

## Results of field-portable X-ray fluorescence analysis of metal contaminants in soil and sediment<sup>☆</sup>

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### Abstract

The US Environmental Protection Agency's Environmental Response Team (US EPA/ERT) has extensively used field-portable X-ray fluorescence (FPXRF) instruments for analyzing metals in soils and sediments at hazardous waste sites nationwide. The US EPA/ERT has used the Outokumpu Electronics Inc. (OEI) model X-MET 880 and the Spectrace Instruments model 9000 FPXRF analyzers. Instrument calibration methods, precision and detection limits are discussed. Both in-situ and prepared soil analysis are described. A statistical comparison of slopes (regression coefficients) is presented comparing AA/in-situ FPXRF and AA/prepared sample FPXRF regression results for data from a battery breakage and scrap metal site. The instruments' analytical capabilities are demonstrated by measurements of chemically analyzed samples from a variety of soil and waste matrices. Additionally, the US EPA's Quality Assurance/Quality Control (QA/QC) procedures for FPXRF analysis of soil and sediment samples is presented.

**Keywords:** Field-portable X-ray fluorescence; Metals in soil; On-site in-situ metals; Lead; Elemental analysis

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### 1. Introduction

Historically, the chemical analytical methods approved for use by the US EPA Contract Laboratory Program (CLP) have been employed for analysis of environmental samples. As a result of increasing documentation of successful application of X-ray fluorescence (XRF) methods to analyze hazardous materials, the environmental community is accepting FPXRF as a viable analytical technique for characterization

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<sup>☆</sup> Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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of environmental samples [1–8]. Time and cost savings over the standard US EPA CLP chemical methods are significant [1–3]. FPXRF is a cost effective method to increase sampling densities. This improves the reliability of decisions based on spatial models delineating the extent of contamination [4].

Energy-dispersive XRF (EDXRF) provides nondestructive near real-time simultaneous multi-element analysis of liquid, powder, solid, and thin-film samples. The US EPA/ERT has used the OEI X-MET 880 and the Spectrace Instruments model 9000 FPXRF analyzers for rapid on-site analysis of hazardous metallic wastes. These instruments were selected for their ability to provide multi-element analysis and sample matrix corrections. The instruments differ in their energy-resolving power and, consequently, in their calibration and analytical methodology. Both instruments have enabled the US EPA/ERT to perform extent of contamination studies, on-site metal analyses to direct removal actions, analysis of paint for Pb content, analysis of air filters for metals, and post-cleanup surveys.

Results from regression of chemical versus FPXRF analysis are presented for samples from hazardous waste sites containing metallic pollutants in a variety of soil and waste matrices. Additionally, FPXRF precision and detection limit data are discussed. Typical target metals analyzed include the following: lead (Pb), zinc (Zn), copper (Cu), chromium (Cr), nickel (Ni), cadmium (Cd), arsenic (As), and barium (Ba). Many of these elements are used in calculations to correct for sample chemical matrix effects.

## 2. Instrumentation and calibration

### 2.1. OEI X-MET 880

The OEI X-MET 880 was equipped with a double-source surface (DOPS) probe for both in-situ soil and XRF sample cup analysis with the probe in the upright geometry and the safety shield attached. The DOPS probe was furnished with 100 mCi  $^{244}\text{Cm}$  and 30 mCi  $^{241}\text{Am}$  radioisotope sources.

The OEI DOPS probe employs a gas proportional detector with a typical energy resolution of 850 eV at the full-width at half-maximum intensity (FWHM) of the manganese (Mn) K X-ray line. The resolution of the detector does not allow for universal and efficient use of a fundamental parameters (FP)-based method to calculate elemental concentrations. An empirical or site-specific calibration that uses elemental standards, site-specific calibration standards (SSCS), and regression mathematics are needed to calibrate the instrument for elemental response and matrix effects. This provides the operator with the flexibility to configure the instrument to analyze for any element from aluminum (Al) through uranium (U).

The chemically analyzed [atomic absorption (AA) or inductively coupled plasma emission spectroscopy (ICP)] SSCS must be representative of the matrix and target element concentration range that will be sampled at the site. The highest and lowest SSCS samples determine the linear calibration range.

The DOPS probe is temperature sensitive. The operator activates a software-controlled gain-control circuit for five minutes for every 3°C change in the ambient

operating temperature, or every half an hour of operation to prevent possible errors due to gain shifts.

The electronic unit of the OEI X-MET 880 FPXRF is capable of holding 32 calibration models. Each calibrated model can analyze up to six target elements. The electronic unit does not provide internal storage for spectrum and analytical results. An RS-232 serial port is provided for downloading data and spectra to a peripheral device.

