

Application of field-portable X-ray fluorescence spectrometers for field-screening air monitoring filters for metals[☆]

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Abstract

Field-portable X-ray fluorescence (FPXRF) spectrometers have been successfully used for on-site rapid characterization of hazardous metallic waste sites. The Outokumpu Electronics, Inc. (OEI), X-MET 880 and the Spectrace Instruments, Inc., Spectrace model 9000 FPXRF spectrometers' ability to analyze filters used in monitoring air quality was evaluated. The instruments differ in their energy resolving power and calibration methodology. Both instruments, representing two different analytical techniques, performed similarly. Typical method detection and quantitation limits, results of an accuracy check, conformational laboratory chemical analysis and results of a blind performance evaluation are presented.

Keywords: Field-portable X-ray fluorescence; Air filters; Metals; Personnel monitoring; NIOSH method 7300; Thin films

1. Introduction

Field-portable X-ray fluorescence (FPXRF) spectrometers have been successfully used for on-site rapid characterization of hazardous metallic waste sites [1–5]. The objective was to evaluate FPXRF as a rapid, nondestructive, on-site alternative for analysis of membrane filters used in National Institute for Occupational Safety and Health (NIOSH) method 7300 for metals using FPXRF spectrometers [6–8]. NIOSH method 7300 is used to monitor or identify off-site migration, sources, indoor air quality, and personnel sampling. Additionally, filters and thin films used in Hi-Vol

[☆] Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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sampling or performing wipe tests could be analyzed with this method. The United States Environmental Protection Agency (US EPA) Environmental Response Team has been using the OEI X-MET 880 and the Spectrace 9000 FPXRF spectrometers to characterize soil and sediment metal contamination at hazardous waste sites [3, 4]. These spectrometers can be adapted to include analysis of membrane filters used to quantify metals in air.

2. Experimental

The following target list of metals was used in evaluating the FPXRF methods: chromium (Cr), manganese (Mn), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), lead (Pb), cadmium (Cd), and tin (Sn).

NIOSH method 7300 uses a 37 mm diameter, 0.8 μm pore, cellulose ester-membrane filter in a sampler connected to a pump with a flow rate of 1–4 l/min for sampling volumes of 0.5–2 m^3 over 8 h. The method calls for chemical ashing of the filter, followed by atomic emission, atomic absorption or inductively coupled argon plasma analysis. The 37 mm filters are prepared for XRF analysis by mounting them on a 40 mm double open-ended X-ray sample cups between two layers of 5 μm polypropylene X-ray film.

Energy-dispersive XRF (EDXRF) provides nondestructive near real-time simultaneous multi-element analysis of thin-film samples. The FPXRF instruments evaluated employ radioisotope source excitation. X-ray excitation was provided in each case by the radioisotopes; ^{109}Cd and ^{241}Am . The ^{241}Am source was used for a measurement time of 800 s for the elements Cd and Sn. ^{109}Cd was used for the other elements with a measurement time of 200 s. A third source, ^{55}Fe , was also used by the Spectrace 9000 for a measurement time of 200 s for a second analysis of the element Cr. In each case, all of the elements excited with a given source are effectively determined in a simultaneous fashion.

Both spectrometer designs provide lightweight, battery-powered, hand-held operation, for practical application to in situ and prepared sample measurement of soils. The instruments differ in their energy resolving power and calibration methodology. The adaption of each to filter measurement is relatively simple, as described below.

3. Methodology

3.1. Outokumpu Electronics, Inc., X-MET 880 HEPS probe

The OEI X-MET 880 can be adapted to perform filter measurement by mounting the surface-analysis probe (SAPS) or the double-source surface (DOPS) probe in the upright geometry and attaching the safety shield. A heavy element powder/liquid (HEPS) probe was used in this evaluation. This eliminates the need to hold the DOPS or SAPS trigger for the 200–800 s measuring times and provides better sensitivity and sample presentation. Two HEPS probes were required, because each probe can be

fitted with only one excitation radioisotope. The probes are temperature-sensitive. The operator activates a software-controlled gain-control circuit for 5 min for every 3 °C change in the ambient operating temperature to prevent possible error due to gain shifts.

The OEI HEPS probe employs a gas proportional detector with a typical energy resolution of 850 eV at the full width at half-maximum (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 program to calculate elemental concentrations. Elemental standards and certified thin-film standards are used for an empirical instrument calibration. This provides the operator with the flexibility to configure the instrument to analyze any element from aluminum (Al) to uranium (U).

