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Evaluation of a Portable X-Ray Fluorescence Instrument for the Determination of Lead in Workplace Air Samples

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Occupational Safety and Health Administration (OSHA) regulations for worker exposure to lead specify worker protection levels based upon airborne concentrations of lead dust. The rapid, on-site determination of lead in air filter samples using a portable x-ray fluorescence (XRF) instrument with an attachment to hold the filter would expedite the exposure assessment process and facilitate compliance with the OSHA standards.

A total of 65 lead in air filter samples were collected at bridge blasting lead-abatement projects using closed-faced, 37-mm cassettes with pre-loaded 0.8 micron pore size mixed cellulose ester membrane filters. The lead loading range of the data set was 0.1–1514.6 micrograms (μg) of lead/sample. Samples were initially analyzed with a field portable XRF (NITON® 700) using an experimental non-destructive XRF method. Samples were subsequently analyzed using National Institute for Occupational Safety and Health (NIOSH) Method 7105 (Graphite Furnace AA) as a reference analytical method. The paired data were not normally distributed; therefore, the non-parametric Wilcoxon signed rank test was used for statistical analysis. There was no statistically significant difference between data from the field portable XRF method and the NIOSH method (p-value = 0.72). Linear regression of the data resulted in a slope of 0.959, a y-intercept of 5.20 μg, and an r^2 of 0.985. The XRF limit of detection and limit of quantitation were determined to be 6.2 and 17 μg of lead/sample, respectively. The XRF method accuracy was ± 16.4% (7.1%–27%, 90% confidence interval).

The data presented in this study indicate that field-portable XRF can be used for the analysis of lead air filter samples over the range of 17 to 1500 μg of lead/sample. The practicing industrial hygienist can use field-portable XRF to produce a rapid, on-site determination of lead exposure that can immediately be communicated to workers and help identify appropriate levels of personal protection. As the method is non-destructive, samples can subsequently be sent to a laboratory for confirmation. Confirmation would be recommended when greater than 16.4 percent accuracy from an analytical method is required. This study provided data of suitable quality for the development of NIOSH Method 7702, "Lead by Field Portable XRF."

Keywords Lead, X-Ray, Fluorescence, Workplace Air, Portable Analysis

The Occupational Safety and Health Administration (OSHA) regulates "all construction work where an employee may be occupationally exposed to lead"(1) and "all occupational exposure to lead."(2) In both standards, occupational exposure to lead is determined by conducting an initial exposure assessment. A field portable instrument for the on-site measurement of lead in air filter samples would facilitate compliance with the standards and improve employee health and safety by providing rapid exposure assessment data which can be used to determine the appropriate level of personal protection. This is of particular interest to the lead abatement community where projects are often of shorter duration than the corresponding laboratory turnaround time for the initial exposure assessment sample analyses.

BACKGROUND

The analysis of lead using XRF is conducted by the excitation of lead atoms. XRF instruments have sealed radioactive sources which release electromagnetic energy in the form of

X rays and/or gamma rays when the shutter is opened. The two radioactive sources most commonly seen in field-portable XRF instruments are Cadmium 109 (^{109}Cd) and Cobalt 57 (^{57}Co). Both ^{109}Cd and ^{57}Co decay by electron capture. Electron capture occurs when the nucleus of a radionucleotide absorbs an orbital electron, converting a proton to a neutron and releasing electromagnetic energy. Both ^{109}Cd and ^{57}Co radionucleotides absorb a K shell electron during electron capture. The K-shell is the innermost electron shell of the atom, followed by the L-shell, the M-shell, and so on. With a ^{109}Cd source, the energy released during electron capture is a 88.037 kiloelectron volts (keV) gamma ray.(3) With a ^{57}Co source, the energy released during electron capture is in the form of two gamma rays, at 122.06135 keV and 136.47434 keV.(3) Following electron capture, the daughter atom is left in an excited state with an electron vacancy in the K shell. This electron vacancy is filled by an outer-shell electron, releasing a secondary emission in the form of an X ray. When a ^{109}Cd source decays, two secondary X rays are released, at 22.1 keV and 25.0 keV.(3) When a ^{57}Co source decays, the secondary emission is at 14.41302 keV.(3) The strongest emission from a ^{109}Cd source is the 22.1 keV X ray, with an absolute intensity of 79.4 percent.(3) The strongest emission from a ^{57}Co source is the 122.06135 keV gamma ray with an absolute intensity of 85.6 percent.(3)

