

FIELD XRF ANALYSIS OF ARSENIC AND LEAD IN SOILS AT A FORMER SMELTER FACILITY

by

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Abstract: Field X-ray fluorescence (XRF) chemical analyses were performed to efficiently and cost-effectively evaluate arsenic and lead concentrations in soils as part of CERCLA-driven remedial investigations at a former lead smelter. Sample preparation and analysis protocols, including extensive quality control (QC) requirements, were developed for the field XRF method that were accepted by the United States Environmental Protection Agency and other regulatory agencies. Over 800 soil samples from approximately 150 borings and test pits were analyzed using the field XRF technique during a three-week period. Measured arsenic and lead concentrations ranged over several orders of magnitude. Costs for using the field XRF technique were about 60 to 70 percent of the costs for traditional wet chemistry (acid digestion and spectrophotometric analysis) methods, which were also used to analyze selected samples for verification. Split samples analyzed during and immediately after the field investigation showed a good correlation between soil concentrations obtained using field XRF methods and concentrations obtained using laboratory analysis (both XRF and wet chemistry). Correlation coefficients (r^2) for split samples compared using linear regression ranged from 0.832 to 0.995. Split-sample comparisons were generally better at lower soil concentrations (<10,000 ppm arsenic, <15,000 ppm lead). Duplicate, blank, and control standard results for the field XRF method were within limits typically achieved by laboratory-based systems. Preparation study results suggested that increased levels of soil-sample preparation may not significantly improve data comparability. Overall, results indicated that the field XRF technique is a dependable method for "screening-level" investigations in which solids are differentiated based on order-of-magnitude differences in arsenic and (or) lead concentrations. The field XRF method allowed rapid turnaround of analytical results while achieving data quality and comparability goals acceptable for a CERCLA remedial investigation.

Introduction

This report summarizes results of using a field XRF instrument to perform "screening-level" testing of soil samples for total lead and arsenic. This technique was used as part of a former smelter facility remedial design investigation in the western United States (US).

Use of the field XRF technique augmented laboratory testing efforts and allowed analytical results to be obtained according to a schedule that permitted daily evaluation of test results. The cost for using the field XRF technique was about 60 to 70 percent of the cost for wet chemistry methods. Field XRF costs did not include development costs, or costs incurred for shipping and expedited turn-around time (typically 24 hours).

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Over 800 field XRF samples were analyzed during a period of about three weeks. Use of this technique enabled interpretation of approximately 60 results a day (with 24-hour turn-around time), which allowed direction and modification of the ongoing field investigation. Critical verification and confirmation samples, as well as appropriate Quality Assurance and Quality Control (QA/QC) samples, were also submitted for laboratory analyses (XRF and wet chemistry). As part of this investigation, a procedural analysis was

performed to assess the effectiveness of each field XRF sample-preparation step used during the investigation.

Based on information received from the US Environmental Protection Agency (EPA Region 8), the portable field XRF method had not been used successfully in the past for this specific application, to quantify relative differences in arsenic concentrations. The protocols developed for this project were scrutinized and accepted by the EPA and other state and local regulatory agencies. The field XRF method developed and reported herein corresponds closely to EPA-accepted laboratory methods typically used in inorganic laboratories. The purpose of this paper is to provide a summary of information regarding this technique, so that it may be used in the future as a tool to complement laboratory analyses when performing exploration, site characterization, or remediation investigations.

Methods Description

To meet the objectives of the recent remedial design investigation, the majority of XRF chemical analyses to evaluate arsenic levels were performed on a "screening" level. The accuracy requirements of this testing consisted of delineating materials with arsenic concentrations on the order of several hundred milligrams per kilogram (mg/kg) or parts per million (ppm), from materials with arsenic concentrations of 10,000 ppm or greater. Lead concentrations in soil were also measured using the field XRF technique. As a part of the procedure, confirmation and verification of arsenic (As) and lead (Pb) analysis results were also performed using accepted laboratory XRF and wet chemistry methods.

Procedures associated with using field XRF techniques as a screening tool were based on information derived from the following sources:

- EPA Draft Method 6200: Field Portable XRF Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment (EPA, 1996).
- Niton Corporation XL Spectrum Analyzer User's Guide to Measuring Metal in Soil.
- Existing laboratory soil analytical procedures.

A field portable XRF instrument (NITON model 702 multi-element bulk-sample analyzer) was used for this investigation. This instrument uses an X-ray spectrophotometer to bombard the sample with X-rays, which in turn causes elements in the sample to fluoresce, producing a specific spectral emission.

