPD range calculated for ICP (0% to 166%, n=61), and similar percentages of the RPDs exceed 25% (32 % for XRF and 33% for ICP). Project planning did not include the setting of a performance goal for precision. However, if one assumes that data generated by ICP were sufficiently precise to meet decision-making goals, then Tables 3 and 4 demonstrate that the XRF analyses, including sample preparation techniques, also were sufficiently precise to meet decision-making goals.

Can the XRF instrument be a useful tool in characterization and clean-up operations?

The XRF technique can be a useful tool in characterization and clean-up operations. Use of the prepared-sample on-site NITON Model 700 Series XRF technology produced data of known quality shown to be sufficiently accurate, sensitive and precise. The XRF data was comparable to data produced by SW-846 Methods 3050/6010 (acid digestion/ICP-AES). The low percentage of false negative and false positive decision errors results around the two action levels (500 ppm and 1000 ppm) gives a high level of confidence in the reliability of using the data for project decision-making purposes. That situation, combined with the high density of sampling possible using the various XRF techniques, produces data sets that support highly-confident project decisions. Generation of results in the field permits rapid selection of analytical technique and sampling location to quickly delineate the boundaries of non-compliant soil requiring excavation. This combination of a dynamic work plan strategy with real-time data shown to be effective for making the specified decisions is the hallmark of highly protective, yet at the same time, less expensive site investigations and cleanup [30].

When considering a field portable XRF analyzer as an analytical tool, attention must be paid to the sample support and preparation issues discussed previously. The effect of sample preparation is illustrated by the data presented in Table 1, which provides comparisons among the various sample preparation methods for XRF and between the XRF and referee methods. As can be seen in Table 1, as

PERFORMANCE EVALUATION (continued)

XRF sample preparation becomes more rigorous and similar to those used for Methods 3050/6010 ICP-AES analysis, the better the agreement between the XRF and ICP-AES measurements becomes.

Another key consideration when using a field portable XRF analyzer is the frequency of verification analyses by a referee technique. The number of verification samples, the way verification samples are selected, and any criteria that might trigger an increase in the frequency of verification samples should be determined on a project-specific basis. The reason for performing verification testing is to manage for any residual analytical uncertainty in the field method and to establish comparability between the field technique and the traditional laboratory technique (which is generally the basis for the regulatory thresholds). For example, verification analysis can help characterize known or suspected analytical interferences that are specific to XRF analysis. The rationale for both the number of verification samples and for how to select those samples should be clearly specified in the QAPP. That rationale should take into account project-specific factors such as the expected concentrations of target analyte, the matrix, the extent of contamination, and the thresholds that will be used for making decisions. A key consideration when selecting verification samples is building confidence that decisions based on field-generated data are being made correctly at critical thresholds (like action levels). Therefore, the selection strategy would emphasize selecting enough samples from around decision points to be able to build this confidence. The rapid availability of XRF results allows this to be easily done. The plan also may specify that the frequency of verification sampling might be higher during early stages of the project until there is sufficient understanding of method performance. The number of verification samples might be decreased after this understanding is achieved, but might be increased again if additional reassurance is needed for certain sensitive site locations or for certain analyte concentrations.

Arsenic Evaluation [8]

Arsenic is a secondary constituent of concern at LSBP, and is addressed here as an example of performance of the NITON Model 700 Series XRF analyzer in the analysis of a constituent other than lead. Table 9 provides XRF arsenic results for three NIST standards and a blank. The XRF results are from samples that were prepared by drying, sieving, grinding, and homogenization. This work was performed during the initial phase of a site study exploring the use of XRF for arsenic analysis.

Table 9.
Prepared-sample XRF Results for Arsenic [8]

NIST Standard	XRF Arsenic Concentration (ppm)	NIST Arsenic Concentration(ppm)
2710	679	626
2711	80.6	105
2709	<27.0	17.7
Zero Blank	<18.0	0.0

The XRF analytical results for NIST standards indicate that the XRF instrument is capable of adequately replicating arsenic concentrations in prepared samples. However, based on the results from the blank sample, the detection limit is at least around 20 ppm, and sample matrix considerations can raise the detection limit. The arsenic detection limit requirement for many remediation activities is between 10 ppm and 20 ppm [8]. Based on the above results, the NITON Model 700 Series XRF instrument might have been adequate to show that a soil sample exceeded arsenic clean-up levels around 20 ppm, but was inadequate to demonstrate compliance with LSBP project action levels. As XRF technology continues to

PERFORMANCE EVALUATION (continued)

advance, the detection limit for arsenic may come down, with XRF instrumentation becoming capable of detecting and quantifying arsenic at lower levels. Potential users should always consult with XRF technology vendors to determine the current status of XRF analyte-specific detection capabilities.

