



Summary of SITE Demonstration Results
XRF Technologies for Measuring Trace Elements in Soil and Sediment

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A performance verification of eight field-portable X-ray fluorescence (XRF) spectrometers for the analysis of trace elements was conducted under the U.S. EPA's SITE program. Table 1 summarizes some key technical specifications for each instrument included in the demonstration and lists the reference number of the innovative technology verification report (ITVR). The ITVRs are posted on the SITE homepage (www.epa.gov/ORD/SITE).

Table 1: Summary of XRF Instruments Included in the SITE Demonstration

Developer	Instrument	Portability	X-ray Source	Mode of Operation	Detector	Calibration	Special Sample Prep.	ITVR No. (EPA/540/)
Niton	XLt 700 Series	Hand-held (3 lbs.)	Tube	ED	Si-PiN	Factory (FP)	None	R-06/004
Niton	XLi 700 Series	Hand-held (2 lbs.)	Isotope	ED	Si-PiN	Factory (FP)	None	R-06/003
Innov-X	XT400	Hand-held (4 lbs.)	Tube	ED	Si-PiN	Compton	None	R-06/002
Oxford	X-Met 3000TX	Hand-held (4 lbs.)	Tube	ED	Si-PiN	Compton	None	R-06/008
Oxford	ED2000	Bench-top (165 lbs.)	Tube	ED	Si-PEF LN	Empirical	Pellet Pressing	R-06/007
Rigaku	ZSX Mini II	Bench-top (264 lbs.)	Tube	WD	Scintillation	Empirical	None	R-06/001
Rontec	PicoTAX	Bench-top (62 lbs.)	Tube	ED	Si-PiN	Ge Int. Std.	Emulsification	R-06/005
Xcalibur	ElvaX	Bench-top (40 lbs.)	Tube	ED	Si-PiN	Empirical	None	R-06/006

Abbreviations: ED = Energy dispersive. FP = Fundamental parameters. Ge Int. Std. = Germanium internal standard. Si-PiN = Silicon PiN diode, thermoelectrically cooled. Si-PEF LN = Silicon Pentafet, liquid nitrogen cooled. WD = Wavelength dispersive.

The demonstration targeted 13 trace elements, including antimony (Sb), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), silver (Ag), vanadium (V), and zinc (Zn). The field demonstration was performed from January 24 through 29, 2005 at NASA's Kennedy Space Center on Merritt Island, Florida. A total of 326 samples were analyzed by each XRF instrument and by a reference laboratory using conventional fixed laboratory methods (EPA SW-846 methods 3050B/6010B and 7471A). These samples were derived from 70 different blends and spiked blends of soil and sediment that originated from nine sites across the U.S. The sample blends were thoroughly dried, sieved, crushed, mixed, and characterized before they were used for the demonstration. Between three and seven replicates of each blend were analyzed.

The results of the demonstration are summarized in Table 2 for three of the primary evaluation objectives, including sensitivity, accuracy, and precision. Specifically, Table 2 lists the target elements in each of four selected ranges to illustrate the sensitivity, precision and accuracy of each instrument. As shown, there were significant differences in instrument performance with respect to the objectives; these differences in performance reflect the variations in instrument components, operation, and calibration. In general, instruments with more established procedures and quantitation algorithms for analysis of environmental samples performed the best.

Figures 1 and 2 summarize the findings for two other primary evaluation objectives; sample throughput and cost, based on the instruments as equipped for the SITE demonstration and on a sampling program of similar size to the demonstration (326 samples, 13 target elements). Sample throughput was higher and per sample costs were lower for the hand-held instruments due to shorter instrument run times and simplified sample handling procedures. For comparison, the cost of a fixed laboratory analysis is about \$20 per element per sample, and greater than \$150 per sample for the full list of target elements included in the demonstration. Conversely, the cost for analysis of a sample using XRF technology is essentially fixed regardless of the number of analytes. Thus, the analysis of multiple elements is substantially less expensive using XRF technology. Further, XRF technology can easily provide rapid-turnaround data in the field to aid in-field decision-making and more cost-effective environmental cleanup.

The findings for the above-described primary objectives, and for other primary and secondary objectives (including interference effects, matrix effects, instrument safety, training, durability, and availability), are described in detail in the ITVRs. Project teams should consider the detailed information in the ITVRs carefully prior to selecting an XRF technology for large-scale data collection. An initial pilot-scale method evaluation, carried out in cooperation with an instrument vendor, can yield site-specific procedures for sample preparation and analysis to ensure that the XRF method will meet data quality needs for accuracy, sensitivity, and comparability.