Two sets of gravimetrically prepared thin-film standards were purchased from OEI for target element model calibration. The standards were fabricated using 37 mm diameter, 0.8 µm pore, cellulose-ester filters. The single element standards were quoted as 5% accurate and the multielement standards as 10% accurate. A thick (approximately 6 mm) piece of high-purity Al was placed directly behind all samples and standards prior to analysis, to provide a constant background/backscatter radiation profile and eliminate possible background from impurities in the probe shield material.

The electronic unit of the OEI X-MET 880 FPXRF is capable of holding 32 calibration models. Each model can be calibrated to analyze for six target elements. The OEI standards were used to develop three calibration models. 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.

3.2. Spectrace 9000

The Spectrace 9000 is adapted to perform filter measurement by placing the surface probe in its laboratory stand and mounting the safety shield. An adaptor ring locates the sample cup in the center of the aperture. Three excitation sources, ⁵⁵Fe, ¹⁰⁹Cd and ²⁴¹Am, are contained in the probe providing an elemental analytical range of sulfur (S) through uranium (U). Calibration is not necessary; only selection of a thin-film FP-based application from a menu is required. A spectrum energy calibration is performed automatically with each analysis to prevent error due to gain shifts.

The Spectrace 9000 utilizes a mercuric iodide (HgI₂) semiconductor detector with an energy resolution of 270 eV at the FWHM of the Mn K X-ray line. The higher energy resolution of the detector allows for efficient use of a FP-based program to calculate elemental concentrations. For thin-film samples such as filters, element concentrations are computed using FP-derived coefficients in an algorithm of the form: Concentration = RS ; where, R is the measured analyte X-ray intensity relative to the pure element and S is a calculated (during factory setup) sensitivity coefficient. A more complex FP based program is used for soil applications.

X-ray intensities, derived from the spectra of the three sources, are processed for 25 elements simultaneously. The application presently analyzes for potassium (K), calcium (Ca), titanium (Ti), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co),

nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), strontium (Sr), zirconium (Zr), molybdenum (Mo), mercury (Hg), lead (Pb), rubidium (Rb), cadmium (Cd), silver (Ag), tin (Sn), antimony (Sb), barium (Ba), thorium (Th), and uranium (U). Therefore, filter samples may be analyzed for any or all of these elements without developing a calibration model. Additionally, the thin-film application calculates and reports Cr results for both ^{55}Fe and ^{109}Cd spectra.

The probe shield design utilizes a high-purity Al metal over the Pb in the shield to prevent excitation and analysis of the lead during thin-film measurements. Therefore, the Spectrace 9000 thin film method did not require placement of a high-purity piece of Al directly behind the thin films prior to analysis.

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

Table 1
OEI X-MET 800 HEPS probe and Spectrace 9000 detection and quantitation limits

Standard number	Target element	Standard deviation ($\mu\text{g}/\text{cm}^2$)	Isotope source	Analysis time (s)	Detection limit ($\mu\text{g}/10.75 \text{ cm}^2$) ^a	Quantitation limit ($\mu\text{g}/10.75 \text{ cm}^2$)
Spectrace 9000						
B-1-031	Cr	0.4	^{55}Fe	200	12.9	43.0
B-1-031	Cr	0.6	^{109}Cd	200	19.4	64.5
B-1-048	Mn	0.8	^{109}Cd	200	25.8	86.0
B-1-031	Fe	0.8	^{109}Cd	200	25.8	86.0
B-1-031	Ni	0.5	^{109}Cd	200	16.1	53.8
B-1-048	Cu	0.5	^{109}Cd	200	16.1	53.8
B-1-031	Zn	0.5	^{109}Cd	200	16.1	53.8
B-1-048	Pb	0.5	^{109}Cd	200	16.1	53.8
B-1-048	As	0.8	^{109}Cd	200	25.8	86.0
B-1-031	Se	0.4	^{109}Cd	200	12.9	43.0
6312	Cd	1.1	^{241}Am	800	35.5	118.3
6312	Sn	1.1	^{241}Am	800	35.5	118.3
OEI X-MET 880 HEPS probe						
B-1-031	Cr	0.7	^{109}Cd	200	22.6	75.3
B-1-048	Mn	0.9	^{109}Cd	200	29.0	96.8
B-1-031	Fe	0.5	^{109}Cd	200	16.1	53.8
B-1-031	Ni	0.5	^{109}Cd	200	16.1	53.8
B-1-048	Cu	0.5	^{109}Cd	200	16.1	53.8
B-1-031	Zn	0.4	^{109}Cd	200	12.9	43.0
B-1-048	Pb	0.6	^{109}Cd	200	19.4	64.5
B-1-048	As	0.4	^{109}Cd	200	12.9	43.0
B-1-031	Se	N/A ^b	^{109}Cd	200	N/A	N/A
6312	Cd	2.1	^{241}Am	800	67.7	225.8
6312	Sn	1.8	^{241}Am	800	58.1	193.5