Incident electromagnetic energy from the radioactive source causes the excitation of the target lead atoms. Once excited, lead atoms return to their original energy state (steady state) by emitting electromagnetic radiation in the form of X rays. The release of this energy is a rare, highly characteristic process of atomic relaxation called fluorescence.(4) Atomic excitation can occur at the K shell and/or the L shell, depending upon the electron-binding energies of the atom and the strength of the incident electromagnetic radiation. K shell XRF is done when a lead K shell electron is excited to the L shell and subsequently falls back to the K shell releasing X rays. L shell XRF is done when a lead L shell electron is excited to the M shell and subsequently falls back to the L shell releasing X rays.

Lead K shell electrons have an electron binding energy of 88.005 keV.(3) Both the ^{57}Co and the ^{109}Cd gamma ray emissions are greater than the K shell electron binding energy of lead and can cause excitation. Excited K shell electrons return to steady state releasing 74.2 keV and 85.4 keV X rays. Lead L shell electrons have an electron binding energy of 15.861 keV, 15.200 keV, and 13.035 keV.(3) The secondary emissions from ^{109}Cd (22.1 keV and 25.0 keV) are greater than the L shell binding energies of lead and can cause excitation. However, the secondary emission from ^{57}Co (14.41302 keV) is greater than only one L shell binding energy and cannot cause complete excitation of the L shell. Excited L shell electrons return to steady state releasing 10.5 keV, 12.6 keV, and 14.8 keV X rays.

The analysis of lead air filter samples is made possible through the excitation and ionization of L-shell electrons and the detection of 10.5 keV, 12.6 keV, and 14.8 keV emissions. For this reason, XRF instrumentation that uses a ^{109}Cd source is preferred over XRF instrumentation that uses a ^{57}Co source. L-shell XRF is used for air filter samples because it is very efficient for thin layer samples with no substrate interferences. Additionally, L-shell XRF has a higher signal to noise ratio. This means that reduced background noise from the instrument improves peak resolution. The improved peak resolution allows for greater sensitivity and lower limits of detection. The NITON 700 XRF instrument was selected for this evaluation because it uses a ^{109}Cd source. The instrument has a Peltier-cooled high-resolution silicone PIN-diode detector with a resolution of 700 electron volts (eV) at 12.6 keV. The detector counts the number of X-ray emissions from the excited lead atoms at each of the three energy levels. Based upon the principles of Beer's law, a plot of the fluorescence power versus the concentration of the analyte is linear at low concentrations. Software within the instrument integrates the counts to produce an analytical result in micrograms of lead per square centimeter of surface area (μg of lead/cm^2).(5)

Individual XRF readings must be applied to an algorithm that will integrate readings into an analytical result. The procedure for converting individual XRF readings with the units of μg/cm^2 to an analytical result with the units of μg/sample is based upon sample geometry. The geometric procedure for analysis is based upon the use of a 37-mm filter with a particulate aerosol impacted surface area of approximately 9.6 cm^2. The instrument has a 2 cm^2 (2 cm × 1 cm) aperture through which a reading is taken.(5)

A five-reading analysis covers 10 cm^2, just slightly greater than the entire surface area of the filter (see Figure 1). Each of the five readings should be given equal weight. Therefore, each reading in μg/cm^2 is multiplied by 2 to account for the 2 cm^2 area of the XRF aperture.

