



SAMPLING AND ANALYSIS PLAN

Kelly Camp Mine Site
Summer 2007 Field Investigation
July 6, 2007

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SUMMER 2007 FIELD EFFORT SAMPLING AND ANALYSIS PLAN

1.0 INTRODUCTION

This document serves as the Sampling and Analysis Plan (SAP) for the site inspection (SI) to be conducted at the Kelly Camp Mine Site (site) in Summer 2007. This document describes specific activities, methods, and procedures that will be used during the SI to collect baseline analytical results for future remediation work at the site. The SAP was developed in conjunction with the site-specific Health and Safety Plan (HSP). These two plans collectively are considered the Project Plan for the Summer 2007 field effort.

Standard operating procedures in this document govern all aspects of field measurements, sample collection, and documentation efforts to ensure that samples collected are representative of conditions in the field, measurements and observations are clearly and concisely documented, and the information obtained is valid.

2.0 BACKGROUND AND RATIONALE

The tasks described in this SAP are being conducted in response to a request by the United States Department of Agriculture Forest Service (USFS) to collect baseline data during the summer of 2007. The tasks described for this SI include X-ray Fluorescence (XRF) soil screening as well as the collection of soil, waste rock, and mine water samples for chemical analysis.

3.0 PROGRAM OBJECTIVES

The overall goal of the SAP is to obtain usable data to aid in the evaluation of the risk associated with potential contamination at the site.

4.0 SCOPE OF WORK

The summer 2007 field work will include the following tasks:

- Task 1 – Collect near-surface soil sampling
- Task 2 – Collect seep/mine water (if present).
- Task 3 – Collect waste rock samples
- Task 4 – Conduct visual survey
- Task 5 – Data Submittal

The data obtained from completing Tasks 1 through 4 will be provided to the Agencies for review. A description of each task is provided in the following subsections. A summary of the samples and associated analyses to be performed is provided in Table 1.

4.1 TASK 1: COLLECTION OF NEAR-SURFACE SOIL SAMPLES

Up to 40 near-surface soil samples will be collected using hand collection methods. Near-surface is defined for this field event as soil from 3 to 6 inches below ground surface (bgs). Samples will be collected near the lower adit waste dump, the upper shaft waste dump, and at a nearby background location exhibiting no apparent mining-related disturbance. Upon arrival at the sample location, field personnel will scout the site and note general site conditions. At each soil sample location, surface soils (0 to 3 inches) will be scraped away to remove the highly oxidized surface layers. A preliminary XRF soil screening will be performed directly on the exposed soil surface prior to soil sample collection. The field personnel using professional judgment will collect soil samples that have a range of XRF concentrations. The soil sample container size and preservation requirements are listed in Table 2.

Soil samples will be collected using a dedicated spoon to scoop soil into the laboratory-provided sample containers. Each sample will be a discrete; homogenization will not be performed. No soil field duplicates will be collected. The spoons will be dedicated use, so no decontamination procedures will be required to avoid cross-contamination.

Three soil samples will be analyzed for the full suite of metals listed below. The analyte list for the remaining soil samples will be contingent upon these preliminary sample results. The three preliminary soil samples will be chosen by the field personnel based on field XRF sample results.

Ag	Silver	Mn	Magnesium
Al	Aluminum	Mo	Molybdenum
As	Arsenic	Na	Sodium
B	Boron	Ni	Nickel
Ba	Barium	P	Phosphorus
Be	Beryllium	Pb	Lead
Bi	Bismuth	Sb	Antimony
Ca	Calcium	Sc	Scandium
Cd	cadmium	Se	Selenium
Co	Cobalt	Si	Silicon
Cr	Chromium	Sn	Tin
Cu	Copper	Sr	Strontium
Fe	Iron	Ti	Titanium
Ga	Gallium	Tl	Thallium
K	Potassium	U	Uranium
La	Lanthanum	V	Vanadium
Li	Lithium	Zn	Zinc
Mg	Manganese		

Soil samples will be stored under chain-of-custody (COC) protocols until delivery to the offsite laboratory for analysis as described in Section 6.4.

4.2 TASK 2: COLLECTION OF SEEP/MINE WATER SAMPLES

Up to three mine water samples will be collected from the mine site if water and/or seeps/springs are present at time of sample collection. Field personnel will record the GPS coordinates and general site conditions at each water sample location.

Water sample collection will be performed using a dedicated bailer to retrieve mine water. Mine water will be poured from the bailer into the laboratory provided sample containers. To collect field-filtered samples, a peristaltic pump will be used to pump water through the filter and into the sample containers. Specific containers requirements are listed in Table 2. No field duplicates will be collected. The use of dedicated sampling equipment eliminates the need for equipment blanks.

A full suite of metals will be analyzed on the three samples. Samples will be stored under COC protocols until delivery to the offsite laboratory for analysis as described in Section 6.4.

4.3 TASK 3: COLLECTION OF WASTE ROCK SAMPLES

Approximately three waste rock samples will be collected from the mine site, near the upper and lower adits. Exact samples locations will be determined by the field personnel. Sample collection will consist of using a gloved hand to place the rock into the proper sample collection containers.

Waste rock will be analyzed for Acid Base Accounting (ABA) including acid neutralization potential, acid generation potential, total sulfur, sulfate sulfur, pyretic sulfur, and non-extractable sulfur, as well as inorganic carbon and particle size. Additionally, a limited set of metals (determined by the three preliminary soil samples) will be analyzed on the three waste rock samples. All samples will be stored and shipped under strict COC procedures as described in Section 6.4.

4.4 TASK 4: VISUAL ASSESSMENTS

Field personnel will visually observe and record the general condition of the site. Photographs will be taken as needed to document conditions.

4.5 TASK 5: DATA SUBMITTAL

Data collected during the Summer 2007 field investigation will be evaluated by onsite field personnel and in the office. The chemical data will be reviewed in accordance with Section 6.5 and summarized in tabular form in an Excel spreadsheet for review.

5.0 SAMPLE DESIGNATION

Sample designation procedures are described in the following subsections for field QA/QC, mine water and soil samples.

5.1 FIELD QA/QC SAMPLES

Field QA/QC samples that will be collected include field duplicate (or field replicate) samples using the XRF device. One field duplicate will be collected for every 20 samples. Field duplicates will be designated by the sample name followed by an "X". No field duplicates will be collected for soil, water, or waste rock samples.

5.2 SAMPLE NAMING

All collected soil, water, and waste rock samples will be labeled according to sample location and date. Seep/mine water samples should be denoted by “SW”, “S” for soil, “WR” for waste rock and “XRF” for XRF readings. For example:

A seep/mine water sample collected at sample location one should be labeled: SW-01. Any changes to the sample nomenclature should be clearly recorded in the field log.

6.0 STANDARD OPERATING PROCEDURES

Standard operating procedures for equipment decontamination, environmental sample collection, flow measurement, and sample handling and shipping are provided in the following subsections.

