Real Time Demonstration Project
XRF Performance Evaluation Report
for

Paducah Gaseous Diffusion Plant AOC 492

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Paducah Real Time Project

Purpose

This activity was undertaken to demonstrate the applicability of market-available XRF instruments to quantify metal concentrations relative to background and risk-based action and no action levels in Paducah Gaseous Diffusion Plant (PGDP) soils. As such, the analysis below demonstrates the capabilities of the instruments relative to soil characterization applications at the PGDP.

Methodology

Four soil samples were collected from the AOC-492 area of the Paducah site, prepared by the State of Kentucky (dried, crushed, sieved, and homogenized), split, and the splits provided to two XRF manufacturers, Innov-X and Niton, for analysis. These four samples included one from a location believed to represent background conditions and one from an area believed to be potentially slightly impacted by uranium contamination. The other two samples targeted areas with the highest observed gross gamma activity. One would expect metals to exist at local background levels for the background soil sample.

The samples were analyzed using two different instruments by Innov-X and one by Niton. The Innov-X instruments included the X-50 and the handheld Classic. The X-50 is a "lunch-box" style tube-based system that is field deployable, but that cannot do in-situ readings. A typical X-50 measurement includes consecutive acquisitions with two different filters applied that allow the instrument to be optimized for specific sets of elements. The Classic is a handheld tube-based system that can do in-situ readings and that also has two different beam settings, one for heavier metals and one for lighter metals. The Niton instrument was an XL3t500 handheld tube-based system. It is similar to the Innov-X instruments in that a measurement includes consecutive acquisitions with different filters (3 filters in the case of the XL3t500) to optimize performance for different sets of elements.

Results

The data in Table 1 summarize observed detection limits for the background soil sample for the different detectors operated at different acquisition times. The elements in Table 1 are listed by atomic mass, from lightest to heaviest. In the case of the Innov-X instruments, different X-ray beam settings were combined with different acquisition times, so the results are broken out in different columns. In the case of the Niton instrument, all beam settings had the same acquisition times and so were combined in the same column.

Consistent with EPA SW-846 Method 6200, the standard definition of detection limit for an XRF is three times the detector-estimated measurement error when the element is

actually not present. In practice, if an XRF reading gives a result that is less than three times the detector-estimated measurement error associated with the reading, the XRF will flag the reading as a non-detect and report the associated detection limit as three times the estimated error. In Table 1, if a measurement was a non-detect, the number provided is the instrument-reported detection limit. If a measurement resulted in a detection, the detection limit is recorded as less than ("<") three times the reported error associated with the measurement. This is because measurement error is a function of concentration; measurement error decreases as concentrations decrease and consequently the detection limit for a "detected" result would be less than three times the reported error for the result.

An instrument with a lower detection limit as compared to a second instrument with the same acquisition times for any particular element would also have lower errors associated with actual readings as well for that element. Errors, and consequently detection limits, decrease as acquisition time increases for any particular detector. One can see this exemplified in the X-50 data set in Table 1, where increasing the count time by a factor of more than four often cuts the detection limit in half.

Table 1 also includes, for comparison purposes, site-specific background concentrations for these metals (if available) based on standard laboratory analyses, risk-based No-Action-Levels (NAL) for a teen recreational user, and risk-based Action Levels (AL) for a teen recreational user as reported by DOE in a 2000 Risk Methods report. The teen recreational user is assumed to be a local resident who has frequent exposure to the area of concern's soils and sediments.

The teen recreational user is the most likely exposure scenario for soil pile areas similar to the area where the four samples were obtained. This scenario provides NAL values that are reasonable points of comparison to XRF detection limits if the purpose of XRF data collection is to clear areas of general, long-term risk concerns. The AL values are reasonable points of comparison to XRF detection limits if the purpose of XRF data collection is to identify areas posing immediate health concerns.

The reported background concentrations are derived from standard laboratory analytical results and are 95%UTL (Upper Tolerance Limit) estimates, and so represent the upper range of expected site-specific background concentrations. Standard laboratory metals analyses such as Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) involve an extraction step before the analysis. ICP-MS measures concentrations in the extract. If the extraction is not complete, ICP-MS will underestimate the total mass of metal present in the original sample. Extraction efficiencies are metal- and matrix-specific. XRF directly measures total metal content. Consequently XRF may appear to over-estimate metal concentrations in some cases when compared to ICP-MS results.