A three-reading analysis covers 6 cm^2; therefore, individual readings must be multiplied by individual coefficients whose sum would account for the entire surface area of the filter. The procedure proposed by the manufacturer gives the greatest weight to the middle reading (see Figure 2). This reflects the commonly seen distribution of particulate on the surface of a closed-faced 37-mm cassette. The center (middle) of the filter is highly impacted with a light distribution of particulate extending to the perimeter of the filter. The middle reading (M) is

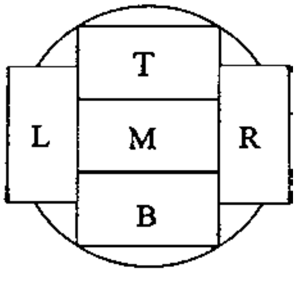

FIGURE 1
Experimental analysis of a 37-mm filter using field-portable XRF. Five readings were taken using a 2 cm × 1 cm aperture (M = middle, T = top, B = bottom, L = left, and R = right).

multiplied by 2 to account for the 2 cm^2 area of the XRF aperture. This leaves 7.6 cm^2 unanalyzed. The top (T) and bottom (B) readings are assumed to represent the remainder of the filter; therefore, each reading is multiplied by 3.8 (see Figure 2).

$$2.0*M + 3.8*T + 3.8*B = \mu g \text{ of lead/ filter}$$

The above algorithm was developed with data used by the manufacturer to pilot test the XRF method. The only reported interference associated with the use of this instrument is bromine.[(5)] The field samples collected were not likely to contain bromine and interferences were not seen in the analysis.

METHODS

The intent of this study was to determine the applicability of field-portable XRF technology for the rapid, on-site determination of lead in workplace air samples. The study design was developed to evaluate the method according to the National Institute for Occupational Safety and Health (NIOSH) criteria for an approved analytical method.[(6)] The NITON® 700 XRF, serial #U508D4193, (NITON Corp., Bedford, Massachusetts) was selected because it uses a ^{109}Cd radioactive source.

Field samples were collected using the standard industrial hygiene sampling protocol described in NIOSH Method 7105 "Lead by HGAAS."[(7)] This protocol calls for the collection of personal air samples using closed-faced 37-mm cassettes with pre-loaded 0.8 um pore size cellulose ester membrane filters. Gelman Science 37-mm three-piece air monitoring cassettes, lot #3112709, were used for all 37-mm samples. MSA Escort Elf Pumps and SKC pumps were used. All pumps were calibrated to 2 (± 0.1) lpm.

Field-Portable Method of Filter Analysis

The samples were first analyzed using the non-destructive, portable XRF analytical method. Filter samples were transferred from their cassettes to a cardboard and acetate sleeve (NITON, Bedford, Massachusetts) specifically designed for XRF air filter analysis. This sleeve is designed so that a 37-mm filter will be sealed between two pieces of acetate, surrounded by cardboard. The top piece of acetate was peeled back from the cardboard backing which is covered with a light adhesive. The 37-mm filter was then removed from the cassette and passed between an antistatic bar. The filter was removed from the backing material and placed onto the bottom piece of acetate. The top piece of acetate was then laid on top of the filter and sealed to the cardboard backing.

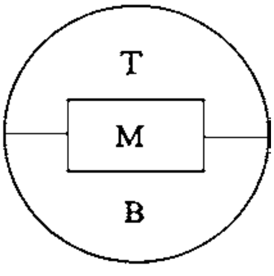

FIGURE 2
Three-reading analysis of a 37-mm filter using field-portable XRF. The three-reading analysis is the most efficient analytical method for the determination of lead in air filter samples. This method uses the algorithm $2*M + 3.8*(T + B)$ where M represents a 2 cm^2 area and T and B each represent a 3.8 cm^2 area.

The sealed sample was placed onto a filter test platform (NITON, Bedford, Massachusetts) designed for filter analysis. This platform is engineered to hold the NITON 700 XRF instrument in place while readings are being taken (see Figure 3). The stand enables the evaluation of an air filter sample without substrate interferences. The platform has pre-cut edges upon which the sleeve is placed to position the filter for the middle (M), top (T), and bottom (B) readings. Additional readings were taken in the left (L) and right (R) positions by moving the filter sleeve into pre-defined positions on the stand. These two additional readings were taken to test additional algorithms for the determination of lead in air filter samples. Figure 1 presents a scaled drawing identifying the locations of the five readings.

Each reading was taken for at least "one source minute." Software within the instrument defines the duration of a one source minute reading, which is equivalent to one real-time minute with a new source. As the source decays over time, a one source minute reading will take longer than one real-time minute. The source used in this study had decayed to a point that one source minute equaled approximately 86 seconds. A one source minute reading ensures an accurate L-shell reading. The five readings taken of each filter were recorded for subsequent statistical analysis.