US EPA/ERT SOP 1707, "X-MET 880 Field Portable X-ray Fluorescence Operation Procedures," [9] and the OEI HAZ-MET 880 Operator's Manual provide guidelines for sampling, preparation of SSCs, calibrating, start-up, check-out, operation, calibration, and routine use of the X-MET 880 for on-site analysis of environmental samples.

## 2.2. Spectrace 9000

The Spectrace 9000 surface probe provides for both in-situ soil analysis and XRF sample cup analysis with the probe in the upright geometry and the safety shield attached. It is furnished with 5 mCi  $^{109}\text{Cd}$ , 50 mCi  $^{55}\text{Fe}$ , and 5 mCi  $^{241}\text{Am}$  radioisotope sources.

The Spectrace 9000 utilizes a mercuric iodide ( $\text{HgI}_2$ ) semiconductor detector with a typical energy resolution of 270 eV at the FWHM of the Mn K X-ray line. The improved energy resolution of the detector allows for efficient use of a FP-based method to calculate elemental concentrations. FP is a mathematical treatment of chemical matrix effects used in conjunction with pure element or known standard element responses to develop an iterative algorithm for analysis of a specific sample type (e.g., soil, oil, thin film, paint). The FP method does not require site-specific calibration samples. Calibration is not necessary; only selection of one of the FP-based applications from a menu is required. Applications for soils, Pb-in-paint (K- and L-lines), and thin films are provided with the instrument. However, only the soils application will be discussed.

X-ray intensities for 25 elements are simultaneously derived from the spectra of the three sources. Therefore, soil samples may be analyzed for any or all of these elements without developing a calibration model. The soil application presently analyzes for potassium (K), calcium (Ca), titanium (Ti), Cr, Mn, iron (Fe), cobalt (Co), Ni, Cu, Zn, As, selenium (Se), rubidium (Rb), strontium (Sr), zirconium (Zr), molybdenum (Mo), silver (Ag), Cd, tin (Sn), antimony (Sb), Ba, mercury (Hg), Pb, thorium (Th), and uranium (U).

An energy calibration is performed automatically with each analysis to prevent error due to gain shifts. The electronic unit provides internal nonvolatile memory for storage of 120 spectra and 300 multi-element analytical reports. An RS-232 serial port is provided for downloading data and spectra to a peripheral device. The multi-element analytical reports and the 2000-channel spectra can be displayed on the instrument's LCD panel.

US EPA/ERT SOP 1713, "Spectrace 9000 Field Portable X-ray Fluorescence Operating Procedure", [10] and the Spectrace 9000 Operator's Manual give guidelines

for start-up, check-out, operation, calibration, and routine use of the Spectrace 9000 for on-site analysis of environmental samples.

### 3. Sample analysis methodologies

#### 3.1. *In-situ FPXRF*

Large rocks and organic debris are removed from the soil within a 25 × 25 cm area to a depth of 2.5 cm. The soil is mixed to reduce gross heterogeneity and flattened with a stainless steel trowel. Flattening the surface is critical since differences in the distance between the source/detector and the sample presentation plane significantly effect results [11]. Two or three different points in the area are analyzed with the FPXRF surface probe positioned flush against the prepared soil surface. The average and range are reported. A sample moisture content of up to 20% is acceptable for most elements [11, 12]. Samples with a moisture content significantly higher than 20% have been successfully analyzed for metals by FPXRF. This is attempted only when confirmation samples are submitted to the laboratory for chemical analysis.

Wet soils and sediments are normally placed in an aluminum pan and allowed to air dry. Large rocks and organic debris are removed from the soil and the sample is mixed to reduce gross heterogeneity. The sample is shaped into a 2.5-cm thick cake and flattened with a stainless steel trowel. Two or three different points are analyzed with the FPXRF surface probe positioned flush against the prepared soil surface, and the average is reported.

Contaminant geological variability is determined when extent of contamination studies are performed. An area with a contaminant level near the action or removal concentration is selected. The area or sample is prepared as described above and eight individual in-situ FPXRF analysis are performed. The mean and coefficient of variation (COV) are reported. This characterization of the contaminant geological variability is used to develop quality assurance protocols for in-situ FPXRF confirmation during removal activities.

#### 3.2. *Prepared sample FPXRF*

Soil or sediment is collected and dried, if needed, by air or in a conventional oven at 105 °C [11]. Air drying is required when analyzing samples containing volatile metals such as Hg. Any organic matter, large rocks, or debris are removed. The sample is broken up and passed through a 10-mesh sieve. The oversized material is discarded, and the undersized portion is thoroughly mixed. A 20-mesh sieve is used when preparing paint chip samples. A 31-mm X-ray sample cup is filled and covered with 3-micron (µm) polypropylene X-ray film. The cup is tapped gently against the table top to pack the soil evenly against the window film and analyzed once with the FPXRF surface probe in the upright geometry.