6.1 DECONTAMINATION OF EQUIPMENT

Equipment used during field sampling will be decontaminated prior to use and during sampling to reduce the potential for the introduction of contamination and cross-contamination in accordance with the guidelines and procedures set forth in this document. These procedures are necessary to ensure quality control in decontamination of field equipment and to serve as a means to identify and correct potential errors in the sample collection and sample handling procedures.

Decontamination of all non-dedicated field sampling equipment and field instruments will be conducted in a thorough and step-wise manner. New disposable nitrile gloves will be worn when handling clean sampling equipment to ensure that the equipment is not contaminated. Decontamination procedures shall be documented in a field notebook.

All non-dedicated sampling equipment used for sample collection will be decontaminated according to the following procedure:

- Rinse thoroughly with potable water
- Scrub with Alconox and water to remove any visible dirt
- Rinse with water

Sampling equipment shall be stored in plastic wrap or plastic bags to prevent contamination during storage and transport.

6.2 GENERAL SAMPLING PROTOCOL

Field observations, notes, and measurements will be recorded daily in waterproof ink by the field personnel in all-weather field logbooks. Each field notebook page will be dated. Upon arrival at the Site, the following procedures will be followed:

1. Record the date and time of arrival, general Site conditions, and other applicable field observations related to the Site.
2. Record sample collection information and sample locations on the appropriate sampling form and/or in the field notebook.

3. Finalize field logs and check sample labels against sampling forms and field notebook. Complete COC forms as samples are packaged in coolers. The project name, location, station, date and time of collection, number of containers, type of analysis, and field team representative's signature and time will be completed on the COC form. Verify that the sample number, request for analyses, date, and time of collection labeled on the sample containers are the same as those entered on the COC form and in the field notebook.
4. Water samples collected will be stored and sealed in ice-filled (or equivalent) coolers prior to transport to the laboratory. Once a sample is collected, it should remain in the possession of the field sampling team. Custody seals will be placed on the cooler to ensure the cooler has not been tampered with during shipment.

6.3 HANDLING & SHIPPING OF ENVIRONMENTAL SAMPLES

Data regarding sample collection and processing will be recorded by sampling personnel on the appropriate sampling report forms and/or in bound field books.

The COC program will be adequate to allow for the tracking and possession and handling of individual samples from the time of field collection through laboratory and field analysis. The laboratory-supplied COC form will be used by personnel responsible for ensuring the integrity of the samples and will be maintained in the project files as documentation of sample handling procedures.

6.3.1 Sample Packaging

Samples collected must be handled and shipped in a manner that will protect against any detrimental effects to the samples or the environment due to breakage, leakage, or spoilage. Sample handling procedures will be closely supervised and recorded to minimize the potential for loss, modification, or tampering during shipment of the analytical laboratory. Package labeling specification will depend on the type of materials being sent, and will be in accordance with Department of Transportation (DOT) regulations (49 CFR, Parts 171 through 177) and CLP guidance (EPA, 2003). Samples of hazardous materials will be stored and handled in accordance with all applicable Federal and State requirements.

6.3.2 Sample Container Preparation

All containers used for sample collection shall be laboratory cleaned. The container type and preservative requirements shall follow the specifications of Table 2.

6.3.3 Procedures to Prevent Cross Contamination

Personnel collecting samples for chemical analyses will take the following precautions to minimize sample contamination or cross-contamination between samples:

- Nitrile gloves will be used while taking all samples and disposed of after equipment has been decontaminated.
- Sampling personnel will not touch the inside of the sampling container.
- Sampling personnel will not walk over any areas where samples will be taken.

- Only equipment that has been properly decontaminated according to the procedures specified in Section 6.1 (Decontamination of Equipment) will be used for environmental sample collection.

Immediately following the collection of the sample, the container will be sealed and the sample will be labeled and entered in the field notebook and/or appropriate sampling record forms.

6.3.4 Sample Identification and Labeling

Each sample shall be identified in the field notebook and on the sample container label. The label shall be filled out as follows:

- Client - URS
- Sample Name - Use nomenclature described in Section 5
- Site – Kelly Camp Mine
- Date - date of sample collection
- Time - time of sample collection
- Sampler - Sampler initials
- Analysis - Test requested
- Comments - Indication of preservation, sample volume limitations, etc.

6.3.5 Field Notebook and Field Report Form

A bound field notebook will be maintained by the sampler to provide a daily record of events. At the beginning of each entry, the following will be recorded:

- Date
- Time
- Meteorological conditions
- Field personnel present
- Level of personnel protection
- List of on-site visitors and the level of personal protection
- Signature of the person making the entry

Field notebook entries will be in as much detail as necessary so that essential information is properly documented. All documentation in field books will be in ink. If an error is made, corrections will be made by crossing a line through the error and entering the correct information. Corrections will be dated and initialed. No entries will be obliterated or rendered unreadable.

If sample locations cannot be indicated on field maps, a simple drawing of the location (not to scale) will be included in the field notebook to provide an illustration of all sampling points.

The cover of each field notebook used will contain:

- Person and organization to whom the book is assigned
- Book number
- Start date
- End date

Entries in the field notebook will include at a minimum the following for each sample date:

- Site identification
- Location of sampling points (e.g., sketch)
- Description of sampling points
- Sample identification number
- Number of samples taken
- Time of sample collection
- Reference to sample location map
- Number of QA/QC samples taken
- Collector's names
- Field observations
- Sample distribution (e.g., split samples, analytical lab)
- All field measurements made (e.g., pH, temperature, specific conductance)

Documentation of sampling procedures will be made on the appropriate sampling report forms and/or field books.

6.3.6 Sample Chain-of-Custody Record Form

In order to maintain an accurate record of sample collection, transport, analysis, and disposal, the following methodologies will be used:

- Samples will be accompanied by a COC form at all times.
- The COC form will be used by personnel responsible for ensuring the integrity of samples from the time of collection until shipment to the laboratory.
- The record will be completed in the field to indicate project, sampling team, etc.
- The person transporting the samples to the laboratory or delivering them for shipment will sign the record form as “Relinquished by _____.”
- If the samples are shipped to the laboratory by commercial carrier, the COC form will be sealed in a watertight container, placed in the shipping container, and the shipping container sealed prior to being given to the carrier.
- If the samples are transported directly to the laboratory, the COC form will be kept in the possession of the person delivering the samples.
- For samples shipped by commercial carrier, the waybill will serve as an extension of the COC record between the final field custodian and receipt in the laboratory.
- Upon receipt in the laboratory, the Sample Receiving Supervisor will open the shipping containers, compare the contents with the COC record, ensure that document control information is accurate and complete, and sign and date the record. Any discrepancies will be noted on the COC form.
- In the event of discrepancies, the samples in question will be segregated from normal sample storage and the field personnel immediately notified.

- The COC form is completed upon receipt of the samples by the analytical service. The completed COC form will be returned to the Project Manager and maintained in the project file.