Laboratory Method of Filter Analysis

Following the non-destructive analysis of the filter using the XRF method, the samples were submitted to the laboratory for analysis using NIOSH Method 7105 "Lead by HGAAS,"[(7)] or Graphite Furnace Atomic Absorption Spectrophotometry (GFAA), as a reference method. This method was chosen over NIOSH Method 7082 "Lead by Flame AAS,"[(7)] and NIOSH Method 7300 "Elements by ICP,"[(7)] due to the lower detection limit of Method 7105 for lead. All three methods show no statistically significant differences in their ability to meet ELPAT performance limits.[(8)]

Sample analysis was performed by the University of Cincinnati, Department of Environmental Health, Hematology and Environmental Laboratory. The exterior of the acetate filter holder was rinsed with double deionized water prepared in the lab using a Wheaton autostill (Fisher, Cincinnati, Ohio). The filter was then cut from the cardboard holder and the acetate and filter were placed into a beaker and digested in 3 milliliters (mL) of concentrated nitric acid (ACS Certified, Fisher, Fair Lawn, New Jersey), and 1 mL of 30 percent hydrogen peroxide (ACS

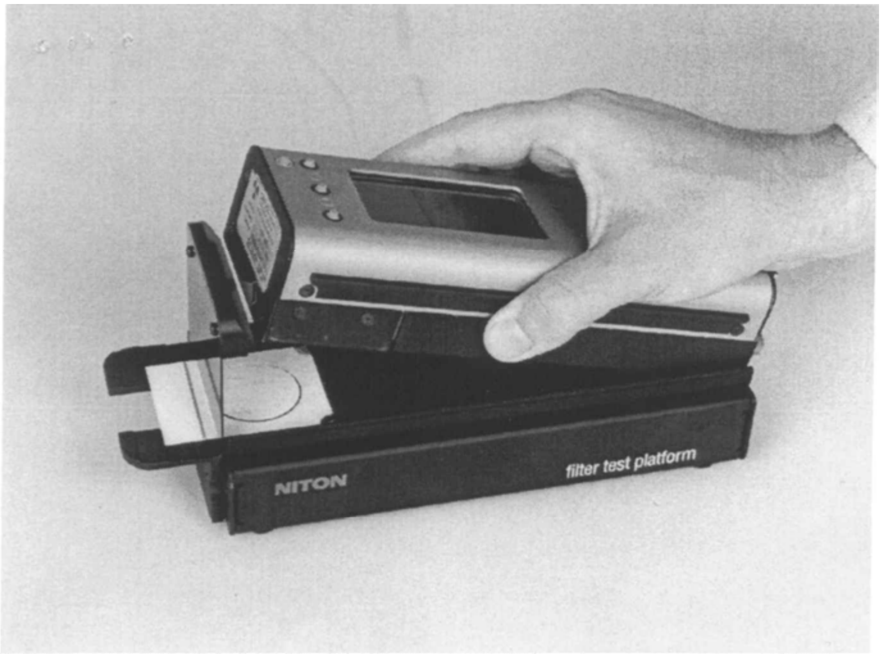

FIGURE 3
Filter analysis using field-portable XRF.

Certified, Fisher, Fair Lawn, New Jersey). The beaker was covered with a watchglass and heated at 140°C on a Lindberg hot plate (Fisher, Cincinnati, Ohio) until the volume was reduced to approximately 0.5 mL. The watchglass and beaker were then rinsed with 3–5 mL of 5 percent nitric acid and evaporated to 0.5 mL in an Isotemp Oven model 630G (Fisher, Cincinnati, Ohio). The solution was quantitatively transferred to a 10 mL volumetric flask and diluted to volume with double deionized water.