### 3.3. Chemical analysis

The confirmation samples (the same 31-mm sample cups analyzed by prepared sample FPXRF) are submitted to the laboratory for digestion and analysis as specified in the US EPA publication, "Test Methods for Evaluating Solid Waste," SW-846, 3rd edition.

## 4. Data QA/QC

The FPXRF method detection limit (MDL) is calculated from the measurement of a soil matrix blank at the start and end of sample analysis, and after approximately every tenth sample (for a minimum of eight measurements per project). The MDL is defined as three times the calculated standard deviation value of the mean for each target element [12].

Precision is monitored by analyzing a sample with target element concentrations above the MQL at the start of and periodically throughout the analysis day (for a minimum of eight measurements per project). Ideally, the sample should have a target analyte concentration near the site action level. The COV is used to calculate XRF method precision. The COV should be  $\leq 20\%$  for the data to be considered adequately precise.

Three equally important QA objectives, QA1, QA2, and QA3, have been defined by the US EPA for assessing and substantiating the collection of data. The characteristics of each of the QA objectives should be evaluated to determine which one or combination thereof fits the data use objective(s) established for the site. All three QA objectives provide useful and valid data for activities such as: enforcement, treatment and disposal, responsible party identification, extent of contamination, site characterization, and cleanup verification.

XRF data is accepted as US EPA QA1 and QA2, according to OSWER Directive 9360.4-01, "Quality Assurance/Quality Control Guidance for Removal Activities-Sampling QA/QC Plan and Data Validation Procedures", April 1990. Determining the appropriate QA objective depends upon site-specific project objectives. QA1 is an objective to afford a quick, cost-effective assessment of site contamination. A calibration or performance check of the method is required in addition to the verification of the detection limit. No specific QA/QC check samples are required. QA2 is a verification objective that requires confirmation of a minimum of 10% of the XRF samples by US EPA-approved laboratory (AA/ICP) methods. The regression analysis of AA/ICP versus XRF data sets must have a coefficient of determination ( $R^2$ ) of 0.7 or greater to meet QA2 objectives [12].

## 5. Results

The target element MDL, precision, and confirmation regression data for the X-MET 880 FPXRF analyses of metal pollutants in a variety of soil and waste matrix

Table 1  
XMET 880 FPXRF Results

Waste type	Element	Analysis method P – prepared I – in-situ	Measurement time in seconds	MDL <sup>a</sup> (mg/kg) <sup>b</sup>	Precision Concentration (mg/kg)	COV (%) <sup>c</sup>	Regression statistics		
							N. Obs. <sup>d</sup>	COD <sup>e</sup>	Slope
Battery breakage	Pb	P	60	123	300	13.7	21	0.97	0.84
		I #1	60	123	300	13.7	21	0.92	0.92
NiCAD production	Ni	I #2	60	81	N/A	N/A	46	0.85	0.85
		P	240	176	277	21.1	8	0.99	0.94
Smelter stack	Cd	P	240	128	221	19.2	7	1.00	0.91
		I	60	102	469	7.2	25	0.94	0.81
Drum scrap metal	Pb	I	60	165	485	11.3	9	0.84	0.53
		P	60	111	159	23.3	22	0.78	1.16
Mine tailings	Zn	P	60	90	319	9.4	23	0.94	1.07
		P	60	336	1306	8.6	9	0.99	0.95
Scrap metals	Cu	P	60	606	N/A <sup>f</sup>	N/A	24	0.64	1.01
		P	60	974	N/A	N/A	18	0.74	0.32
Industrial slag	Pb	P	60	73	1513	16.1	14	0.98	1.21
		I	60	129	266	16.2	26	0.89	0.96
Smelter waste	Pb	P	60	119	256	15.6	261	0.98	0.96
		P	240	645	958	24.4	23	0.89	1.13
Cr plating waste	Cr	P	240	258	1124	7.6	34	0.93	0.85
		P	240	186	551	11.3	34	0.99	6.50
Scrap metal	Pb	I	240	93	772	4.0	30	0.89	1.98
		P	240	93	772	4.0	70	0.92	1.78
	Zn	I	240	111	556	6.7	25	0.96	1.85
		P	240	111	556	6.7	66	0.95	1.85

<sup>a</sup> Minimum detection limit.

<sup>b</sup> Milligrams-per-kilogram.

<sup>c</sup> Coefficient of variation in percent.