[NITON: do you have any recent info to place here?]

COST COMPARISON

Based on the cost comparison conducted as part of this study, the approach to lead level characterization at the LSBP site resulted in considerable savings compared to traditional lead characterization approaches. Therefore, the use of the NITON Model 700 Series XRF analyzer (combined with limited fixed laboratory analyses using a reference method to verify the XRF analyses) allowed cost-effective site characterization and soil excavation. The analytical costs alone are estimated to be nearly 50% less than the cost of using conventional methods alone. This level of savings is consistent with analytical savings reported by NITON regarding use of a field portable XRF analyzer at another site containing lead-contaminated soil [23].

Site remediation activities included soil excavation/treatment and debris removal activities at AECs, which consisted primarily of upland soils. The remediation called for the excavation of contaminated soils, stockpiling of contaminated soils on a CAMU and treatment or disposal of the soils. The estimated cost savings in this case study are based on actual and future costs and take into account the number of lead samples required to characterize each AEC.

For comparison of the baseline cost to field XRF costs, it was assumed that the same number of samples would be required, regardless of the analytical methods used. This assumption is based on the fact that the number of samples taken was determined statistically to confirm attainment of the cleanup goals specified by the state cleanup standards.

A breakdown of project costs is shown in Tables 10 and 11. Based on data obtained during Remedy I, soil analyses using only conventional fixed laboratory methods (i.e., SW-846 Methods 3050/6010 used as referee technologies in this study) would have resulted in costs of approximately \$424,000 (see Table 11, Baseline Costs). The actual total cost for delineation, confirmation-of-compliance sampling, and post-excavation sampling with limited verification analyses was estimated at approximately \$219,000, resulting in a cost saving of approximately \$205,000. Note that calculated cost savings would likely be higher if the evaluation accounted for costs associated with the reduction of contractor down time, the efficiency of real-time lead analysis in the field and the quick turn around time provided by XRF.

In addition, the total cost per sample was estimated at \$27.61 ($\$218,933 \div 7,930$ samples), a calculation that includes both the XRF analyses and the cost of QA/QC, including the off-site Methods 3050/6010 referee/verification analyses. The cost per sample for XRF analyses alone was estimated at \$18.31. Consumable costs were estimated at \$0.32 per sample. Total labor cost for sampling and analysis was estimated at \$143,481, accounting for about 65% of the sampling and analysis costs. Waste disposal costs were not included based on the assumption that any investigation-derived waste, such as plastic bags, could be disposed as nonhazardous municipal solid waste.

COST COMPARISON (continued)**Table 10. Field XRF Analysis Costs Including Costs for Verification Analysis By Referee Methods 3050/6010**