Samples were then diluted 1:10 using 0.5% nitric acid (instrument grade, Baker, Phillipsburg, New Jersey) and transferred to a sample cup (Perkin Elmer, Bodenseewerk, Germany). The sample was analyzed by a Perkin Elmer 5100ZL Atomic Absorption Spectrophotometer (Perkin Elmer, Bodenseewerk, Germany). Eppendorf® pipets and pipet tips (Brinkeman Instruments Inc., Westberg, New York) were used to transfer samples and create the dilutions. Samples were analyzed according to NIOSH Method 7105 with the exception of a slight modification to the injection times and temperatures. The samples were dried at 120°C for 20 seconds followed by 140°C for 30 seconds. The samples were charred at 900°C for 20 seconds and atomized at 1500°C for 5 seconds. The instrument was calibrated using a calibration blank, 2 part per billion (ppb) standard, 12.5 ppb standard, 25 ppb standard, 50 ppb standard, and 75 ppb standard. Standards were prepared using a 1000 ppm lead stock Lead Reference Solution (Fisher, Fair Lawn, New Jersey). Quality control was performed after every 10 samples analyzed using three blanks, a National Institute for Standards and Technology 35.4 ppb standard (NIST, Gaithersburg, Maryland), a Fisher 75 ppb certified reference standard, and a Continuing Calibration Verification 20.0 ppb standard. Method control samples were prepared using NIST Buffalo River Sediment, Standard Reference Material (SRM) #2704 containing 161 ± 17 μg of lead/g of sediment (NIST, Gaithersburg, Maryland).

Data Management

As previously discussed, the individual XRF readings must be applied to an algorithm which will integrate the readings into an analytical result in units of μg of lead/sample. The algorithm was developed by defining the best fit coefficients for the readings taken with the XRF device using NIOSH Method 7105 (GFAA) as the reference method. Best fit coefficients were determined for both a three-reading analysis and a five-reading analysis using statistical analytical software (SAS)$^{(9)}$ with multiple variable linear regression with no intercept:$^{(10)}$

$$\text{GFAA analytical value} = \alpha_1 * \mathrm{M} + \alpha_2 * \mathrm{T} + \alpha_3 * \mathrm{B} + \alpha_4 * \mathrm{L} + \alpha_5 * \mathrm{R}$$

and/or

$$\text{GFAA analytical value} = \beta_1 * \mathrm{M} + \beta_2 * \mathrm{T} + \beta_3 * \mathrm{B}.$$

The paired analytical data collected from each sample (XRF data vs. GFAA reference method data) were evaluated to determine whether a statistically significant difference existed between the two analytical results. Different algorithms for the XRF analytical result were tested for statistical significance. The algorithm which defined the most statistically significant similarity between the methods was further developed. This algorithm was used to define the instrumental limit of detection

(LOD), instrumental limit of quantitation (LOQ), method precision, method bias, and method accuracy.

The LOD and LOQ were estimated using a slight variation of NIOSH Standard Operating Procedure (SOP) 018(6) and an Environmental Protection Agency (EPA) method.(11) The EPA method uses the term method detection limit (MDL) rather than LOD. The MDL is "the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero." The MDL was estimated through the repeat analysis of one sample within the range of the estimated MDL (2–8 μg of lead/sample).

NIOSH SOP 018 defines LOD as "the mass of analyte which gives a mean signal 3 standard deviations (σ) above the mean blank signal, where σ is the standard deviation of the blank signal." The LOQ is defined as "the mass corresponding to the mean blank signal $+ 10\sigma$." NIOSH SOP 018 generally calls for the evaluation of low-level spiked samples and the construction of a calibration curve. Spiked samples could not be prepared for this method evaluation; therefore, matrix blanks were used for the determination. The use of matrix blanks instead of low-level spiked samples requires the following two assumptions: (1) that there is no bias within the method and (2) that the intercept of the regression line defining the slope of the XRF response vs. the true analyte concentration is zero. The use of matrix blanks defines the instrument signal at which a statistically significant determination can be made that the analyte is not a blank. This is a common statistical method for the determination of analytical LODs.(12)

The XRF method bias estimate was determined by subtracting the GFAA analytical value in terms of μg of lead/sample from the XRF analytical value in units of μg of lead/sample, and dividing by the GFAA analytical value in μg of lead/sample at each data point. This produced point bias estimates for each sample. The total bias of the data set was determined by taking the mean of the point bias estimates. The 95 percent confidence interval was determined by multiplying the appropriate t-value by the standard deviation and dividing by the square root of the sample size. NIOSH criteria for method development require that the 95 percent confidence interval for method bias include a value less than $\pm$ 0.10.(6)