6.3.7 Sample Packaging

Samples will be immediately placed in the sample cooler. Once the cooler is filled with samples, the cooler will be sealed with two custody seals initialed and dated by the person packing the cooler. The following protocol will be used for packaging of samples:

- Only waterproof coolers will be used.
- Strapping tape and custody seals will be placed around the lid of all sample coolers.
- Samples will be packed so that the bottles will not dislodge and/or break during shipment.
- The sample containers will be placed upright in the cooler. In addition, all sample containers will be placed in clear, plastic, leak proof bags. Care will then be taken to ensure that sample labels are legible through the bag.
- Additional packaging material will be placed in the cooler to partially cover the sample containers. Ice (or equivalent) will be placed in plastic bags and then around, among and on top of the sample containers.
- The COC form will be placed in a waterproof plastic bag and taped on the inside of the lid of the cooler. Methodology of shipment, courier name(s), and other pertinent information will be recorded on the COC form.
- The completed shipping label will be attached to the top of the cooler.
- All records pertaining to the shipment of a sample will be retained.

6.4 QUALITY CONTROL

The overall quality assurance objectives for field sampling and laboratory analysis are to produce data of known and appropriate quality to support the project objectives. Appropriate procedures and quality control checks will be used so that known and acceptable levels of accuracy and precision are maintained for each data set. Field quality control and laboratory quality control samples will be employed to evaluate data quality. Quality control samples are controlled samples introduced into the analysis stream whose results are used to review data quality and to calculate the accuracy and precision of the chemical analysis program. The purpose of each type of quality control sample, collection and analysis frequency, and evaluation criteria are described in this section. Laboratory quality control samples, as described in the referenced methods, will be followed.

The quality of field and laboratory measurements will generally be determined by the quality control requirements and quality criteria described in analytical methods. All quality control measurements and data assessment for this project will be conducted on project-specific samples when possible.

Quality control checks for sample collection will be accomplished by a combination of chain-of-custody protocols, field quality control samples, and laboratory QA as described in the sampling and analytical

methods sections of this document. The QC measures may include the following: rinsate and method blanks; matrix, surrogate, and laboratory control spikes; and field and laboratory duplicate samples. The laboratory will notify the URS Project Chemist of any quality control exceedances outlined in this SAP immediately.

6.4.1 Field Quality Control Samples

Field quality control samples are collected to evaluate the quality of the field sampling program. Specifically, field duplicate samples are collected to monitor the variability associated with sample collection techniques and equipment rinsate blank samples are collected to monitor the effectiveness of decontamination procedures. Field quality control samples will be selected by the sampling team and designated in the field logbook, as appropriate.

Field Duplicates

Field duplicate samples measure the variability associated with sample collection. Field duplicates consist of two duplicate samples that are collected from the same sampling point at the same date and time with both samples sent to the same laboratory. Field duplicates will be collected using the XRF sampling device as detailed in Appendix A in *Assessing The Components of Measurement Error*. Field duplicates will not be collected for the seep/mine water, soil or waste rock samples.

Rinsate Blanks

Rinsate blanks monitor cross-contamination of samples by sampling equipment. No rinsate blank will be collected for this sampling event due to the use of dedicated sampling equipment.

Field Blank

The field blank will be analyzed under the same analytical conditions as the primary samples. No field blank will be collected for the soil, mine water, and waste rock samples.

6.4.2 Laboratory Quality Control Samples

Laboratory QC checks are accomplished by analyzing initial and continuing calibration samples, method blanks, surrogate spikes, laboratory control samples (LCS), and laboratory duplicate samples. Not all of these QC samples will be required for all methods.

Method Blanks

Method blanks are used to check for laboratory contamination and instrument bias. Laboratory method blanks will be analyzed at a minimum frequency of 5 percent or one per analytical batch.

Analytical results for each sample shall be clearly associated with a particular method blank. In order to evaluate low level determinations of target compounds in samples, the laboratory will report any detected concentration found in method blanks that exceed control criteria specified in this SAP.

Laboratory Control Samples

Laboratory control samples (LCS) are used to monitor the laboratory's day-to-day performance of routine analytical methods, independent of matrix effects. The LCS is prepared by spiking deionized water with standard solutions prepared independently of those used in establishing instrument calibration. The LCS are extracted and analyzed with each batch of samples. Results are compared on a per-batch basis to established control limits and are used to evaluate laboratory performance for precision and accuracy. LCS may also be used to identify any background interference or contamination of the analytical system that may lead to the reporting of elevated concentration levels or false positive measurements.

Matrix Spike/Matrix Spike Duplicate (MS/MSD) Samples

Matrix spikes are used to assess sample matrix interferences and analytical errors, as well as to measure the accuracy of the analysis. Known concentrations of analytes are added to environmental samples; the MS/MSD samples are then processed through the entire analytical procedure and the recovery of the analytes is calculated. Results are expressed as percent recovery of the known spiked amount. MS/MSD pairs will be analyzed at a minimum frequency of one per twenty samples or one per analytical batch. The MS/MSD samples will be analyzed for the same parameters as the associated field samples in the same analytical batch.

MS/MSD samples will be identified on the COC form, and additional sample volumes will be provided to the laboratory. MS/MSD analyses not meeting quality control criteria specified in this SAP will be reanalyzed once. If subsequent analyses result in out of control recoveries, both results will be reported by the laboratory and the corresponding data flagged.

Laboratory Duplicate Samples

Precision of the analytical system is evaluated by using laboratory duplicates. Laboratory duplicates are two portions of a single homogeneous sample analyzed for the same parameter. Laboratory duplicates will be analyzed at a minimum frequency of 1 in 20 samples or one per analytical batch.

6.4.3 Analytical Data Quality Indicators

Analytical data quality indicators of precision, accuracy (bias), representativeness, comparability, completeness, and sensitivity are defined below [USACE 2001a]. Any data that fall outside of these criteria must be justified, and the effects on decisions must be assessed.

6.4.3.1 Precision

Precision is defined as the degree of agreement between or among independent, similar, or repeated measures. Precision is related to analytical variability and can be expressed as a standard deviation, or as percentage of the mean of the measurements, by relative range or relative standard deviation (coefficient of variation). For this project, analytical variability will be measured as the relative percent difference (RPD) between results for laboratory duplicate pairs. Precision will be calculated as the RPD as follows:

$$\%RPD_i = \frac{2|O_i - D_i|}{(O_i + D_i)} \times 100\%$$

where:

$\%RPD_i$	=	Relative percent difference for compound i
O_i	=	Value of compound i in original sample
D_i	=	Value of compound i in duplicate sample

The resultant RPD will be compared to acceptance criteria specified in this SAP. If the criteria are not met, the laboratory will justify why the acceptability limits were exceeded and implement appropriate corrective actions. The RPD will be reviewed during data quality review, and the reviewer will note any deviations from the specified limits and comment on any effects on the data.

6.4.3.2 Accuracy

Accuracy is the amount of agreement between a measured value and the true value. Laboratory accuracy will be measured as the percent recovery of matrix spike samples and laboratory control samples. Additional potential bias will be quantified by the analysis of method blank samples. Accuracy shall be calculated as percent recovery of the target analyte as follows:

$$\%R_i = (Y_i \div X_i) \times 100\%$$

where:

$\%R_i$	=	percent recovery for compound i
Y_i	=	measured analyte concentration in sample i
X_i	=	known analyte concentration in sample i

The resultant percent recoveries will be compared to acceptance criteria as listed in analytical methods and laboratory inhouse criteria. If the objective criteria are not met, the laboratory will justify why the acceptability limits were exceeded and implement appropriate corrective actions. Percent recoveries will be reviewed during data quality review, and the reviewer will note any deviations from the specified limits and comment on any effects on the data.