When comparing detection limit results for instruments from Innov-X and Niton it is important to note that the two companies have slightly different definitions of "acquisition time". For an Innov-X unit, the acquisition time is the clock time associated with the reading. The true "live time" of the detector is something less than this (usually

around 60% - 70% of the clock time). For the Niton instrument, the acquisition time is the "live time" of the detector, and so the clock time associated the reading may be something longer. Consequently, all else being equal, for the same acquisition time one would expect the Niton instrument to do slightly better from the perspective of detection limits since it acquires its spectra longer than the Innov-X instrument.

The data in Table 2 summarize results for the Innov-X X-50 and the Niton XL3t500 for the four samples submitted for analysis. The elements in Table 1 are listed by atomic mass, from lightest to heaviest. In the case of the Innov-X instrument, the results are from a 120-second acquisition for heavy metals and a 60-second acquisition for lighter metals. In the case of the Niton instrument, 60-second acquisitions were used for all three of its beam settings. Results reported as non-detects are shown as "<" the measurement-specific detection limit (defined to be three times the reported measurement error for that measurement).

Table 2 also includes background, NAL, and AL values for the Paducah site as points of comparison as described previously for Table 1.

Several observations and associated conclusions can be drawn from these data regarding detection limits pertinent to the deployment of XRF technologies at Paducah:

- For all elements listed in Table 1 with Site AL's provided, the XRF has detection limits below teen recreational user AL values with reasonable acquisition times. **The conclusion**: for all elements measured by these XRF units the XRF can achieve detection limits below PGDP AL standards for a teen recreational user.

- For most elements listed in Table 1 with Site teen recreational NAL's provided, the XRF has detection limits below NAL values with reasonable acquisition times. The exceptions are chlorine, vanadium, manganese, arsenic, antimony, mercury, and thallium. With the exception of chlorine (for which there is no reported site-specific background), the Site NAL levels for these elements are either less than or close to reported background levels. In the case of arsenic and manganese, XRF detection limits are below background. **The conclusion** for those two elements is that the XRF can distinguish between natural background concentrations and elevated concentrations due to anthropogenic activities. Antimony is a special case which will be discussed later. For mercury, thallium, and vanadium XRF results averaged over an area may still potentially provide usable information regarding the average levels of contamination relative to their respective NAL values.

- There was not a significant disparity in performance as measured by detection limits between the Niton and Innov-X systems. As a generalization, the Innov-X X-50 appeared to perform better for very light elements (e.g. P through Mn) and for some heavy elements (e.g. U). The Niton appeared to perform better for mid-range mass elements (e.g., Fe through Sb). However, there were exceptions to these generalizations. **The conclusion**: from a strictly performance perspective

(as measured by detection limits and measurement error), the latest XRF tube-based units from either company should be equally applicable to PDGP needs. Site-specific deployment protocols (e.g., acquisition time, thoroughness of sample preparation, etc.) will likely have a greater influence on XRF performance than choice of vendor.

The following observations and conclusions can be drawn from Table 2:

- Chromium is clearly elevated above the background sample's concentration for the two samples with the highest levels of uranium. The chromium concentration in sample 5017 exceeded the teen recreational exposure scenario NAL for the site.

- Zinc is present above the concentration present in the background sample in the two samples with the highest levels of uranium, although the levels observed did not exceed the teen recreational NAL for zinc.

- Molybdenum is present above background levels in the two samples with the highest levels of uranium. There was disagreement between the Niton and the Innov-X units regarding the actual level of molybdenum present in each of the samples, with the Innov-X unit providing concentrations that were approximately ten times higher than those from the Niton. The Innov-X reported some results as above the teen recreational NAL, while the Niton reported all as below the NAL.