The XRF method precision estimate was determined by conducting three repeat readings of filter samples whose lead loading range represented the target loading range of the method, that is, 3 to 500 μg of lead/sample. These three readings were averaged for each sample and the precision was defined as the standard deviation divided by the mean at each sample point. The point precision estimates were then averaged to determine the total precision of the method. The 95 percent confidence interval was determined by multiplying the appropriate t-value by the standard deviation and dividing by the square root of the sample size. Precision estimates at and around the OSHA action level and PEL are of interest for compliance sampling purposes. One sample was analyzed three times in the 30-μg lead loading range and one sample was analyzed three times in the 50-μg lead loading range.

The accuracy of the XRF method was estimated using the bias and precision of the XRF method with the Nomogram Relating Accuracy to Precision and Bias.(6) The bias and precision estimates included the appropriate 95 percent confidence interval. Using the 2.5 percent, 50 percent, and 97.5 percent confidence statistics for bias and precision with the Bonferroni Procedure,(6) the 5 percent, 50 percent, and 95 percent confidence statistics for accuracy were determined. NIOSH method development guidelines require that the 90 percent confidence interval for accuracy be entirely below a 25 percent accuracy criterion for a fully evaluated method.

RESULTS

Workplace air samples were collected from bridge lead-based paint abatement projects. Sixty-one area air samples were collected at an abrasive blasting bridge lead-abatement project. Area samples were collected for periods ranging from 30 seconds to 2 hours to obtain a wide distribution of lead particulate loadings. Four personal air samples were collected from employees performing manual scraping at a bridge lead-abatement project. A total of 65 samples were collected for analysis.

The samples were analyzed with the non-destructive XRF method, taking five readings as shown in Figure 1. These individual readings are presented in Table I. The samples were then analyzed using GFAA. The GFAA results are also presented in Table I. GFAA method control recoveries from spiked filters and beaker digestions averaged 88 percent throughout the study. This recovery is consistent with prior studies evaluating SRM 2704 with GFAA and is likely due to the presence of lead bound in silicates, which the digestion procedure cannot break down.(13–15) The data set represented a lead loading range of 0.1–1514.6 μg of lead/sample, based upon the GFAA analytical results.

Using three of the five XRF readings (M, T, and B), multiple variable linear regression with no intercept produced the best fit coefficients:

$$\text{GFAA analytical result} = 1.788*(M) + 4.110*(T) + 3.777*(B).$$

Two permutations of this algorithm that matched the geometric procedure of analysis were tested: $1.8*(M) + 3.9*(T + B)$ and $2.0*(M) + 3.8*(T + B)$. Using the five readings (M, T, B, L, and R), multiple variable linear regression with no intercept produced the best fit coefficients:

$$\begin{aligned}\text{GFAA analytical result} = {} & 1.769*(M) + 0.490*(T) + 2.481*(B)\\ & + 3.015*(L) + 2.038*(R).\end{aligned}$$

Due to the variability of the coefficients for the five-reading algorithm, the average was taken for all five readings. This was done to simplify the algorithm and give equal balance to each reading. The resulting algorithm was $1.96*(M + T + B + L + R)$.

Each of the five algorithms produced data that were compared to the GFAA data. The Wilks Shapiro test for normality