^a These numbers are equivalent to the concentration in air expressed as $\mu\text{g}/\text{m}^3$ if 1 m^3 of air is sampled through a 37 mm diameter filter.

^b Not analyzed.

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.

4. Accuracy check, detection and quantitation limit methodology

The element detection and quantitation limits were determined by performing 10 measurements of the approximate $10 \mu\text{g}/\text{cm}^2$ ($20 \mu\text{g}/\text{cm}^2$ for Cd and Sn) per element multi-element standards. Alternatively, a blank sample could be used for these measurements with the Spectrace 9000 FPXRF since it has the ability to report negative values. The method detection and quantitation limits, in Table 1, were calculated as three times and ten times the standard deviation of the measurements and are quoted in micrograms of element per sample, whose deposit area is 10.75 cm^2 (area of a 37 mm filter). These units are equivalent to the concentration in air expressed as $\mu\text{g}/\text{m}^3$ if 1 m^3 of air is sampled through a 37 mm diameter filter.

The accuracy of the application models was checked by analyzing a set of single and multi-element gravimetrically prepared standards purchased from Micromatter Co. The standards were quoted as $\pm 5\%$ accurate. The results are in Tables 2 and 3.

5. Performance evaluation sample methodology

Two cellulose-ester thin-film multi-element standards were gravimetrically prepared by OEI for use as performance evaluation standards. Sample 1 was loaded with approximately $10 \mu\text{g}/\text{cm}^2$ Cr, Fe, Ni, and Zn. Sample 2 was loaded with approximately $10 \mu\text{g}/\text{cm}^2$ Cu, As, Pb, and Cd. The $\mu\text{g}/\text{cm}^2$ certified values were multiplied by 10.75 for units in $\mu\text{g}/10.75 \text{ cm}^2$ (area of a 37 mm filter). These standards were used to evaluate the performance of both FPXRF instruments and the chemical ashing metal analysis methodology. The standards were first analyzed by both instruments and then sent to the Spectrace Instruments Inc., laboratory for independent XRF analysis by a high resolution tube excited Spectrace 6000 instrument. Quantitative analysis was performed by the 6000 using a FP model that was calibrated using Micromatter Co. standards numbered 6304, 6308, 6310, 6311, and 6314. The certified values for these standards are in Tables 2 and 3. The cellulose-ester standards were then sent blind (with a set of 16 site samples) to a contract laboratory for ashing and chemical analysis. The results of all four analyses are in Table 4.

6. Discussion of results

6.1. OEI X-MET 880 HEPS probe

The OEI X-MET 880 HEPS probe model Se calibration was not checked because the Se calibration standard provided by OEI was unstable, invalidating the Se

Table 2
Spectrace 9000 thin film application accuracy check results using micromatter Co. standards