6.4.3.3 Representativeness

Representativeness is a qualitative parameter that expresses the degree to which sample data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, or an environmental condition. Representativeness is a parameter that focuses primarily on the proper design of the sampling program or the subsampling of a given sample.

6.4.3.4 Comparability

Comparability is a qualitative parameter that expresses the confidence with which data from one study can be compared with data from another. This goal will be achieved by using standard techniques to collect and analyze representative samples and by reporting analytical results in appropriate units. Comparability will be evaluated during the data quality review.

6.4.3.5 Completeness

Completeness for usable data is defined as the percentage of usable data out of the total amount of planned data. Completeness for usable data shall be defined as 95% for each individual analytical method. Completeness will be calculated as follows:

$$\%C = \frac{A}{I} \times 100\%$$

where:

$\%C$	=	Percent completeness (analytical)
A	=	Measurements that are judged to be usable (based on project-specific requirements)
I	=	Intended number of measurements

Invalid data (i.e., data qualified as “R,” rejected) will be identified during the data quality review.

6.4.3.6 Sensitivity

The sensitivity of the analytical methods (i.e., method reporting limits) identified for this project are sufficient to allow comparison of project results to decision criteria.

6.5 EQUIPMENT MAINTENANCE

Laboratory instrumentation will be examined and tested prior to being put into service and will be maintained according to the manufacturer’s instructions. All laboratory instruments will be maintained as specified in the project laboratory’s QA plan and according to manufacturers’ instructions. Manufacturer’s instructions will be followed for any additional equipment that is required for this project.

6.6 INSTRUMENT CALIBRATION

Laboratory instrument calibration will be conducted in accordance with the QC requirements identified in the manufacturers' instructions and the laboratory SOP. General requirements are discussed below.

6.6.1 Laboratory Instruments

As stated in EPA SW-846 and applicable laboratory SOPs, calibration of all analytical instrumentation is required to ensure that the analytical system is operating correctly and functioning at the sensitivity required to meet project objectives. Each instrument will be calibrated with standard solutions appropriate to the instrument and analytical method, in accordance with the methodology specified and at the QC frequency specified in the laboratory SOP.

The calibration and maintenance history of the fixed laboratory instrumentation is an important aspect of the project's overall QA/QC program. As such, all initial and continuing calibration procedures will be implemented by trained personnel following the manufacturer's instructions and in accordance with applicable EPA protocols to ensure the equipment is functioning within the tolerances established by the manufacturer and the method-specific analytical requirements.

6.6.2 Standard Solutions

A critical element in the generation of quality data is the purity/quality and traceability of the standard solutions and reagents used in the analytical operations. To ensure the highest purity possible, all primary reference standards and standard solutions will be obtained from a reliable commercial source. The laboratories will maintain a written record of the supplier, lot number, purity/concentration, receipt and preparation date, preparer's name, method of preparation, expiration date, and all other pertinent information for all standards, standard solutions, and individual standard preparation logs.

Standard solutions will be validated prior to use. Validation procedures can range from a check for chromatographic purity to verification of the concentration of the standard solution using another standard solution prepared at a different time or obtained from a different source. Stock and working standard solutions will be checked regularly for signs of deterioration, such as discoloration, formation of precipitates, or change of concentration. Care will be exercised in the proper storage and handling of standard solutions, and all containers will be labeled as to compound, concentration, solvent, expiration date, and preparation data (initials of preparer/date of preparation). Reagents will be examined for purity by subjecting an aliquot or subsample to the corresponding analytical method as well.

6.7 DATA MANAGEMENT

6.7.1 Laboratory Data Deliverables

The laboratory data reports will consist of data packages containing the documentation necessary to complete an independent data review of analytical results. Each laboratory data report will include the following:

- Case narrative identifying the laboratory analytical batch number. The narrative shall be signed by the laboratory manager or their designee.
- Matrix and number of samples included.

- Analyses performed and analytical methods used.
- Description of any problems or exceedances of QC criteria and corrective action taken.
- Copy of COC records for all samples included in the analytical batch.
- Tabulated sample analytical results with units, data qualifiers, percent solids, sample weight or volume, dilution factor, laboratory batch and sample number, field sample number, and dates sampled, received, extracted, and analyzed all clearly specified. Surrogate percent recoveries will be included for all organic analyses.
- Blank summary results indicating samples associated with each blank.
- Matrix spike/matrix spike duplicate result summaries with calculated percent recovery and relative percent differences.
- Laboratory control sample results, when applicable, with calculated percent recovery.
- Electronically formatted data deliverable results

6.8 DATA REVIEW, VERIFICATION AND VALIDATION

The purpose of the data quality review is to eliminate unacceptable analytical data and to designate a data qualifier for any data quality limitation discovered. The data quality review will include a review of laboratory performance criteria and sample-specific criteria. The reviewer will determine whether the measurement quality objectives have been met, and will calculate the data completeness for the project. The following guidelines will be used for data validation of all analyses:

- Test Methods for Evaluating Solid Waste, SW-846, USEPA
- USEPA "Laboratory Program National Functional Guidelines for Inorganic Data Review," EPA 540-R-01-008, October 2004, where appropriate

A summary validation will be performed on all data generated by the laboratory. A “summary” data validation review refers to conducting reviews that involve evaluating only the data summary and QA/QC summary sheets provided with all data packages. The “summary” reviews do not involve spot-checking the raw data packages and calculations.

If “summary” reviews indicate potential problematic areas within a data set, a “standard” data validation review may be conducted. A “standard” data validation review refers to conducting a data validation review that requires spot-checking the laboratory’s raw data package and calculations in accordance with the EPA Functional Data Validation Guidelines (USEPA, 2004). The QA/QC Manager will contact the laboratory to discuss the problematic areas; however, if questions still exist, the QA/QC Manager may elect to conduct a “standard” review of the data. The “summary” review will include verification of the following:

- Compliance with this SAP
- Chain-of custody records
- Case Narrative
- Proper sample collection and handling procedures

- Holding times
- Field QC results
- Laboratory blank analysis
- Method detection and reporting limits
- Laboratory duplicate precision
- Matrix spike (MS) recoveries
- Laboratory Control Spike (LCS) recoveries
- Surrogate compound recoveries
- Data completeness and format
- Data qualifiers assigned by the laboratory
- Verification of reported data in electronic data deliverable with the hard copy deliverable

Qualifiers will be added to data during the review as necessary. Qualifiers applied to the data as a result of the review will be limited to:

- U The analyte was analyzed for but was not detected above the reporting limit.
- J The analyte was detected at a concentration less than the laboratory reporting limit, and the result is therefore considered an estimated quantity.
- UJ The analyte was not detected above the sample reporting limit. However, the reporting limit is approximate and may or may not represent the actual limit of quantitation necessary to accurately and precisely measure the analyte in the sample.
- R The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet QC criteria. The presence or absence of the analyte cannot be verified. No associated value is reported.