Element concentrations in the soil sample are quantified by comparing the intensities of spectral emissions in the sample to a calibration curve generated from standards with known concentrations. The detection limit for soil analyzed by field XRF techniques varied with individual samples. Generally the detection limit was less than 100 ppm.

In addition to the field portable XRF instrument, other equipment used to perform the analyses consisted of testing materials (including sample cups, mylar film, filter paper, and storage and shipping supplies), soil grinder, sample dryer, portable lab trailer with a ventilated hood, sieves, air compressor, laptop computer, and health and safety equipment (including gloves and respirator).

Based on experience with this investigation, two people can comfortably perform the field sample preparation, analyses, and reporting tasks. Initially, a third person may prove useful in setting up and getting started. Two people can handle about 40 to 60 samples per day (maximum of 80).

The following is a summary of the field XRF procedures developed for the investigation. Field procedures focused on sample homogenization using various preparation procedures (sieving, drying, grinding), QA/QC, and XRF instrument operation. Additional XRF testing to evaluate the effectiveness of each sample preparation step is discussed in the Sample Preparation Process Evaluation Section.

Field XRF Sample Preparation, Calibration, Analytical Quality Control Procedures:

1. Collect sample (1000 to 2000 grams).
2. Homogenize sample by hand, and remove a representative aliquot for processing by the cone and quartering method. The remaining sample is archived.
3. Air or oven dry samples.
4. Disaggregate and sieve sample (#10 mesh); decontaminate equipment between samples.
5. Machine grind, decontaminate equipment between samples.
6. Sieve ground sample (#60 and #120 mesh), decontaminate equipment between samples.
7. Bag ground, sieved sample, and produce any required splits.
8. Place prepared samples into plastic XRF cups.
9. Samples analyzed in groups of 20 (one batch) for total arsenic and lead.
10. Calibration - The Niton model 702 instrument is auto-calibrating; the self-calibration is performed

once per hour of continuous use, according to the manufacturer's recommendation.

11. Site-specific Matrix Correction - A set of samples from the project site which have been previously used to calibrate the laboratory XRF instrument are analyzed using the field instrument prior to analyzing any investigation samples. A correlation curve is developed for the project by which instrument readings from the field can be corrected, if necessary.
12. Quality control samples -
 - Calibration verification - Percent recovery is recorded using a sample of known concentration (one per batch).
 - Instrument and (or) method blank - A blank sample of clean silica sand processed as a routine sample (one per batch).
 - Field duplicate - Submitted to field lab blind (one per batch).

A preliminary set of site-specific samples previously characterized using laboratory-based methods (XRF and wet chemistry) were analyzed with the field XRF instrument to assess the necessity of bias correction to achieve comparable results. The comparison of field XRF and wet chemistry results is shown in Table 1. This level of agreement between field XRF and wet chemistry results was deemed adequate for purposes of "screening"-level soil characterization.

A data summary form was completed as field XRF testing proceeded. Soil samples were processed and analyzed in batches of 20, with appropriate field QA/QC samples (duplicates, blanks and standards). The data summary form also accommodates laboratory

Verification and confirmation data generated subsequent to completion of the field analyses. Completion of this form concurrently with ongoing field activities provides prompt data summaries for field interpretation, and allows flagging of samples with potential interference problems which may require laboratory analysis.

A critical aspect of XRF analysis (both laboratory and field-based methods) is proper resolution of arsenic and lead peaks in the fluorescence spectrum. Peak overlap in samples with high lead concentrations can cause under-reporting of arsenic concentrations. The field XRF instrument used during this investigation was factory-calibrated to measure arsenic as accurately as possible, even in samples with high lead concentrations. In addition, samples with reported field XRF lead: arsenic concentration ratios of 2:1 or greater were flagged for confirmatory laboratory analysis.

Quality Assurance/Quality Control

The precision and accuracy of field XRF measurements were evaluated using field and laboratory QA/QC samples, the results of which are presented in Tables 2 and 3. Duplicate, standard, and blank analyses indicate that the field XRF measurement technique provides data with accuracy and precision acceptable for the purpose of this investigation. Typical control limits for duplicate analyses consisted of relative-percent-difference (RPD) values of 35 percent or less. These limits were routinely achieved for field and laboratory, duplicate and split, samples.