TABLE I

Analytical results

Sample #	M^A (middle)	B^A (bottom)	T^A (top)	L^A (left)	R^A (right)	XRF [2*M + 3.8*(T + B)]^B	GFAA^B
1	4.01	2.55	2.38	2.57	2.2	26.754	23.1
2	0.18	0.19	-0.01	0.34	-0.01	1.044	0.1
3	0.44	-0.5	0.5	0.2	-0.33	0.88	0.61
5	0.98	0.85	0.98	0.82	0.75	8.914	5.73
1A-37C	14.62	5.22	5.68	6.16	3.3	70.66	48.2
1B-37C	25.44	6.7	5.56	5.93	3.99	97.468	57.2
2A-37C	20.77	6.19	4.31	2.74	3.26	81.44	100
2B-37C	20.07	6.86	3.75	3.91	2.76	80.458	48.4
3A-37C	10.98	8.18	5.48	5.68	3.36	73.868	74.8
3B-37C	11.07	5.25	7.66	5.87	3.71	71.198	64.9
4A-37C	20.39	11.8	10.33	11.96	9.32	124.874	93.8
4B-37C	15.19	9.84	12.14	11.07	8.35	113.904	104
5A-37C	11.9	12.86	11.5	10.3	10.9	116.368	102
5B-37C	19.02	13.72	12.57	16.86	12.18	137.942	126
6A-37C	12.35	2.33	5.2	3.74	2.7	53.314	34.9
6B-37C	13.4	3.74	4.02	3.99	4.23	56.288	45.3
7A-37C	14.76	14.39	15.07	9.59	11.98	141.468	113
7B-37C	14.69	12.52	14.17	12.41	11.03	130.802	161
8A-37C	19.48	17.5	14.69	16.69	14.9	161.282	137
9A-37C	12.09	10.77	13.79	11.62	11.03	117.508	98.3
9B-37C	40.1	20.66	15	9.98	38.97	215.708	301
10A-37C	10.41	10.15	42.42	43.75	52.3	220.586	301
11B-37C	18.39	10.19	10.93	15.76	21.3	117.036	142
12A-37C	-0.09	0.23	1.63	0.87	0.74	6.888	5.8
12B-37C	3.34	1.82	0.62	1.11	1.15	15.952	10.3
13A-37C	12.29	7.92	8.77	9.61	6.07	88.002	77
13B-37C	9.17	8.43	5.63	6.53	8.33	71.768	72.4
14A-37C	11.06	9.85	12.12	11.04	7.64	105.606	221
14B-37C	12.29	8.57	11.47	9.27	7.74	100.732	84.8
15A-37C	16.22	8.45	7.48	5.65	4.95	92.974	60.9
15B-37C	20.69	11.11	6.1	5.28	7.56	106.778	87
16A-37C	13.94	17.74	22.03	18.25	18.03	179.006	171
16B-37C	58.54	48.33	34.84	36.83	37.9	433.126	361
17A-37C	17.75	18.46	24.4	20.71	16.17	198.368	179
17B-37C	28.66	22.73	18.94	16.23	21.4	215.666	210
18A-37C	18.87	18.33	19.25	19.27	19.01	180.544	181
18B-37C	18.77	12.91	15.23	16.58	16.05	144.472	136
19A-37C	16.42	20.72	21.75	23.81	15.79	194.226	240
19B-37C	20.36	20.09	16.41	17.32	24.33	179.42	204
20A-37C	44.51	71.69	86.84	66.66	65	691.434	612
20B-37C	20.57	24.19	22.41	21.38	19.38	218.22	220
21A-37C	16.29	22.88	20.35	22.2	22.14	196.854	220
21B-37C	54.46	82.7	76.63	96.27	65.74	714.374	803
22A-37C	16.65	16.37	19.9	22.43	19.44	171.126	198
22B-37C	10.23	88.74	103.36	72.32	100.52	750.44	707
23A-37C	51.52	137.47	114.08	128.2	107.43	1058.93	1091
23B-37C	16.74	19.75	20.35	18.05	15.16	185.86	175
24A-37C	8.62	72.47	94.8	98.19	88.5	652.866	741.85
24B-37C	13.1	17.6	15.46	21.94	21.83	151.828	210

(*Continued on next page*).

TABLE I

Analytical results (*Continued*)

Sample #	M[A] (middle)	B[A] (bottom)	T[A] (top)	L[A] (left)	R[A] (right)	XRF [2*M + 3.8*(T + B)][B]	GFAA[B]
25A-37C	0.37	-0.09	0.09	-0.06	0.08	0.74	1.3
25B-37C	62.64	168.25	185.5	164.67	178.99	1469.53	1514.6
26A-37C	40.1	140.55	157.9	162.02	159.48	1214.31	1241
26B-37C	16.11	21.95	19.92	19.75	21.78	191.326	214
28-37-DS	0.46	0.89	-0.38	-0.19	0.03	2.858	1.92
28-37-CM	32.96	32.38	23.58	35.74	25.9	278.568	333
28-37LB	1.37	0.52	-0.02	-0.24	0.34	4.64	2.51
28-37FS	13.33	13.44	17.47	13.77	14.74	144.118	140
29A-37C	33.62	16.65	18.8	17.54	22.31	201.95	215
29B-37C	15.17	15.2	15.92	14.03	9.58	148.596	132
30A-37C	15.56	22.46	19.8	19	14.29	191.708	239
30B-37C	30.65	25.33	39.33	30.98	20.36	307.008	273
32A-37C	27.06	27.03	12.46	15.73	9.25	204.182	195
32B-37C	16.27	20.35	11.39	14.36	12.15	153.152	128
33A-37C	7.68	3.32	2.41	2.45	3.21	37.134	36.3
33B-37C	11.54	3.6	3.39	1.93	2.58	49.642	37.8