Results of the data quality review will be included in a data quality review report that will provide a basis for meaningful interpretation of the data quality and evaluate the need for corrective actions and/or comprehensive data validation.

7.0 REFERENCES

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USEPA, 2004. USEPA Contract Laboratory Program, National Functional Guidelines for Inorganic Data Review, October.

Table 1. Summary of Analytical Analysis

Sample Matrix	Analytes	Number of Samples Collected	Number of Sample Analyzed
Soil	Arsenic (As ^{III} and As ^V)	Up to 40	5
	Chromium (Cr ^{VI})		5
	Mercury		36
	Total Metals		3
Seep/Mine Water	Total Arsenic (As ^{III} and As ^V)	Up to 3	2
	Total Chromium (Cr ^{VI})		2 ¹
	Total Mercury		2
	Total Metals		2
	Dissolved Arsenic (As ^{III} and As ^V)	Up to 3	2
	Dissolved Chromium (Cr ^{VI})		2 ¹
	Dissolved Mercury		2
	Dissolved Metals		2
Waste Rock	ABA	3	3
	Inorganic Carbon		
	Particle Size		

Notes:

Metals: Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Sc, Se, Si, Sn, Sr, Ti, Tl, U, V, Zn

ABA - Acid Base Accounting

TBD - To Be Determined. An initial total metals analysis will be performed on 3 samples, analysis of the remaining samples is contingent upon the initial analytical results.

¹ Due to the 24-hour hold time for chromium, this analysis will be run on all samples collected

Table 2. Summary of Sample Containers, Preservation and Hold Times

Sample Matrix	Analytes	Analytical Method	Container	Hold Time
Soil	Arsenic (As ^{III} and As ^V)	Not promulgated method	8oz glass jar	6 months at 4°C
	Chromium (Cr ^{VI})	ASA Memograph 9		6 months at 4°C
	Mercury	7471A		28 days at 4°C
	Total Metals	6010B		6 months at 4°C
Seep/Mine Water	Arsenic (As ^{III} and As ^V) (Total)	Not promulgated method	125 mL PP, HCL preserved, no headspace	6 months at 4°C
	Arsenic (As ^{III} and As ^V) (Dissolved)		125 mL PP, no headspace	
	Chromium (Cr ^{VI}) (Total)	D1687	500mL PP, no preservation, no headspace	24 hrs at 4°C
	Chromium (Cr ^{VI}) (Dissolved)			
	Total Mercury (Total)	EPA 245.1	500mL PP, HNO ₃ , pH<2	28 days at 4°C
	Total Mercury (Dissolved)		500mL PP	
	Total Metals (Total)	EPA 200.7	500mL PP, HNO ₃ , pH<2	6 months at 4°C
	Total Metals (Dissolved)		500mL PP	
Waste Rock	ABA	Modified Sobek	small Ziploc bag	none
	Inorganic Carbon	TBD		
	Particle Size	TBD		
	Metals	6010B/7471A		

Notes:

Metals: Ag, Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Sc, Se, Si, Sn, Sr, Ti, Tl, U, V, Zn

ABA - Acid Base Accounting

TBD - To Be Determined

PP - polypropylene bottle

* The total Mercury and Total Metals can be placed in the same 500mL collection container

* The dissolved Mercury and Total Metals can be placed in the same 500mL collection container

* Dissolved samples will be filtered at the laboratory.

APPENDIX A

Comparing Field Portable X-Ray Fluorescence (XRF) To Laboratory Analysis Of Heavy Metals In Soil

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ABSTRACT

Field portable x-ray fluorescence (XRF) continues to gain acceptance as a complement to traditional laboratory testing of metal contaminated soil. The quality of data produced by field XRF varies with site conditions, soil composition, and sample preparation. Quality assurance protocols for the field method usually require that a number of field samples be split and sent to a laboratory for confirmatory analysis. This confirmatory analysis can provide valuable information of the effectiveness of the field methodology.

We present field and confirmatory data from a variety of contaminated sites that show the effectiveness of field XRF under different site conditions, with different methods of sample preparation. In general, we find that field sample preparation (drying, grinding, sieving, homogenization) significantly improves data quality, compared to unprepared, in-situ measurement. The level of data quality provided by rapid, low-cost in-situ or abbreviated preparation methods can be predicted in the field by the comparison of representative field samples to fully prepared split samples, and can be proven by laboratory confirmation.

We find that the method with which one performs sample splitting for confirmatory analysis can greatly affect the correlation of the field results to the laboratory results. Unexpectedly poor correlation often arises from the introduction of error in the confirmatory sample splitting and sample handling procedures, and which may be misinterpreted as a deficiency of the field method. We discuss ways to avoid the introduction of such error. We also discuss how to use confirmatory analysis to determine the quality of field-obtained XRF data, and we discuss procedures for comparing the field XRF method to the laboratory method.

THE UTILITY OF FIELD METHODS

Field methods can offer significant advantages over laboratory methods, provided they are sufficiently accurate and well-documented to support field decision-making. Field analysis is frequently less expensive per sample than laboratory analysis because of less need for sample handling, transportation,

and chain-of-custody documentation. In addition, the rapid analytical turn-around of a field method can provide timely support for field decision-making, and greatly reduce overall project cost. The lower cost-per-sample allows for denser, more complete sampling. And field methods offer the ability to rapidly delineate contaminated areas or "hot-spots", supporting interim control measures and guiding remediation.

Field portable x-ray fluorescence (XRF) is an exemplary field method, offering extremely rapid, cost-effective screening of heavy metals in soil by *in-situ* measurement. It is also versatile enough to provide *ex-situ*, prepared-sample analysis in the field with accuracy that can rival that of standard laboratory analysis. Even in cases where laboratory analysis is required, field XRF can be used to rapidly pre-screen samples (directly through the plastic sample bag), to obtain the optimal utility from the laboratory sampling effort. Since XRF is completely non-destructive, any sample collected and measured in the field can be retained for verification by a laboratory.

While field XRF cannot generally provide the low detection limits attained by laboratory methods, it can often provide detection limits well below regulatory levels. For example, field XRF can easily provide detection limits for lead-in-soil of less than 100 ppm, well below typical regulatory levels of 300 to 1500 ppm.^[1,2,3]

FIELD SAMPLE PREPARATION FOR XRF

The *in-situ* XRF measurement requires little or no sample preparation. Although the instrument can measure undisturbed soil directly, we recommend a minimal preparation protocol. First, the field operator should remove any debris, such as leaves, twigs, grass, and stones, from the measurement surface. Second, the operator should loosen the soil to a depth of 1.5 to 2.5 cm over an area of at least 10 cm diameter, and stir the loosened soil to achieve some homogenization. The loosened soil may be allowed to dry in the sun for a few hours before the measurement, to improve accuracy. Just before the measurement, the operator should mix and level the loose soil and pack it down gently. For improved accuracy, the operator may screen or comb the loose soil with a 2 mm mesh to remove stones, roots, broken glass, metal fragments, paint chips and other such objects.