Generally, field XRF results agree well with laboratory results. For both arsenic and lead, field XRF results tend to be higher than laboratory XRF results at concentrations greater than 15,000 ppm. Wet chemistry and laboratory XRF duplicate results indicate

Table 1 - Preliminary Comparison of Project Soil Sample Results

WET CHEMISTRY RESULTS		FIELD XRF RESULTS		RELATIVE PERCENT DIFFERENCE (RPD)	
As (ppm)	Pb (ppm)	As (ppm)	Pb (ppm)	As	Pb
32,560	3292	33,800	3043	2	8
15,840	655	12,600 ^(a)	606 ^(a)	23	8
15,840	655	13,300 ^(a)	541 ^(a)	17	19
2356	1283	1908	1060	21	19

^(a) Duplicate Field XRF results (separate analyses of the same sample)

Table 2 - Summary of Field XRF QA/QC Information

QC SAMPLE TYPE	FREQUENCY COLLECTED	AVERAGE RPD (PERCENT) (or other, as indicated)	
		ARSENIC	LEAD
Field blind duplicate for lab XRF analysis	At least 5 percent of field XRF samples	14	24
Field instrument duplicate	At least 5 percent of field XRF samples	11	8
Field (lab) method duplicates	At least 5 percent of field XRF samples	14	20
Lab control sample (calibration verification)	At least 5 percent of field XRF samples	14	20
Field instrument/ method blank (clean silica sand)	At least 5 percent of field XRF samples	69 percent of samples below arsenic detection limit; 97 percent of samples below 150 ppm arsenic	
Lab XRF comparison sample	At least 25 percent of field XRF samples	29	23
Lab wet chemistry comparison sample	At least 5 percent of field XRF samples	29	16
Raw lab XRF duplicates	15 samples	29	23
Other splits	4 samples	50	62

Table 3 - Comparison of Arsenic and Lead Results (38 Samples)

METHODS COMPARED	AVERAGE RPD (PERCENT)	
	ARSENIC	LEAD
Field XRF/Wet Chemistry	29	17
Lab XRF/Wet Chemistry	16	23

that field XRF results for arsenic may be biased high for concentrations greater than 20,000 ppm. Improvements in the comparison between field and laboratory XRF concentrations were observed for arsenic at concentrations less than about 15,000 ppm and for lead at concentrations less than about 7,500 ppm.

The QA/QC protocols followed during validation of the results reported herein are in accordance with specific data-quality objectives. These objectives include precision, accuracy, representativeness, completeness, and comparability. These sampling and analytical specific objectives are consistent with guidelines provided by the EPA (EPA, 1994; EPA, 1993a; EPA, 1993b; EPA, 1993c).

Evaluation of the Process for Preparing Samples

In conjunction with this investigation, an evaluation of field-XRF sample-preparation procedures were performed. This evaluation consisted of using 20 soil samples and measuring arsenic and lead

concentrations with the NITON field XRF instrument after each of the following sample preparation steps (treatments).

- **Treatment 1:** Measured in-situ.
- **Treatment 2:** Collected and homogenized sample in ziploc bag.
- **Treatment 3:** Sample placed in XRF sample cup (no grinding).
- **Treatment 4:** Sample dried and ground (60 mesh), placed in XRF sample cup (full sample preparation).

One set of QA/QC samples (field duplicate, laboratory duplicate, blank, and standard) was also analyzed in conjunction with the four preparation procedures. QA/QC testing results were within established limits discussed above. Arsenic and lead results for the sample preparation study are summarized in Tables 4 and 5, respectively.

**Table 4 - Summary of Field XRF Sample Preparation Process Evaluation
Soil Arsenic (As)**

Lab ID	Field XRF As Concentration (ppm) Treatment Number				Wet Chemistry Concentration As (ppm)	Field XRF/Wet Chemistry RPD Treatment Number			
	1	2	3	4		1	2	3	4
001	146	145	139	169	277	62%	63%	66%	48%
002	187	290	153	333	378	68%	26%	85%	13%
003	664	506	658	703	976	38%	63%	39%	33%
004	756	515	542	528	758	0%	38%	33%	36%
005	541	429	558	490	705	26%	49%	23%	36%
006	1531	1052	1121	1097	1574	3%	40%	34%	36%
007	1430	1178	1348	1472	1853	26%	45%	32%	23%
008	228	367	338	319	521	58%	35%	43%	48%
009	341	295	335	343	549	47%	60%	48%	46%
010	<54	<53	<50	<50	41	nc	nc	nc	nc
011	115	103	<57	103	140	20%	30%	nc	30%
012	145000	113000	197000	280000	154907	7%	31%	24%	58%
013	32800	37700	40700	47300	38970	17%	3%	4%	19%
014	1188	1456	1528	1548	904	27%	47%	51%	53%
015	4566	3094	2993	4115	4228	8%	31%	34%	3%
016	<44	<44	<43	<42	<20	nc	nc	nc	nc
017	442	<58	<58	<59	51	159%	nc	nc	nc
018	167	126	<69	<83	141	17%	11%	nc	nc
019	2185	2241	2480	2228	2923	29%	26%	16%	27%
020	7020	412	4876	7014	6508	8%	45%	29%	7%
Average:						34%	38%	37%	32%