Table 2. Comparative Evaluation of Sensitivity, Accuracy, and Precision for Eight XRF Instruments

Objective	Criterion	Hand-held Instruments				Bench-top Instruments			
		XLt	XLi	XT400	X-Met	ED2000	ZSX Mini II	PicoTAX	ElvaX
Mean MDL (Calculated per 40 CFR 136)	1 to 20 ppm	As, Pb, Hg, Se, V	Se	As, Cu, Pb, Hg, Se, Zn	As, Se	Sb, Cd, Cu, Se, Ag, V	Cu, Hg, Ni, Se, Zn	Se	Sb, Hg
	20-50 ppm	Cu, Ag, Zn	As, Pb, Hg	Sb, Cd, Ag, V	Cd, Cu, Pb, Hg, Ag, Zn	As, Cr, Pb, Ni, Hg, Zn	As, Pb, Ag, V	As, Cu V	As, Cu, Ni, Ag, V, Zn
	50 to 100 ppm	Cr, Ni	Sb, Zn	Cr, Ni	Ni	None	Sb, Cd, Cr	Hg, Ni, Zn	Cd, Cr, Pb
	> 100 ppm	Sb, Cd	Cd, Cr, Cu, Ni	None.	Sb, Cr, V	None	None	Cd, Cr, Pb, Ag	Se
Accuracy (Median RPD vs. reference laboratory; bias assessed through correlation plots)	RPD < 10%	Cu, Se	Se	Cd	Cd, Se	Ni	None	None	None
	RPD 10-25%	As, Cd, Cr, Fe, Pb, Ag, Zn	As, Cd, Cr, Cu, Fe, Pb, Ni, Zn	As, Cu, Pb, Se, Zn	As, Fe, Pb, Ni	Cd, Cr, Cu, Pb, Hg, Ag, Zn	None	As, Cr, Cu, Fe, Pb, Ni, Se, Ag, V, Zn	Cd, Fe, Ni, Ag
	RPD 25- 50%	Ni, V	None.	Sb, Cr, Fe, Hg, Ni, Ag	Cr, Cu, Hg, Ag, V, Zn	As, Se, V	As, Cr, Cu, Ag, V, Zn	Hg	Sb, As, Cr, Cu, Zn
	RPD > 50%	Sb, Hg	Sb, Hg, Se, V	V	Sb	Sb, Fe	Sb, Cd, Fe, Pb, Hg, Ni, Se	Cd	Pb, Hg, Se, V
	Low Bias	Hg, V	Cr, Hg	V	None	Se	As, Cr, Cu, Fe, Pb, Hg, Ni, Se, Zn	Hg	Sb, Cr, Fe, Hg, V
	High Bias	As, Pb, Ni, Ag	Sb, As, Cd, Pb, Ag, V, Zn	As, Cr, Fe, Pb, Ni, Ag, Zn	Sb, As, Pb, Ag, V, Zn	As, Fe, Zn	None	Cd, Pb	Cu, Pb, Se, Ag
Precision (Median RSD of replicate analyses)	RSD < 5%	Cd, Fe, Pb, Se, Zn	Fe, Pb, Zn	As, Cd, Cu, Fe, Pb, Hg, Se, Zn	Cd, Fe, Hg, Se	Sb, As, Cd, Cu, Fe, Hg, Ni, Se, Ag, Zn	Cd, Cu, Fe, Hg, Pb, Ni, Se, Ag, Zn	None	Cu, Fe
	RSD 5-10%	Sb, As, Cr, Cu, Hg, Ni, Ag, V	Sb, As, Cd, Cu, Hg, Ni, Se, V	Sb, Cr, Ni, Ag, V	As, Cu, Pb, Ni, Ag, Zn	Cr, Pb	Sb, V	Se	Sb, Cd, Pb, Ni, Se, Ag, Zn
	RSD 10-20%	None	Cr, Ag	None	Sb, Cr, V	V	As, Cr	As, Cu, Fe, Pb, Ni, V, Zn	As, Cr, Hg
	RSD > 20%	None	None	None	None	None	None	Cd, Cr, Hg, Ag	V

Abbreviations: CFR = Code of Federal Regulations. MDL = Method detection limit. ppm = Parts per million. RPD = Relative percent difference. RSD = Relative standard deviation.