Ex-situ measurement offers a variety of sample preparation strategies. A core sampling device may be used to collect the sample to a well-defined depth. A composite sample may be formed by combining soil from several spots in the sample area, mixing thoroughly before measuring. The sample may be dried by spreading it out on a paper and exposing it to sunlight and air, or by using a small field stove or oven. The dried sample can be screened with a 2 mm mesh to remove large objects, and placed in a sample bag, or prepared further. The ultimate field sample preparation for XRF is to grind and sieve the soil to reduce the particle size to less than 0.250 mm (or preferably to less than 0.125 mm), homogenize well, and then sub-sample 3 to 5 grams of the dry, well-ground soil and place in an XRF sample cup for analysis.

The various stages of sample preparation require time and effort, but provide improved measurement accuracy. Core sampling improves the accuracy of the sample definition. Compositing increases the sample support, improving the sample's ability to represent a particular sample area, or "sampling unit". Drying the sample removes the diluting influence of moisture, and facilitates further sample preparation stages of grinding and sieving. Screening the sample with a 2 mm mesh removes the influence of large non-soil particles. Grinding facilitates thorough homogenization of the sample, reducing the effects of fundamental (particle) error and XRF particle-related bias. Sieving with grinding assures complete and accurate particle size reduction. Thorough homogenization assures accurate, unbiased sub-sampling. And the XRF sample cup assures consistent, accurate sample presentation to the XRF instrument. A

companion paper^[4] discusses the importance of particle-related effects and their control in detail.

QUALITY ASSURANCE FOR THE LABORATORY AND FIELD METHODS

Quality assurance (QA) is a basic requirement of any analytical method. No measurement has value for decision-making unless its accuracy is known and understood. A quality assurance program should aim to assess the quality and accuracy of all stages of the measurement process, from sample selection and collection through sample handling and preparation and analysis. Significant levels of error can occur at all stages in the measurement process, and accuracy requires that errors at all stages be controlled. Laboratories concentrate a great deal of effort on their QA programs, which assess and control laboratory sample preparation and analytical error. At present, relatively little QA effort focuses on sample collection and sample handling. That is a pity, because much, if not most, of the overall measurement error occurs in the field, not the laboratory. If we do not assess the errors in the field stages, we cannot know the true accuracy of the laboratory-based measurement.

QA programs generally include calibration checks at several concentrations (typically at "background" or low-level, and at moderate to high level), and replicates (collocated or split samples) to assess variation. QA for a field method usually includes verification or confirmatory analysis of some samples, typically by laboratory. Laboratory confirmatory backup may be required for field methods used in decision-making, and assures that the field method is appropriate, effective, and of sufficiently accurate for its purpose. For in-situ XRF, the accuracy can vary significantly from site to site. Fully prepared ex-situ XRF offers the potential for field-based verification of the in-situ XRF method.

The laboratory confirmatory method should match the field method as well as possible. For example, since XRF is a total element method, the confirmatory method should also be a total element method. For lead, most laboratories use atomic absorption spectrometry (AAS) or inductively coupled plasma atomic emission spectrometry (ICP-AES). Both of these methods require that the soil sample be introduced to the instrument as a solution, so the lab must perform sample extraction or digestion. Laboratory analysis of total lead requires a strong acid total digestion to achieve complete dissolution of the sample. Weak acid extraction and leaching-based methods, such as the toxicity characteristic leaching procedure (TCLP), are not appropriate confirmatory methods for the total element XRF method. The most appropriate confirmatory method for XRF would completely digest siliceous minerals, as does EPA draft method 3052. However, total digestion is relatively difficult and expensive, and seldom used in environmental analysis. More commonly used strong acid-based extractions such as EPA methods 3050 and 3051 generally recover most of the heavy metal content, but they cannot recover metals locked within an undissolvable silicate.

ASSESSING TOTAL MEASUREMENT ERROR

Error includes the components of bias and precision (or variation). It is difficult to determine the true measurement bias, because we do not generally know the true concentration of the contaminant in the sampling unit. Instead, we must be satisfied to compare our measurement results against confirmatory results. We can assess the total measurement precision by replicate sampling the sampling unit, and observing the variation of the resulting measurements. To avoid spatial bias in our assessment, we avoid taking replicates from identical sampling locations. Ideally, we select replicate sampling locations randomly throughout the sampling unit. The sampling unit is the volume of soil a particular sample is intended to represent. For example, suppose the sampling unit is a plot running along a 10 meter long wall, from the wall to 2 meters from the wall, and from the surface to a depth of 2.5 cm. The total area of the sampling unit is then 20 square meters, and the total soil volume is 0.5 cubic meters. If the sampling protocol calls for a composite sample of 6 randomly located cores, then replicates should be

sampled and composited exactly the same way: as 6 randomly located cores. The greater the number of replicate samples, the more accurately we can determine the total measurement precision. For routine work, it may be sufficient to take only two replicates (that is, one duplicate pair) per sampling unit. The precision may be expressed in terms of relative standard deviation (RSD), or coefficient of variation (COV), which is simply the standard deviation of the set of replicate sample results divided by the mean of the set.

Total measurement variation may be substantially larger than you expect! It includes the variation in sample representation, sample collection, sample handling, sample preparation (including subsampling and homogenization), and analysis. Particle effects, including fundamental error, can generate serious variation in sampling and subsampling, depending on the particulate form of the contaminant. Soil contaminated by paint chips can exhibit severe particle effects, with relative errors easily exceeding 20 percent; this is discussed in detail in a companion paper.^[4] Another significant contributor to total error is the representativeness of the sample collected. The contaminant is not likely to be distributed evenly through the sampling unit. If we ignore spatial variation and let a single point represent a large area, we can expect relative errors of at least 20 percent. To reduce the effect of spatial variation, we must "increase sample support"; composite a sample from several points in the sampling unit. The total measurement variance, σ_{total}^2 , is given by the sum of the individual component variances:

$$\sigma_{total}^2 = \sigma_{sample\ representation}^2 + \sigma_{sample\ collection}^2 + \sigma_{sample\ handling}^2 + \sigma_{sample\ preparation}^2 + \sigma_{analysis}^2,$$

where the σ 's denote the errors introduced at each stage of the measurement process. The error due to the analytical stage itself, $\sigma_{analysis}$, may be a minor, even negligible contributor to the total error.

Suppose our field method has an analytical error of 10 percent, while the lab method has an analytical error of only 1 percent. You might expect that your choice of field or lab method will seriously affect the total measurement error. Not necessarily so. Suppose the total relative error using the super accurate (1%) lab analysis is 30 percent. Then the total relative error using the field method (precision 10%) ought to be

$$\sigma_{total} = \text{SQRT}((30\%)^2 - (1\%)^2 + (10\%)^2) = 31.6\%.$$

The difference in total error (31.6% versus 30%) is of little or no practical significance. In general, a component of error will affect total error only if it is large relative to the other components. If analytical error is much smaller than sampling and preparation-related errors (and it often is), then it will little affect total measurement error.