Description	Quantity	Unit	Unit Cost	Totals	Computation of Unit Cost				
					Production Rate (units/hr)	Duration (hr)	Labor Item	\$/Hr	Other
Equipment Rental and Supplies									
Sample jars (for ICP samples) (see note 1)	793	EA	\$ 3.00	\$ 2,379.00					\$36/dz
Plastic bags (for all XRF except in-situ) (see note 2)	6	1000/cs	\$ 30.00	\$ 180.00					
NITON XRF instrument (see note 3)	0.4	EA	\$ 21,000.00	\$ 8,400.00					
Soil Sample Collection									
Move equipment	7930	EA	\$ 5.72	\$ 45,357.79		0.08333	2MT	\$ 68.64	
Measure off area	7930	EA	\$ 4.58	\$ 36,287.68	15		2MT	\$ 68.64	
Position survey tool	7930	EA	\$ 0.86	\$ 6,803.94	80		2MT	\$ 68.64	
Take sample and containerize (for ICP analyses only)	793	EA	\$ 11.44	\$ 9,071.92	6		2MT	\$ 68.64	
Soil Analysis									
Equipment set-up (see note 4)	50	EA	\$ 18.33	\$ 916.34		0.267	2MT	\$ 68.64	
XRF daily calibrations (see note 5)	250	EA	\$ 11.44	\$ 2,860.00	6		2MT	\$ 68.64	
Prepared-sample XRF analysis (including sample prep) (see note 6)	2644	EA	\$ 0.57	\$ 1,512.37	60		1MT	\$ 34.32	
Sample preparation for "prepared" XRF analysis (see note 7)	2644	EA	\$ 7.50	\$ 19,830.00					See Note 8.
In-situ XRF (see note 8)	2644	EA	\$ 0.76	\$ 2,016.49	90		2MT	\$ 68.64	
Bagged-sample XRF (see note 8)	2644	EA	\$ 0.76	\$ 2,016.49	90		2MT	\$ 68.64	
Deliver field data (XRF only) (see note 9)	250	EA	\$ 40.02	\$ 10,004.28		0.583	2MT	\$ 68.64	
Fixed lab analysis (Pb in soil by ICP including sample prep)	793	EA	\$ 75.00	\$ 59,475.00					
Sample labeling and prep for shipping	793	EA	\$ 8.58	\$ 6,803.94	8		2MT	\$ 68.64	
Sample transport to lab for fixed analysis (see note 10)	793	EA	\$ 2.00	\$ 1,586.00					
Data Validation	50	SDG	\$ 68.64	\$ 3,432.00		1	1 SrChem	\$ 68.64	
Total (see note 11)				\$ 218,933.24					

COST COMPARISON (continued)**Table 10 Notes and Abbreviations:**

1. Assumes 793 jars, representing 10% of all samples
2. Assumes 5,287 bags, representing 2/3 of all 7,930 samples
3. Assumes unit cost amortized over 5 years, and used at site full time for 2 years.
4. Assumes once per 2 weeks for 2 yrs
5. Assumes 250 field days
6. Assumes analysis performed on 1/3 of all samples, at 60 readings per hour
7. Assumes 1.75 hours of 1MT @ \$34.32/hr to prep each batch of 20 samples (sample transfers, placement in/out of oven, weighing, sieving), plus \$4.50 fixed fee per sample for grinding (particle-size reduction).
8. Assumes analysis performed on 1/3 of all samples, at 90 readings per hour
9. Assumes field data delivered once per day of sampling
10. Assumes 20 samples will fit in a cooler, and \$40 FedEx to ship cooler to lab (i.e., \$2.00/sample)
11. Costs do not include preparation of the SAP/QAPP or other preplanning activities, excavation and removal of soil to the CAMU, backfilling, regrading, and revegetation.

MT = mid level technician or scientist

SDG = sample delivery group

SrChem = Senior chemist

COST COMPARISON (continued)

Table 11. Baseline Costs for Analysis by Conventional Methods Alone at Off-site Laboratory

Description	Quantity	Unit	Unit Cost	Totals	Computation of Unit Cost				
					Production Rate (units/hr)	Duration (hr)	Labor Item	\$/Hr	Other
Equipment Rental and Supplies									
Sample jars (for ICP samples)	7930	EA	\$ 3.00	\$ 23,790.00					\$36/dz
Move equipment	7930	EA	\$ 5.72	\$ 45,357.79		0.08333	2MT	\$ 68.64	
Measure off area	7930	EA	\$ 4.58	\$ 36,287.68	15		2MT	\$ 68.64	
Take sample and containerize	7930	EA	\$ 11.44	\$ 90,719.20	6		2MT	\$ 68.64	
Soil Analysis									
Fixed lab analysis (Pb in soil by ICP including sample prep)	7930	EA	\$ 17.75	\$ 140,757.50					
Sample labeling and prep for shipping	7930	EA	\$ 8.58	\$ 68,039.40	8		2MT	\$ 68.64	
Sample transport to lab for fixed analysis (see note 1)	7930	EA	\$ 2.00	\$ 15,860.00					
Data Validation	50	SDG	\$ 68.64	\$ 3,432.00		1	1 SrChem	\$ 68.64	
Total				\$ 424,243.57					

Table 11 Note and Abbreviations:

- 1. Assumes 20 samples will fit in a cooler, and \$40 FedEx to ship cooler to lab (i.e., \$2.00/sample).
- MT = mid level technician or scientist
- SDG = sample delivery group
- SrChemist = Senior chemist

OBSERVATIONS AND LESSONS LEARNED

Based on the set of data evaluated as part of this technology evaluation, the use of the NITON Model 700 Series XRF analyzer during a site characterization and remediation effort is cost-effective and can provide analytical results of sufficient quality. The results showed a good correlation with more conventional, off-site laboratory analyses. Other observed advantages include the lack of investigation-derived waste, the availability of real-time or quick turn-around data, instrument portability and relative ease of use, and the non-destructive nature of the analysis. Significant disadvantages that may be encountered include a difficulty in obtaining sufficiently low detection limits because of matrix interference and, depending on the analyte of concern, the achievable detection limits may not be low enough in relation to the site action levels. Recommended conditions for the reliable use of field portable XRF analysis include:

- As part of a systematic planning process, a QAPP should be carefully developed involving appropriate QA/QC procedures and criteria to document the sampling and analytical procedures and the quality of the data.
- The sampling and analysis procedures should take into account opportunities for error introduction based on both sampling and analytical procedures and the related impacts on decision quality. This includes errors that may be introduced during sample collection and sample preparation procedures involving a heterogenous matrix such as lead in soil.
- The sampling and analysis procedures should take into account the necessary level of sample preparation based on the purpose of the analysis (e.g., less sample preparation when XRF is used for identification of sample collection locations, and more sample preparation when XRF is used to determine compliance with site action levels).
- As part of the site-specific QA/QC program, comparability of the XRF results with a more conventional analytical technology should be conducted with a frequency that should be determined on a project-specific basis. If the XRF results will be used to determine action level compliance or other critical decision-making, selection of samples for verification should focus on building confidence that decisions are being made correctly around those action levels. Ideally, sample splits for this verification should occur after sample preparation procedures to ensure a comparison that is not affected by error introduced from differences in sample support, collection and preparation. Otherwise, a poor correlation might be misinterpreted as a deficiency in the XRF analysis. Field portable XRF analysis can correlate well with more conventional technologies if variation from sample support, collection, and preparation is minimized.

Emphasizing the importance of appropriate sample preparation, it was seen in the LSBP study that analytical results on minimally prepared samples by in-situ and bagged-sample XRF analysis were not as comparable with the off-site laboratory ICP-AES results as were the prepared-sample on-site laboratory XRF results. Specifically, overall result agreement with a conventional technology result was highest when XRF analysis was used on fully prepared samples, and agreement was lowest when it was used as part of in-situ or bagged-sample analysis involving less intensive sample preparation. The more the soil samples are prepared (e.g., drying, grinding, sieving, and homogenizing) for XRF analyses, the better the agreement between sample pairs (field portable XRF analysis vs. more conventional analysis such as Method 6010). Nevertheless, in-situ or bagged-sample analysis using XRF with minimal sample preparation can provide rapid, low-cost measurement of soil to map out contamination patterns or select sample collection sites for prepared-sample XRF analysis. Accuracy of results from these approaches can be assessed by comparison with the prepared-sample XRF results.

OBSERVATIONS AND LESSONS LEARNED (continued)

In addition, it appears that, as the concentration of lead decreases, the accuracy of the test also decreases. If the reliability of results at these lower levels is important to project decision-making, additional samples should be sent to a conventional laboratory to better manage this analytical uncertainty.

The cost savings realized from use of the NITON Model 700 Series XRF analyzer at the LSBP, as compared with the cost of conventional laboratory analysis alone, are significant at approximately 50%. Documented savings would no doubt increase with inclusion of the cost benefits from time and labor savings as a result of expediting the field work as a result of real-time decision-making to guide soil excavation. The use of real-time or rapid turn around results from a field portable analytical technology during site characterization, in lieu of waiting for results from an off-site laboratory, can greatly speed certain removal and remedial activities [27].

Based on the above observations, field portable XRF technologies can have a significant and important role in site remediation efforts. For example, such technologies can provide reliable and economical assessments of Brownfields sites that are slated for redevelopment and productive reuse.