<sup>d</sup> Number of observations.

<sup>e</sup> Coefficient of determination (R-square) for the regression.

<sup>f</sup> Not analyzed.

Table 2  
Spectrace 9000 FPXRF results

Waste type	Element	Analysis method P – prepared I – in-situ	Measurement time in seconds	MDL <sup>a</sup> (mg/kg) <sup>b</sup>	Precision Concentration (mg/kg)	COV (%) <sup>c</sup>	Regression Statistics		
							N. Obs. <sup>d</sup>	COD <sup>e</sup>	Slope
Cr tanning waste	Cr(Cd109)	P	100	516	N/A <sup>f</sup>	N/A	18	0.80	0.98
	Cr (Fe55)P	P	100	264	1103	8.0	23	0.80	0.97
Cr plating waste	Cr (Cd109)	P	240	1383	4462	10.3	32	0.94	0.37
	Pb	P	240	114	1124	3.4	32	0.71	0.67
Scrap metal	Pb	I	240	123	972	4.4	40	0.87	1.09
	Pb	P	240	123	972	4.4	72	0.83	1.04
Auto junkyard	Zn	I	240	159	783	6.8	40	0.95	0.78
	Zn	P	240	159	783	6.8	72	0.97	0.59
Battery breakage	Pb	P	60	30	136	19.1	12	0.86	1.17
	Cu	P	60	96	N/A	N/A	12	0.96	1.07
Battery breakage	Zn	P	60	75	N/A	N/A	11	0.97	0.73
	Pb	I	60	42	1049	5.0	20	0.97	0.69
Smelter waste	Pb	I	60	33	1750	4.3	13	0.99	1.62
	Pb	I	30	36	1766	8.2	23	0.91	1.11
Smelter waste	Cu	I	30	135	N/A	N/A	23	0.95	0.86
	Zn	I	30	135	N/A	N/A	23	0.97	0.75
Smelter waste	As	I	30	81	N/A	N/A	N/A	N/A	N/A
	Pb	P	60	38	1151	8.0	180	0.89	1.34
Burned electronics	As	P	60	58	N/A	N/A	180	0.58	0.62
	Pb	I&P	30	42	935-1233	4.7	213	0.89	0.94
Wood treatment	Zn	I&P	30	103-206	N/A	N/A	215	0.94	0.60
	Cu	I&P	30	93-192	N/A	N/A	206	0.84	0.87
Wood treatment	Ba	I&P	30	39-78	N/A	N/A	218	0.76	0.80
	Cu	P	240	75	2851	11.0	24	0.95	1.09
Scrap metal	Zn	P	240	56	6277	10.0	37	0.94	1.16
	As	P	240	49	N/A	N/A	27	0.89	1.14
Scrap metal	Zn	P	60	120	1938	7.0	51	0.98	1.09
	Pb	P	60	90	1094	7.8	50	0.94	1.16
Paint chips	Cd	P	60	170	N/A	N/A	N/A	N/A	N/A
	Pb	P	60	50	N/A	N/A	5	0.99	1.10

<sup>a</sup>Minimum detection limit.

<sup>b</sup>Milligrams-per-kilogram.

<sup>c</sup>Coefficient of variation in percent.

<sup>d</sup>Number of observations.

<sup>e</sup>Coefficient of determination (R-square) for the regression.

<sup>f</sup>Not analyzed.

types are summarized in Table 1. Similar data for the Spectrace 9000 FPXRF analyzer are summarized in Table 2.

Additionally, several sites have been investigated where most or all of the FPXRF and confirmatory AA results were below the FPXRF MDL; this data is not presented.

## 6. Discussion of results

### 6.1. Evaluation of in-situ and prepared sample methodologies for lead analysis

The in-situ and prepared sample methodologies for Pb analysis were evaluated at a battery breakage and a scrap metal site using the OEI X-MET 880 (the first and last sites in Table 1). Additionally, these methodologies were also evaluated with the Spectrace 9000 at the scrap metal site (the third site in Table 2). Both the in-situ and prepared sample FPXRF results for these sites met QA2 data objective requirements.

A statistical comparison of slopes (regression coefficients) was performed to compare AA/in-situ FPXRF and AA/prepared sample FPXRF regression results for data from the battery breakage and scrap metal sites. A methodology was utilized which is similar to that for testing the difference between two population means with the Student's *t*-test [13]. The null hypothesis for this test is  $\beta_1 = \beta_2$ , where  $\beta$  represents the true population regression coefficient. The alternative hypothesis is:  $\beta_1$  does not equal  $\beta_2$ . In all cases, alpha, the probability of rejecting the null hypothesis when it is in fact true, was set equal to 0.05.