ASSESSING THE COMPONENTS OF MEASUREMENT ERROR

To assess the variation due to a particular stage of the measurement process, we prepare identical (replicate) splits and carry the replicates individually through the stage and the remainder of the measurement process. The variance due to a particular stage is calculated from the variance of the identical replicate results, minus the variances due to the remaining measurement stages.

The easiest measurement stage to assess for precision is the final, analytical stage. Analytical replicates entering analysis must be as identical as possible. For XRF this condition is particularly easy to satisfy:

replicates can be repeat measurements of the same sample. For the laboratory, analytical replicates can be splits from a well-mixed digestate liquid.

Variance due to the final subsample and packing of the XRF sample cup can be assessed by preparing replicate sample cups from a well-mixed container of ground, sieved sample material. The variance due to subsampling and cupping is the variance of the replicates minus the variance of the analytical replicates.

COMPARING AND CORRELATING DIFFERENT ANALYTICAL METHODS

If you want to compare two different analytical methods, the most accurate assessment of their equivalence will derive from the analysis of identical sample material. The sample material should be split as late as possible in the measurement process to assure that the two analytical methods see similar material. Otherwise, variance will be introduced in intermediate stages that will ultimately degrade the accuracy of the assessment, even if such variance is carefully measured and subtracted from the total.

Suppose we wish to compare two atomic spectrometry methods, AAS and ICP-AES. The sample preparation is identical; both require sample digestion. So we split the sample *after* the digestion. The two methods will measure identical liquid digestate. Any difference between the two measurement results can then be attributed to the analytical stage, not to the sample collection, sample handling, or sample preparation. If we wish to assess variation in the sample preparation stage, that assessment should be performed separately.

Suppose instead we wish to compare AAS with prepared sample XRF. We split the sample after the final stage of XRF sample preparation. The dried, ground, sieved and mixed material will split accurately, giving uniform analyte concentration to each method. Alternately, instead of splitting, we can send the analyzed XRF cup to the lab, assuring that the sample is truly identical. Of course, we do not compare XRF directly to AAS, but to the combination of the digestion method and AAS analysis. We can attribute differences in the results to the digestion and to the analytical methods, but not to variation in the sample collection and handling stages.

But if we wish to compare in-situ XRF with lab AAS, we must split the sample early in the measurement process, since the in-situ method requires so little sample preparation. We should still strive to make the sample splits as identical as possible. The in-situ XRF method measures a small area of ground, only a few square centimeters. As nearly as possible, the sample taken to the lab for comparison to AAS should be removed from the same spot measured by the in-situ method.

When we observe differences between analytical methods, we must bear in mind that significant variation results from the sample collection, handling, and preparation stages. We should always consider the big picture: total measurement error. Unless two analytical methods differ by a more than a few percent, the impact on total measurement error will probably be insignificant.

EXPERIMENTAL DETAILS

The data presented in this paper come from the study of samples from three lead-in-soil sources. The first source was a site around a highway bridge in Smithtown, Long Island, New York. The soil around the bridge had been contaminated by leaded paint that had come off the bridge through the aging and weathering of the painted surfaces, and through bridge maintenance activities. We observed visible paint chips in many of the samples. The second source was an archive of Massachusetts residential lead-in-soil samples collected by Environmental Science Laboratory, Inc. We believe most of the lead in these

samples was derived from paint chips. The third source was a low-income residential tract in Northbridge, Massachusetts where lead-in-soil had been determined to be the cause of 6 childhood lead poisoning cases. The Massachusetts Department of Environmental Protection (MA-DEP) was overseeing remedial activities in the neighborhood at the time the measurements were performed. Since paint chips were not visible in the soil at this site, we believe that most of the lead was contained in finely-dispersed particles. Many of the samples measured high in zinc as well as lead, indicating that the likely contaminant origin was paint. The samples from the three sources represented a variety of soil types and textures, from sandy to loamy to clayey.

All XRF data were collected with a NITON XL equipped with a 10 mCi cadmium-109 radioisotope source, silicon PIN diode detector (750 eV resolution), and the Lead-In-Soil Analysis (LISA) software package. The LISA software reports concentrations in parts per million (ppm) for lead, arsenic, zinc, and copper in soil with matrix corrections determined by Compton normalization.[1] A newer model, the NITON 700, offers similar performance for lead, but with expanded multiple element capability.

In-situ XRF measurements were prepared minimally, by removing debris, loosening the soil, stirring the soil, and flattening the soil before measurement. The bridge samples of approximately 250 grams each were transported raw in heavy plastic bags and measured by the in-situ XRF method in the laboratory. In-situ measurements were 30 seconds in duration, adjusted for source decay. Ex-situ samples of approximately 100 grams each were field-prepared by air and/or sun drying, screening with a 2 mm sieve, then grinding and sieving to 0.250 mm or 0.125 mm. We measured prepared samples in Mylar window XRF cups for 120 seconds duration, adjusted for source decay.

Environmental Science Laboratory (Medway, MA), an ELPAT proficient and A2LA accredited laboratory, analyzed the Long Island bridge samples and the Massachusetts residential samples by flame-AAS. The MA-DEP Wall Experiment Station (Lawrence, MA) analyzed the Northbridge samples by ICP-AES. Both laboratories used microwave-assisted strong acid extractions, and achieved recoveries of 80 to 93 percent on reference materials (RMs). Since Wall Experiment Station reported results in mg/kg wet mass, we calculated mg/kg dry mass with water content determined by gravimetry. We adjusted both laboratory data sets by constant factors to give mean recoveries of 100 percent on RMs.

RESULTS AND DISCUSSION

The XRF method gave excellent performance on reference materials. (Graph 1) A set of 14 measurements on NIST Standard Reference Material (SRM) soils and Environmental Lead Proficient Analytical Testing Program (ELPAT) soils gave a linear regression slope of 0.996 and an R^2 of 0.996. For the 10 reference soils with more than 100 ppm lead, the mean recovery of the XRF was 0.992 and the standard deviation of the recovery was 0.058, for an RSD of 5.8 percent.

Fully prepared XRF samples showed excellent correlation with laboratory AAS for material split after the final grinding, sieving, and homogenization. (Graph 2) A set of 20 fully prepared XRF samples (oven dried, ground to 0.125 mm), including 11 bridge site samples, 6 residential lead samples, and 3 NIST SRM soils, gave a linear regression slope of 1.004 and an R^2 of 0.995. For the 17 samples with lead concentrations above 100 ppm, the mean recovery of the XRF relative to AAS was 0.952 and the standard deviation of the recovery was 0.068, for an RSD of 7.1 percent. The subset of 11 bridge site samples gave a linear regression slope of 0.958 and an R^2 of 0.994. The subset of 6 Massachusetts residential samples gave a linear regression slope of 1.010 and an R^2 of 0.994. We were pleased to observe such strong correlation of widely different analytical methods, especially considering the possibility of less than total lead recovery by the laboratory extraction.