nc = Not calculated due to measurement below detection limit.

**Table 5 - Summary of Field XRF Sample Preparation Process Evaluation
Soil Lead (Pb)**

Lab ID	Field XRF Pb Concentration (ppm) Treatment Number				Wet Chemistry Concentration As (ppm)	Field XRF/Wet Chemistry RPD Treatment Number			
	1	2	3	4		1	2	3	4
001	146	208	243	266	343	81%	49%	34%	25%
002	378	499	682	666	708	61%	35%	4%	6%
003	637	562	556	654	766	18%	31%	32%	16%
004	414	324	319	444	501	19%	43%	44%	12%
005	276	208	254	275	344	22%	49%	30%	22%
006	692	470	450	571	528	27%	12%	16%	8%
007	548	537	585	748	701	24%	26%	18%	6%
008	329	322	357	413	462	34%	36%	26%	11%
009	281	330	349	422	482	53%	37%	32%	13%
010	106	117	111	121	149	34%	24%	29%	21%
011	129	146	206	236	263	68%	57%	24%	11%
012	23200	25900	25800	38800	37887	48%	38%	38%	2%
013	8697	9363	11600	17600	17617	68%	61%	41%	0%
014	2662	4323	5068	5123	7576	96%	55%	40%	39%
015	2312	1352	1543	2668	3556	42%	90%	79%	29%
016	<20	<20	<20	<19	21	nc	nc	nc	nc
017	88.8	120	88.2	176	139	44%	15%	45%	23%
018	337	286	346	458	574	52%	67%	50%	22%
019	3763	4518	4739	5606	6363	51%	34%	29%	13%
020	11100	8800	10700	13800	13760	21%	44%	25%	0%
					Average:	45%	42%	33%	15%

nc = Not calculated due to measurement below detection limit.

In most cases, good agreement was obtained for the four treatments field XRF sample-preparation and laboratory wet-chemistry results. No "order-of-magnitude" differences were observed associated with arsenic and lead concentrations. The differences between various field XRF sample preparation results and wet-chemistry results have been quantified by calculating the RPD for each field XRF and wet chemistry data pair. For the purpose of this investigation, the wet chemistry results are assumed to be more accurate and are used as the independent

variable. However, wet-chemistry data may not be equivalent to the "true" concentration of the sample because an analytical measurement of any kind (wet chemistry or XRF) has an associated error.

Average RPD values for arsenic were similar (near 35 percent) for each of the preparation treatments (Table 4). Overall agreement between field XRF and wet-chemistry data was not significantly improved by increasing the level of sample preparation (see average RPD values in Table 4). However, different trends are

evident when examining the RPD results for samples with arsenic concentrations above and below 400 ppm. It appears that by performing at least some level of sample preparation (Treatment 2 or Treatment 4), variability due to sample arsenic concentration levels can be reduced, and similar RPD values can be obtained for both high- and low-concentration samples. For Treatment 1 and Treatment 3, low-concentration samples exhibited much higher RPD values than relatively high-concentration samples, as presented in Table 6.

In addition to arsenic RPD calculations, least-squares linear regression analyses were performed for each of the four sample treatments using wet-chemistry values as the independent variable and field XRF measurements as the dependent variable. For comparisons of this type, regression parameters of slope = 1, intercept = 0, and r-squared = 1.00 indicate near perfect agreement between analytical methods. The regression parameters for each treatment are shown in Table 7.