- Potassium, chromium, nickel, barium, antimony, and uranium were reported as being present at levels higher than the reported background 95%UTL for the site. There are several potential reasons for this observation. The first is that the "background" sample may in fact have had some low level site impacts, particularly in the case of uranium and chromium. The second is potential calibration issues or interference effects for these elements with the XRF units at low concentrations. The third is the fact that some elements may have relatively low extraction efficiencies for standard laboratory analyses (e.g. ICP-MS), resulting in under-estimates of the true elemental mass concentration present that would be reflected in site 95%UTL values. In other words, the XRF may actually be providing more accurate estimate of background mass concentrations than the 95%UTL estimate which was based on standard laboratory analyses. This is potentially the case with antimony and barium. **The conclusion**: if the site chooses to use the XRF more intensively in the future and comparisons of XRF results to background values are important, the development of background values specific to the XRF is encouraged.

- There was significant disagreement between the two systems regarding the concentration of barium present across all four samples. In general the Innov-X unit reported barium concentrations three times higher than the Niton unit.

- Both the Niton and the Innov-X units identified elevated uranium in the three samples from areas suspected to be impacted. There were, however, significant

differences in their reported values. In particular the Niton reported approximately twice as much uranium as the Innov-X. In discussing this with the vendors, Niton reported having a uranium standard available for calibration purposes, but Innov-X did not. Innov-X acknowledged that their calibration might be off, but that this could be corrected with the availability of an appropriate uranium standard. **The conclusion**: this difference underscores the critical need for appropriate standards when working with XRF technologies, both to properly calibrate the system and to monitor calibration as work proceeds. This is particularly true for uranium since uranium is typically a non-standard calibration for XRF units, but also applicable to any other element measurable by the XRF that will potentially drive decision-making at the site. Standards can take the form of NIST soil standards, procured spiked samples with known elemental concentrations, or well-characterized samples with appropriate concentrations from the site. In the case of standards, it is important that the standard's concentrations of the metals of concern are well within the expected calibration range of the instrument, and preferably as close to the level important for decision-making as possible, and that the standard's soil matrix is comparable to the type of matrix expected to be encountered at the site.

References

US Department of Energy, 2000. Methods for Conducting Risk Assessments and Risk Evaluations at the Paducah Gaseous Diffusion Plant, Paducah, Kentucky Volume 1. Human Health.

Table 1 Detection Limit Performance (ppm) for Various XRF Configurations

Element	Innov-X X-50 1st Beam		Innov-X X-50 2nd Beam	Innov-X Hand Held 1st Beam	Innov-X Hand Held 2nd Beam	Niton XL3t500		Site NAL (ppm)[1]	Site AL (ppm)[1]	Site Background (ppm)[2]
	600 sec	120 sec	60 sec	120 sec	60 sec	60 sec	30 sec			
P			7,028							
S			1,746			11,527	15,824			
Cl			1,332					301	100,000	
K			<798		<1,290	<780	<1018			1,300
Ca			<387		<663	411	553			200,000
Sc						22	30			
Ti			<315	<846	<528	<240	<315			
V						77	100	2.12	3,090	38
Cr			<21	<99	<39	<30	<41	227	100,000	16
Mn			<33	<81	<57	<84	<126	29	39,100	1,500
Fe	<408	<435		<516	<1,011	<358	<528	1,350	100,000	28,000
Co				<114		103	155	1,390	100,000	14
Ni	<12	<27		32		40	59	161	100,000	21
Cu	40	86		17		20	32	331	100,000	19
Zn	<9	<15		<12		<15	<22	1,800	100,000	65
As	4	9		<6		7	10	0.35	314	12
Se	17	37				3	5	65	44,700	0.8
Rb				<6		<6	<9			
Sr	<3	<6		<6		<7	<10	3,600	100,000	
Zr	<6	<15		<12		<17	<25			
Mo	3	6		7		5	8	56.4	41,700	
Pd	8	18				8	12			
Ag	10	23		29		6	9	27	27,100	2.3
Cd				29		8	12	14.7	45.3	0.21
Sn				45		<12	<17	1,810	100,000	
Sb	18	41		50		<14	<20	0.24	344	0.21
Te	8	19				<38	<55			
Cs						<12	<17			
Ba	<222	<510			<129	<36	<52	148	100,000	200

	Innov-X X-50 1st Beam	Innov-X X-50 2nd Beam	Innov-X Hand Held 1st Beam	Innov-X Hand Held 2nd Beam	Niton XL3t500		Site NAL (ppm)[1]	Site AL (ppm)[1]	Site Background (ppm)[2]
Ta	7	14							
W	1	3			51	79			
Pt	9	19	2						
Au	1	3	2						
Hg	6	13	8		8	12	0.63	100,000	0.2
Tl	<2	3					0.48	611	0.21
Pb	<6	<15	<9		<9	<12	400	400	36
Bi	<3	<6							
Th	5	12			<6	9			
U	<3	<3	4		<9	13	14.7	683	4.9

[1]NAL for a teen recreational user and AL for a child resident as reported in Risk Methods document (DOE 2000), with the exception of lead. The lead NAL has been updated to reflect current State of Kentucky guidance. The teen recreational user is assumed to be a local resident who has frequent exposure to the area of concern's soils and sediments.