Standard number	Target element	Density deposit ($\mu\text{g}/\text{cm}^2$)	Isotope source	Analysis time (s)	Instrument reading ($\mu\text{g}/\text{cm}^2$)	% Error ^a
6301	Cr	21.0	¹⁰⁹ Cd	200	20.7	– 1.4
6302	Mn	17.0	¹⁰⁹ Cd	200	16.0	– 5.9
6303	Fe	20.4	¹⁰⁹ Cd	200	19.4	– 4.9
6304	Ni	18.5	¹⁰⁹ Cd	200	21.0	13.5
6305	Cu	20.0	¹⁰⁹ Cd	200	18.1	– 9.5
6306	Zn	19.2	¹⁰⁹ Cd	200	19.9	3.6
6311	Pb	21.9	¹⁰⁹ Cd	200	26.7	21.9
6307	As	34.2	¹⁰⁹ Cd	200	40.4	18.1
6308	Se	18.6	¹⁰⁹ Cd	200	N/A ^b	N/A
6313	Pb	21.4	¹⁰⁹ Cd	200	15.5	–27.6
	As	34.4	¹⁰⁹ Cd	200	41.0	19.2
	Se	19.7	¹⁰⁹ Cd	200	N/A	N/A
6314	Cr	18.6	¹⁰⁹ Cd	200	25.2	35.5
	Mn	16.1	¹⁰⁹ Cd	200	19.2	19.3
	Fe	19.0	¹⁰⁹ Cd	200	22.8	20.0
	Ni	18.2	¹⁰⁹ Cd	200	21.9	20.3
	Cu	19.7	¹⁰⁹ Cd	200	18.3	– 7.1
	Zn	18.7	¹⁰⁹ Cd	200	19.9	6.4
6309	Cd	18.9	²⁴¹ Am	800	20.3	7.4
	Se	13.2	¹⁰⁹ Cd	200	N/A	N/A
6310	Sn	18.8	²⁴¹ Am	800	21.8	16.0
6312	Cd	21.0	²⁴¹ Am	800	27.8	32.4
	Se	14.7	¹⁰⁹ Cd	200	N/A	N/A
	Sn	18.2	²⁴¹ Am	800	17.2	– 5.5
Blanks	Cr, Mn, Fe,	0	¹⁰⁹ Cd	200	All requests were below the element direction limits	
	Ni, Cu, Zn,	0	¹⁰⁹ Cd	200		
	Se, Pb, As,	0	¹⁰⁹ Cd	200		
	Cd, Sn	0	²⁴¹ Am	800		

^a % error = [(instrument reading – certified value)/certified value] (100).

^b Not analyzed.

calibration. Additionally, the Americium 241 HEPS probe was unavailable when the performance evaluation samples were analyzed, so Cd analysis was not performed on these samples. The method detection limit range was from 12.9 to 67.7 $\mu\text{g}/10.75 \text{ cm}^2$ (Table 1). The error of the accuracy check ranged from –27.6% to 35.5% (Table 2). The error of the performance evaluation check ranged from –41.7% to 30.3% (Table 4).

Table 3
Spectrace 9000 thin film application accuracy check results using micromatter Co. standards

Standard number	Target element	Density deposit ($\mu\text{g}/\text{cm}^2$)	Isotope source	Analysis time (s)	Instrument reading ($\mu\text{g}/\text{cm}^2$)	% Error ^a
6301	Cr	21.0	⁵⁵ Fe	200	18.2	– 13.3
6301	Cr	21.0	¹⁰⁹ Cd	200	20.5	– 2.4
6302	Mn	17.0	¹⁰⁹ Cd	200	18.4	8.2
6303	Fe	20.4	¹⁰⁹ Cd	200	22.2	8.8
6304	Ni	18.5	¹⁰⁹ Cd	200	23.2	25.4
6305	Cu	20.0	¹⁰⁹ Cd	200	21.8	9.0
6306	Zn	19.2	¹⁰⁹ Cd	200	20.0	4.2
6311	Pb	21.9	¹⁰⁹ Cd	200	24.1	10.0
6307	As	34.2	¹⁰⁹ Cd	200	38.9	13.7
6308	Se	18.6	¹⁰⁹ Cd	200	22.4	20.4
6313	Pb	21.4	¹⁰⁹ Cd	200	22.2	3.7
	As	34.4	¹⁰⁹ Cd	200	40.3	17.2
	Se	19.7	¹⁰⁹ Cd	200	23.8	20.8
6314	Cr	18.6	⁵⁵ Fe	200	15.1	– 18.8
	Cr	18.6	¹⁰⁹ Cd	200	22.2	19.4
	Mn	16.1	¹⁰⁹ Cd	200	16.4	1.9
	Fe	19.0	¹⁰⁹ Cd	200	21.7	14.2
	Ni	18.2	¹⁰⁹ Cd	200	22.0	20.9
	Cu	19.7	¹⁰⁹ Cd	200	19.4	– 1.5
	Zn	18.7	¹⁰⁹ Cd	200	17.9	– 4.3
6309	Cd	18.9	²⁴¹ Am	800	25.2	33.3
	Se	13.2	¹⁰⁹ Cd	200	15.4	16.7
6310	Sn	18.8	²⁴¹ Am	800	23.5	25.0
6312	Cd	21.0	²⁴¹ Am	800	25.7	22.4
	Se	14.7	¹⁰⁹ Cd	200	17.2	17.0
	Sn	18.2	²⁴¹ Am	800	21.9	20.3
Blanks	Cr	0	⁵⁵ Fe	200	All results were below the element detection limits	
	Cr, Mn, Fe	0	¹⁰⁹ Cd	200		
	Ni, Cu, Zn	0	¹⁰⁹ Cd	200		
	Se, Pb, As	0	¹⁰⁹ Cd	200		
	Dc, Sn	0	²⁴¹ Am	800		

^a %error = ([instrument reading – certified value]/certified value) (100).