Comparison of X-MET 880 battery breakage Pb AA versus in-situ FPXRF, and AA versus prepared sample FPXRF regression results indicated slopes of 0.92 and 0.84, respectively. When applying the Student's *t* methodology, no significant difference could be found between these two slopes ( $p$ -value > 0.50), indicating that they came from the same  $\beta$  population and that the regression lines can be assumed to be parallel.

Similar results were achieved for scrap metal comparisons for X-MET 880 and Spectrace 9000 regressions. Results of the X-MET 880 Pb in-situ FPXRF regression (slope = 1.98) vs. the prepared sample FPXRF regression (slope = 1.78) also showed no statistical difference between the slopes with  $0.10 < p$ -value < 0.20. Spectrace 9000 comparisons gave the same results as well, with the Pb in-situ FPXRF slope = 1.09, prepared sample FPXRF slope = 1.04, and  $0.20 < p$ -value < 0.50.

In all the three cases the null hypothesis could not be rejected, which supports the theory that the true population regression coefficients are in fact the same between AA/in-situ and AA/prepared sample FPXRF results. Therefore, the pairs of regression lines can be assumed to be parallel in each case.

### 6.2. FPXRF precision and detection limits

Lead is a primary target analyte in many extent of contamination studies and removal programs. FPXRF analyzers have proven to be well suited for the analysis of lead. FPXRF detection limits in Table 1 and Table 2 are significantly below typical Pb



action levels of 400–2000 mg/kg, and precision is normally less than 20% relative for analysis times of 30–60 s. FPXRF Pb results generally meet QA2 data objectives with close to 1:1 proportionality between AA/ICP and XRF data sets.

Additionally, FPXRF analyzers have proven to be well suited for the analysis of several other typical target metals (Ni, Cu, Zn, Ba, Cd, and As in the absence of Pb) and have met QA2 data objectives with close to 1:1 proportionality between AA/ICP and XRF data sets.

The severe Pb/As spectral overlap adversely affects As quantitation in XRF analysis as the sample Pb/As concentration ratio approaches 10:1, for example, 400 mg/kg of Pb makes it difficult to quantitate 40 mg/kg of As.

Cr has proven difficult to analyze by FPXRF because detection limits are high, and the Cr X-ray intensity is subject to interferences from both particle size variations and sample moisture content.

### 6.3. XRF round-robin results

Recently, an XRF round-robin was conducted by The Mineral Lab, Inc., Lakewood, Colorado. It included 12 laboratory EDXRF and wavelength dispersive XRF (WDXRF) units, and the field-portable Spectrace 9000 EDXRF unit. Splits of an unknown, ground and homogenized sample were sent to each laboratory for analysis. The metal results produced by the Spectrace 9000 soils application correlated well with the results of the more sophisticated laboratory EDXRF and WDXRF units. Spectrace 9000 Ti, Fe, Cu, Zn, Sr, Zr, Cd, Ba, and Pb results fell within two standard deviations of the mean for values reported by seven or more of the laboratories. Both laboratory XRF and Spectrace 9000 Cr, Rb, Mo, Sn, Sb results indicated very low or nondetectable concentrations.

### 6.4. Chemical analysis results

Chemical extraction recovery efficiency is addressed in a recent issue of *American Laboratory* [14]. Significant variance is reported for extraction recovery of different metals. Additionally, variance is reported among laboratories and different soil matrices. Therefore, it is important to understand that the confirmatory chemical analysis extraction recoveries are dependent upon the sample matrix, the chemical extraction methodology, and the laboratory analyzing the samples. Performance evaluation samples (blind) and field blanks are encouraged to validate laboratory performance.

## 7. Conclusions

FPXRF analyzers have proven to be a viable, effective approach to meet the on-site metals analysis needs of many US EPA/ERT hazardous waste site evaluation/removal programs. QA2 data objectives have been achieved that provide quick on-site multi-element analysis of large numbers of in-situ and prepared samples. Additionally,

statistical evaluations of in-situ and prepared sample FPXRF analyses infer that both methods produce identical confirmation slopes (regression coefficient). Therefore, in-situ analysis should be considered when characterizing large areas requiring large sample populations or when confirming removal activities at sites exhibiting large contaminant geological variability.

The on-site availability of reliable FPXRF analyses provides managers with the near real-time data necessary for guidance of critical field decisions in removal actions. Simultaneously, cost and time savings have been realized when FPXRF analysis is compared with off-site laboratory AA/ICP analysis. Furthermore, by cost effectively increasing sampling densities, the reliability of decisions based on spatial models delineating the extent of contamination has increased.

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