REFERENCES

1. NITON Corporation. *XL-309 & 700 Series User's Guide Version 5.0 (HTML)*. Available on-line at: <http://www.niton.com/support.html>
2. U.S. Environmental Protection Agency. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846)*. Method 3050B: Acid Digestion of Sediments, Sludges, and Soils. Available on-line at: <http://www.epa.gov/epaoswer/hazwaste/test/3xxx.htm#Three>
3. U.S. Environmental Protection Agency. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846)*. Method 6010B: Inductively Coupled Plasma-Atomic Emission Spectrometry. Available on-line at: <http://www.epa.gov/epaoswer/hazwaste/test/6xxx.htm>
4. See the Clean-Up Information (CLU-IN) website for EPA documents discussing dynamic work plans: http://www.cluin.org/char1_edu.cfm#dyna_work
5. See the Superfund Programs website for EPA guidance and other resources regarding systematic planning and dynamic work plans involving the use of field based analytical methods (including XRF analyzers): <http://www.epa.gov/superfund/programs/dfa>.
6. See the Clean-Up Information (CLU-IN) website for EPA documents discussing sampling variability: http://www.cluin.org/char1_edu.cfm#stat_samp
7. Corporate Remediation Group. An Alliance between DuPont and The W.C. Diamond Group. Wilmington, DE 19880. *Stratford Corrective Measures Completion Report, Lake Success Business Park, Bridgeport, Connecticut*. DSLS7022. 1999.
8. Northey, Scott T., Woodward-Clyde Diamond Group. The URS Corporation. Wilmington, DE 19805. *The Utilization of XRF Lead Screening and XRF Lead Analysis at a RCRA Corrective Action Site*. No date.
9. Crumbling, D. M. *Current Perspectives in Site Remediation and Monitoring: Clarifying DQO Terminology Usage to Support Modernization of Site Cleanup Practice*. EPA 542-R-01-014. October 2001. Available on-line at <http://clu.in.org/tiopersp/issue.cfm>
10. U.S. Environmental Protection Agency. *Guidance on Quality Assurance Project Plans*. QA/G-5. EPA/600/R-98/018. February 1998. Available on-line at http://www.epa.gov/quality/qa_docs.html
11. U.S. Environmental Protection Agency. *Guidance for the Data Quality Objectives Process for Hazardous Waste Sites*. QA/G-4HW. EPA/600/R-00/007. January 2000. Available on-line at http://www.epa.gov/quality/qa_docs.html
12. Shefsky, Stephen. NITON Corporation. Bedford, MA. *Sample Handling Strategies for Accurate Lead-in-Soil Measurements in the Field and Laboratory*. 1997. Available on-line at <http://www.niton.com/shef01.html>
13. U.S. Environmental Protection Agency. Office of Research and Development. Washington, DC. *Environmental Technology Verification Report — Field Portable X-ray Fluorescence Analyzer, Niton XL Spectrum Analyzer*. EPA/600/R-97/150. March 1998. Available on-line at <http://www.epa.gov/etv/verifrpt.htm#monitoring>

REFERENCES (continued)