6.2. Spectrace 9000

The method detection limit ranges was from 12.9 to 35.5 $\mu\text{g}/10.75 \text{ cm}^2$ (Table 1). The error of the accuracy check ranged was from –18.8% to 33.3% (Table 3). The error of the performance evaluation check ranged from –40.2% to 37.0% (Table 4).

Table 4
Performance evaluation sample analysis results

Element	Certified ($\mu\text{g}/10.75\text{ cm}^2$)	Analytical results ($\mu\text{g}/10.75\text{ cm}^2$) ^a			
		AA ^b	Spectrace 6000	OEI X-MET 880	Spectrace 9000
Cr	131.2	140	126.3	167.7	159.5 ^c 179.8 ^d
Fe	118.3	110	116.6	145.8	134.7
Ni	122.6	160	117.7	159.7	153.5
Cu	107.5	37	74.4	62.7	91.3
Zn	127.9	130	119.2	157.4	148.2
As	98.9	30	67.5	84.4	80.0
Pb	123.6	43	84.7	81.5	98.4
Cd	114.0	42	67.5	NA ^e	68.2

Element	Percent error ^f			
	AA	Spectrace 6000	X-MET 880	Spectrace 9000
Cr	6.7	– 3.7	27.8	21.6 ^c 37.0 ^d
Fe	– 7.0	– 1.4	23.2	13.9
Ni	30.5	– 4.0	30.3	25.2
Cu	– 65.6	– 30.8	– 41.7	– 15.1
Zn	1.6	– 6.8	23.1	15.9
As	– 69.7	– 31.7	– 14.7	– 19.1
Pb	– 65.2	– 31.5	– 34.1	– 20.4
Cd	– 63.2	– 40.8	NA	– 40.2

^a Micrograms per 10.75 square centimeters (total area of a 37 millimeter diameter filter). These numbers are equivalent to the concentration in air expressed at $\mu\text{g}/\text{m}^3$ if 1 m^3 of air is sampled through a 37 mm diameter filter.

^b Atomic absorption.

^c ^{55}Fe excitation.

^d ^{109}Cd excitation.

^e Not analyzed.

^f Percent error = $([\text{instrument reading} - \text{certified value}]/\text{certified value}) (100)$.

6.3. Spectrace 6000

Method detection limits were not determined. The error of the performance evaluation check ranged from -1.4% to -40.8% (Table 4).

6.4. Chemical ashing and metal analysis

The error of the performance evaluation check ranged from -69.7% to 30.5% (Table 4). Additionally, half of the errors were both negative and greater than 60%.

7. Conclusions

All of the elements evaluated (with the exception of As and Ni currently identified by NIOSH as occupational carcinogens) by both FPXRF spectrometers had detection limits (assuming a minimum of 1 m³ sample air volume for a 37 mm diameter filter) below the exposure limits (as the element, i.e., lead dust as Pb) published in the NIOSH Pocket Guide To Chemical Hazards, US Department of Health and Human Services, September, 1990.

Generally, the XRF performance-evaluation results agreed well and had similar differences with the certified gravimetric values. The atomic absorption metal-analysis performance-evaluation results had the widest range and the largest negative errors (up to -70%) indicate a loss during the analytical procedure. Blind-performance evaluation samples are recommended when submitting samples for chemical ashing and metal analysis.

FPXRF analysis provides a rapid nondestructive on-site technique for prescreening filters and wipes. This technique could be adapted by the users of the OEI X-MET 880 FPXRF unit by using the appropriate HEPS probe and standards for the metal(s) of interest. This technique could be adapted by the present users of the Spectrace 9000 through use of the thin-film application model currently provided with the unit. Both instruments, representing two different calibration approaches, performed similarly.

The reported method detection limits are based on repetitive measurements of filters loaded with 10 µg/cm² (20 µg/cm² for Cd and Sn) of the target element(s). Lower method detection limits, by generally a factor of 2, could be calculated by measurement of a blank filter reducing the counting statistical error. Additionally, the inclusion of lot and trip blanks are recommended for all field analytical activities.

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