The Massachusetts residential samples yielded an unexpected observation of variation due to standard laboratory protocol for sample preparation. These archive samples had already been dried and ground to pass a 0.500 mm mesh, subsampled, digested and measured by AAS according to standard lab protocol. We ground the samples further, to pass a 0.125 mm mesh, in order to prepare for XRF analysis. We then submitted a 1.0 gram subsample of the finely ground material to the lab for a second analysis, and it is that data which gave an impressive R^2 of 0.994 against XRF. Interestingly, when we compared the XRF data to the original lab data for the same samples, the correlation was decidedly less impressive: R^2 was only 0.958. In fact, the XRF readings correlated with the final AAS readings far better than the original AAS readings did! (Table 1) We believe the better correlation was due to better control of fundamental (particle) error in the laboratory subsampling by the reduction of particle size from 0.500 mm to 0.125 mm. The recovery of the original AAS readings versus the final AAS readings ranged from 0.962 to 1.226, with an RSD of 11.3 percent. This finding supports the argument that fundamental error in subsampling can have a major impact on the precision of the laboratory sample preparation method. If you require better precision than the standard laboratory protocol delivers, consider preparing the sample yourself, by drying, grinding, sieving, mixing, and subsampling, before submitting it to the lab.

Seven field-prepared composite samples (mixed, air and sun dried, ground to 0.250 mm or less) from the Northbridge site, when correlated against the adjusted lab ICP-AES values, gave a linear regression slope of 1.004 and an R^2 of 0.982. (Graph 3 and Table 2) The mean recovery of these 7 samples was 0.997 and the standard deviation of the recovery was 0.066, for an RSD of 6.6 percent.

As expected, in-situ XRF samples did not correlate with the lab as well as did prepared samples, and the performance of the in-situ method varied by site. (Graph 4) The bridge site in-situ method results had a slope of 0.548 and an R^2 of 0.737; negative bias was pronounced on the highest concentration samples. The bridge site in-situ data were all single, uncomposited in-situ readings. The Northbridge in-situ samples, given as mean values of several spots in the sampling unit and compared against a composite sample sent to the lab gave a regression slope of 0.969 and an R^2 of 0.915. We attribute the better in-situ performance at the Northbridge site to a well-dispersed, small particle contaminant.

To examine the effect of spatial variation on single spot in-situ measurements, we recorded individual readings for each of 5 to 6 spots in each of 5 sampling units at the Northbridge site. The five sampling units varied in area from a drip line approximately 10 m long by 0.5 m wide (5 m^2) to a rectangular yard of approximately 50 m^2 area. Compared with the lab analysis of the sampling unit composites, the set of 28 individual spot in-situ readings showed a mean recovery of 0.966 with a standard deviation of 0.320, giving an RSD of 33.1 percent. The means of the 5 to 6 spot in-situ readings per unit gave better correlation with the lab composites: mean recovery was 0.986 with a standard deviation of 0.150, giving an RSD of 15.2 percent. (Graph 5 and Table 2) By averaging 5 to 6 spot in-situ scattered through each sampling unit, we effectively "composite" a sample mathematically, improving sample support. We also retain the spatial data from the individual spot readings, giving us useful insight into site specific spatial variability and representativeness.

CONCLUSIONS AND RECOMMENDATIONS

Field prepared XRF can correlate extremely well with laboratory atomic spectrometry. The total measurement quality depends as much on sample support, collection, handling, and preparation procedures as it does on choice of analytical method. We can determine total measurement precision through replicate sampling within the sampling unit. We can better control overall measurement quality by paying close attention to sampling, handling, and preparation protocols. We can compare different analytical methods most effectively by splitting the sample as late as possible in the measurement

process to eliminate variation caused by sample handling and preparation.

In-situ XRF provides rapid, low-cost measurement of heavy metals in soil with a minimum of sample preparation. While the in-situ XRF method is not generally as accurate as the ex-situ prepared sample method, it allows for more thorough sampling of an area to map out contamination patterns and assess spatial variation. The accuracy of the in-situ method depends on site-specific conditions of contaminant particle size and distribution; the accuracy can be assessed in the field by comparison to the prepared sample XRF method.

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Table 1: Massachusetts residential lead-in-soil samples measured by AAS before and after XRF sample preparation. The original samples had been dried and ground to 0.500 mm before subsampling for the microwave-assisted strong acid digestion and AAS analysis. Afterward, the dried ground samples were further ground to 0.125 mm, mixed, subsampled for XRF analysis, and then subsampled for a final microwave digestion and AAS analysis. Correlation coefficient (R^2) between the XRF and AAS values improved from 0.958 with the original AAS results to 0.994 with the final AAS results.

Sample	AAS-original (ppm)	XL-LISA (ppm)	AAS-final (ppm)
9502445	3251	2715	2652
9502446	508	549	524
9502557	605	500	535
9502448	2230	2310	2271
9502449	5487	6512	5704

Table 2: Northbridge samples first measured in-situ (composites averaged), then manually composited (where noted), field prepared and measured by XRF, then split and measured by laboratory ICP-AES. Agreement of in-situ XRF with field prepared XRF predicts agreement with the lab.

Sample	Composite sample?	In-situ XRF mean (ppm)	Field prep'd XRF (ppm)	Lab ICP-AES (ppm), adj.
Dripline C	Y	2561	3155	3004
Dripline 1	N	2512	2325	2354
Yard C	Y	1546	1637	1520
Yard 1	N	2347	2096	2217
Cover area C	Y	1132	1174	1328
Play area C	Y	942	796	774
Doghouse C	Y	932	944	940
Doghouse 1*	N	3632*	N/A*	15213*

*This sample was not dried and ground for field prepared XRF analysis before the laboratory split. Post-split preparation of the sample in a laboratory environment yielded an XRF reading of 12100 ppm. The sample came from a highly localized hot-spot which would not have been discovered without field XRF. Five in-situ method measurements of this non-composite sample ranged from 2976 ppm to 5885 ppm, indicating highly inhomogenous composition. The moisture content was 24.1 percent.

Graph 1: Performance of field portable XRF for lead-in-soil reference materials: NIST SRM numbers 2709, 2710, and 2711, and ELPAT soil samples from rounds 016 and 017.

NITON {GRAPH 1}

Graph 2: Comparison of fully prepared XRF (oven dried, screened, ground to 0.125 mm or less, and cupped) and laboratory AAS results on Long Island bridge site soil samples, Massachusetts residential lead-in-soil samples and NIST Standard Reference Materials.

NITON {GRAPH 2}

Graph 3: Comparison of field prepared XRF (field dried, screened, ground to 0.250 mm or less, and cupped) and laboratory ICP-AES for Northbridge lead-in-soil samples.

NITON {GRAPH 3}

Graph 4: Comparison of in-situ XRF results with laboratory AAS and ICP-AES. The Long Island bridge site in-situ measurements exhibit strong negative bias, probably due to the concentration of lead in relatively large particles (paint chips).

NITON {GRAPH 4}

Graph 5: Comparison of individual spot in-situ readings and averaged in-situ readings with laboratory ICP-AES measurement of composite samples. Samples from Northbridge site.

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