14. U.S. Environmental Protection Agency. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846). (Draft Update IVA.)* Method 6200: Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment. Available on-line at <http://www.epa.gov/epaoswer/hazwaste/test/up4a.htm>
15. Sackett, Donald and Martin Kenneth. NITON Corporation. *EPA Method 6200 and Field Portable X-ray Fluorescence*. 1998. Available on-line at <http://www.niton.com/martin.html>
16. Shefsky, Stephen. NITON Corporation. Bedford, MA. *Comparing Field Portable X-Ray Fluorescence (XRF) to Laboratory Analysis of Heavy Metals in Soil*. 1997. Available on-line at: <http://www.niton.com/shef02.html>
17. U.S. Environmental Protection Agency. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846)*. Chapter Two: Choosing the Correct Procedure. Available on-line at <http://www.epa.gov/epaoswer/hazwaste/test/main.htm>
18. U.S. Environmental Protection Agency. Office of Research and Development. *A Rationale for the Assessment of Errors in the Sampling of Soils*. EPA 600/4-90/013. May 1990. Available on-line at <http://clu.in.org/download/stats/rationale.pdf>
19. Ramsey, Charles A. and Jennifer Suggs. Improving Analytical Performance Through Scientific Subsampling Techniques. *Environmental Testing & Analysis*, March/April 2001, pp. 13-16. Article available on-line at <http://clu.in.org/download/stats/etasubsamplingarticle.pdf>
20. The Woodward-Clyde Diamond Group. The URS Corporation. Wilmington, DE 19805. *Evaluation of XRF Lead Concentrations, Lake Success Business Park, Bridgeport, Connecticut*. April 1999.
21. The Woodward-Clyde Diamond Group. The URS Corporation. Wilmington, DE 19805. *Evaluation of XRF Lead Concentrations, Lake Success Business Park, Bridgeport, Connecticut*. November 1997.
22. The Woodward-Clyde Diamond Group. The URS Corporation. Wilmington, DE 19805. *Evaluation of XRF Lead Concentrations, Lake Success Business Park, Bridgeport, Connecticut*. October 1998.
23. U.S. Environmental Protection Agency. *Guidance on Data Quality Indicators*. QA/G-5i. Peer Review Draft. September 2001. Available on-line at http://www.epa.gov/quality/qa_docs.html
24. The Woodward-Clyde Diamond Group. The URS Corporation. Wilmington, DE 19805. *Evaluation of XRF Lead Concentrations, Lake Success Business Park, Bridgeport, Connecticut*. October 1999.
25. NITON Corporation. *Soil Abatement with NITON XRF*. Article in NITON Connects. July 1999.
26. NITON Corp., Bedford, MA. *NITON XL-700 Series Standard Resolution Instruments, Elemental Limits of Detection in Soils, mg/kg (ppm)*. 1999.
27. U.S. Environmental Protection Agency. Region I. Office of Environmental Measurement and Evaluation. *Standard Operating Procedure for Elemental Analysis Using the X-MET 920 Field X-Ray Fluorescence Analyzer*. 1996. Available on-line at: <http://www.epa.gov/region1/measure/xray/xrayfluor.html#download>

REFERENCES (continued)

28. U.S. Department of Energy. Office of Science and Technology. Innovative Technology Summary Report DOE/EM-0402. *Portable X-Ray Fluorescence Spectrometer*. December 1998. Available on-line at <http://apps.em.doe.gov/ost/itsrall.html>
29. U.S. Environmental Protection Agency. Cost and Performance Report: Soil Washing at the King of Prussia Technical Cooperation Superfund Site. March 1995. Available at <http://bigisland.ttclients.com/frtr/pdf/kop.pdf>
30. Crumbling, D.M. Current Perspectives in Site Remediation and Monitoring: Applying the Concept of Effective Data to Environmental Analyses for Contaminated Sites. EPA 542-01-013. October 2001. Available on-line at <http://clu.in.org/tiopersp/issue.cfm>

APPENDIX
ESTIMATED DETECTION LIMITS FOR SOIL MEASUREMENTS
USING A NITON XL-700 SERIES STANDARD RESOLUTION (¹⁰⁹CD Isotope) INSTRUMENT
Source: Reference 24

According to NITON, XRF detection limits are dependent upon testing time, matrix, and level of statistical confidence. The following table of limits of detection by NITON [24] assume a 99.7% confidence level for the testing time shown. According to NITON, individual limits of detection improve as a function of the square root of the testing time. The table provides detection limits for both the "optimal" matrix of sand and a typical soil matrix represented by NIST Standard Reference Materials (SRM). Two testing times are given, illustrating the lowering of detection limits with an increase in testing time. The levels given for arsenic represent low levels of lead. High levels of lead might increase arsenic detection limits.

Analyte	60 Second Testing Time		120 Second Testing Time	
	Detection Limit in Sand Matrix (ppm)	Detection Limit in SRM Matrix (ppm)	Detection Limit in Sand Matrix (ppm)	Detection Limit in SRM Matrix (ppm)
Arsenic (As)	60	100	45	60
Chromium (Cr)	1400	3500	1000	2500
Cobalt (Co)	300	700	180	420
Copper (Cu)	130	200	90	130
Iron (Fe)	500	1000	350	600
Lead (Pb)	45	70	35	45
Manganese (Mn)	1000	2200	600	1600
Molybdenum (Mo)	20	25	15	30
Nickel (Ni)	200	500	120	300
Rubidium (Rb)	30	45	20	30
Strontium (Sr)	20	30	15	20
Zinc (Zn)	100	150	70	90
Zirconium (Zr)	20	30	15	30