The regression analyses show that, for the purposes of "screening-level" XRF analysis, all four field preparation treatments showed reasonable agreement between field XRF and wet chemistry results. The higher slope and intercept values for Treatment 4 suggest a lower level of overall comparability for field XRF and wet chemistry analyses. However, the arsenic values compared in the regression analysis range over four orders-of-magnitude (from less than 100 to greater than 100,000 ppm), and examination of the data in Table 4 show that

in most cases, the level of agreement is acceptable for "screening-level" analyses. In addition, there is the possibility that treatment 4 XRF data may be a better estimate of the true arsenic concentration than the wet chemistry concentration.

The results associated with the evaluation of the process for preparing samples for lead, in contrast to arsenic, show that increasing levels of sample preparation did affect lead RPD values (Table 8). Overall average RPD values for field XRF and wet-chemistry results decrease consistently with increasing levels of preparation. RPD values for samples with lead concentrations both greater than and less than 1000 ppm (based on wet chemistry measurements), indicate only Treatment 4 had slightly lower RPD values for high-concentration samples (>1000 ppm) than for low-concentration samples (<1000 ppm). Treatment 4, the most intensive level of sample preparation, also produced the best agreement (lowest RPD) for both high- and low-concentration lead samples with essentially identical average RPD values for both data ranges.

The Draft EPA Field XRF Protocol (EPA, 1996) incorporated the results of a study of the effects of preparation procedures on the precision and comparability of XRF sample results. The preparation steps studied by the EPA were generally similar to the four treatments outlined above. The EPA study assessed the performance of the field XRF instruments relative to wet-chemistry methods by performing linear regression, and estimated the effects on precision of results from each step by comparing the relative standard deviations of ten replicate measurements on 12 soil samples covering a range of arsenic, lead and other metal concentrations. Results of the EPA study indicated that precision was relatively unaffected by

Table 6 - Summary of Average Arsenic (As) RPD Results (Field XRF/Wet Chemistry)

Data Range	Treatment 1	Treatment 2	Treatment 3	Treatment 4
<400 ppm As	65%	33%	76%	31%
>400 ppm As	23%	39%	32%	33%

Table 7 - Summary of Arsenic Regression Analysis Results (Field XRF/Wet Chemistry)

Parameter	Treatment 1	Treatment 2	Treatment 3	Treatment 4
slope	0.93	0.74	1.26	1.79
intercept	-107	323	-931	-1928
r-squared	0.999	0.993	0.998	0.994

Table 8 - Summary of Average Lead (Pb) RPD Results (Field XRF/Wet Chemistry)

Data Range	Treatment 1	Treatment 2	Treatment 3	Treatment 4
<1000 ppm Pb	41%	37%	30%	15%
>1000 ppm Pb	55%	54%	42%	14%

preparation procedure, although the EPA method measured primarily instrument precision (overall method precision was not evaluated). Relative standard deviations showed no significant trends when comparing different levels of sample preparation.

The EPA comparability study suggests that increasing levels of preparation do improve the agreement between field XRF and laboratory wet chemistry data for all analytes (arsenic, copper, barium, lead, chromium, and zinc). Regression parameters improved (i.e., r-squared increased, and slopes moved closer to the "ideal" comparison value of 1.0) with each preparation step, with the greatest improvement generally observed between steps 1 and 2 (similar to treatment 1 and treatment 2), where the sample was removed from the ground surface and homogenized. The only EPA data showing a similar trend to this preparation study was low-concentration arsenic data (<400 ppm), where average RPD decreased from 65 percent to 33 percent between Treatment 1 and Treatment 2.

Overall, the results of the EPA study are similar to the results obtained in the study presented herein, in that they indicate that preparation may result in slight improvements in data comparability. However, the benefit of these improvements must be weighed against the increased time and cost required for more advanced levels of preparation. The EPA recommends homogenization (Treatment 2) as a worthwhile preparation step, and concludes that, "based on the data quality objectives for the project, an analyst must decide if it is worth the extra time required to dry and grind the sample for small improvements in comparability."

Summary

The following information was obtained during the portable field XRF investigation:

- Field XRF techniques provide a reliable and efficient means for differentiating arsenic and lead concentrations in soil on a "screening-level" (discerning order-of-magnitude differences in arsenic and lead concentrations).

- Results can be obtained on a daily basis to aid on-going field investigations.
- Costs for using the portable field XRF method are generally less than costs for using more conventional (wet chemistry) methods.
- Protocols for using this field XRF method were accepted by the US EPA and other regulatory agencies.
- Analytical data acquired with this field XRF method correlates well with laboratory data.
- The level of sample preparation required for using the field XRF technique depends on potential interferences, desired accuracy and precision, and cost constraints.

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