[2]Background values represent the 95%UTL observed in background results.

Table 2 XRF Results Summary for Four Samples

Element	Innov-X X-50				Niton XL3t500				Site NAL (ppm)[1]	Site AL (ppm)[1]	Site Background (ppm)[2]
	Backgrnd (5011)	High 1 (5014)	High 2 (5017)	Low (5020)	Backgrnd (5011)	High 1 (5014)	High 2 (5017)	Low (5020)			
P	<7,028	<6,154	<6,742	<5,927							
S	<1,746	<1,517	<1,474	<1,437	<11,527	<10,132	<10,734	<9,928			
Cl	<1,332	<1,189	<1,188	<1,121					301	100,000	
K	11,840	10,162	10,105	9,889	14,548	13,150	12,471	13,437			1,300
Ca	5,146	3,582	3,349	2,951	6,196	4,885	4,402	4,027			200,000
Sc					<22	<19	<19	<18			
Ti	4,669	4,992	4,801	4,886	5,084	5,163	5,233	5,197			
V					<77	<73	77	81	2.12	3,090	38
Cr	64	123	521	48	65	121	736	61	227	100,000	16
Mn	413	514	380	880	353	545	358	889	29	39,100	1,500
Fe	18,392	13,758	14,346	12,977	16,044	11,201	12,460	11,045	1,350	100,000	28,000
Co					<103	108	<93	<85	1,390	100,000	14
Ni	37	<23	31	34	<40	<39	<41	41	161	100,000	21
Cu	<86	<96	<101	<88	<20	21	42	22	331	100,000	19
Zn	55	81	212	43	60	87	213	42	1,800	100,000	65
As	<9	<9	<10	<8	<7	<7	<8	<7	0.35	314	12
Se	<37	<42	<45	<39	<3	<3	<4	<4	65	44,700	0.8
Rb					55	46	47	47			
Sr	105	104	86	96	100	91	79	95	3,600	100,000	
Zr	468	636	616	645	604	747	762	746			
Mo	<6	76	105	<7	<5	7	17	<6	56.4	41,700	
Pd	<18	<17	<17	<17	<8	12	21	<8			
Ag	<23	<22	<22	<22	<6	<5	<5	<6	27	27,100	2.3
Cd					<8	<7	<7	<8	14.7	45.3	0.21
Sn					15	<11	<10	<11	1,810	100,000	
Sb	<41	<39	<39	<39	28	<13	<12	16	0.24	344	0.21
Te	<19	<18	<18	<18	89	<35	<34	75			
Cs					51	<11	<11	32			

9

	Innov-X X-50				Niton XL3t500						
Ba	914	651	813	868	372	231	163	313	148	100,000	200
Ta	<14	<16	<17	<15							
W	<3	<4	<4	<3	<51	<52	<53	<51			
Pt	<19	<22	<23	<20							
Au	<3	<4	<5	<3							
Hg	<13	<14	<15	<13	<8	<8	<8	<8	0.63	100,000	0.2
Tl	<3	4	<4	<3					0.48	611	0.21
Pb	21	18	37	23	23	24	28	18	400	400	36
Bi	8	9	6	12							
Th	<12	<14	<14	<13	9	9	10	12			
U	11	273	377	60	10	717	942	129	14.7	683	4.9

[1]NAL for a teen recreational user and AL for a child resident as reported in Risk Methods document (DOE 2000), with the exception of lead. The lead NAL has been updated to reflect current State of Kentucky guidance. The teen recreational user is assumed to be a local resident who has frequent exposure to the area of concern's soils and sediments.

[2]Background values represent the 95% UTL observed in background results.