[A] M, T, B, L, and R numbers are in the units of μg of lead/cm^2.
[B] XRF and GFAA numbers are in the units of μg of lead/sample.

was applied to each of the five pairs of data to determine their distribution.(10) All five paired data sets were non-normally distributed, p-value < 0.05; therefore, the Wilcoxon signed-rank test, a non-parametric t-test, was used to determine statistical significance for the paired data sets.(10) The five sets of paired data were tested and produced p-values > 0.05. This indicated that all five algorithms tested produced XRF analytical results that were not statistically significantly different than the GFAA analytical results over the range 0.1–1514.6 μg of lead/sample.

Because the five-reading algorithms require two additional measurements and produced results similar to the three-reading algorithms, both five-reading algorithms were discarded. Of the three-reading algorithms, the 2.0*(M) + 3.8*(T + B) algorithm was the original algorithm defined in the geometric procedure for filter analysis. Additionally, the data used by the manufacturer to pilot test and develop this method used this algorithm of analysis. Hundreds of slight variations in the three-reading algorithm can produce XRF data that are not statistically significantly different than the GFAA data. The 2.0*(M) + 3.8*(T + B) algorithm was selected because it was consistent with the geometric procedure for analysis, was consistent with the data from pilot studies by the manufacturer (unpublished), and three measurements take less time to perform than five measurements. Future data sets evaluating this method may find slightly different "best fit" algorithms; however, the 2.0*(M) + 3.8*(T + B) algorithm should work for these data sets and was further developed in this study. Analytical results using this algorithm are presented in Table I under the XRF [2*M + 3.8*(T + B)] header.

Linear regression of the entire data set (0.1–1514.6 μg of lead/sample) defined the slope, the y-intercept, and r^2 value. The slope of the regression line was 0.959, the y-intercept was 5.20 μg, and the r^2 was 0.985 (see Figure 4). Linear regression of the data was also performed by limiting the data to less than 250 μg of lead/sample to evaluate the method at and around the PEL. The slope of the regression line was 0.826, the y-intercept was 20.0 μg, and the r^2 was 0.884 (see Figure 5). The data used in Figure 5, $n = 53$, were tested for statistical significance using the Wilcoxon signed-rank test. There was no statistically significant difference between the field-portable XRF method and the laboratory graphite furnace method over the range 0.1–240 μg of lead/sample, p-value = 0.109.

NIOSH SOP 018 was applied to 29 blank filters using the XRF method with a three-reading analysis (see Table II). The mean blank signal was 1.57 and the standard deviation of the blank signal was 1.55; therefore, the LOD is $3*(1.55) + 1.57 = 6.22$ μg of lead/sample. The LOQ is calculated as $10*(1.55) + 1.57 = 17.1$ μg of lead/sample.

The EPA method was applied to a sample whose laboratory-determined lead loading was 3.2 μg of lead. This sample was in the range of the estimated MDL (2–8 μg of lead). This sample was analyzed five times using the XRF method. The results of these repeat analyses were 2.418, 6.062, 3.082, 5.844, and 3.708. The mean of these five readings is 4.22 and the standard deviation is 1.65. The t-table was obtained and $t_{4,99} = 3.747$. Therefore, 1.65 was multiplied by 3.747 to obtain an estimated MDL of 6.18 μg of lead/sample.

The point bias estimates of each paired data point ranged from 0.93 to -0.50. Seven values below 6.2 μg of lead/sample (as determined by GFAA) were eliminated from the data set, because they are below the LOD and should be reported as

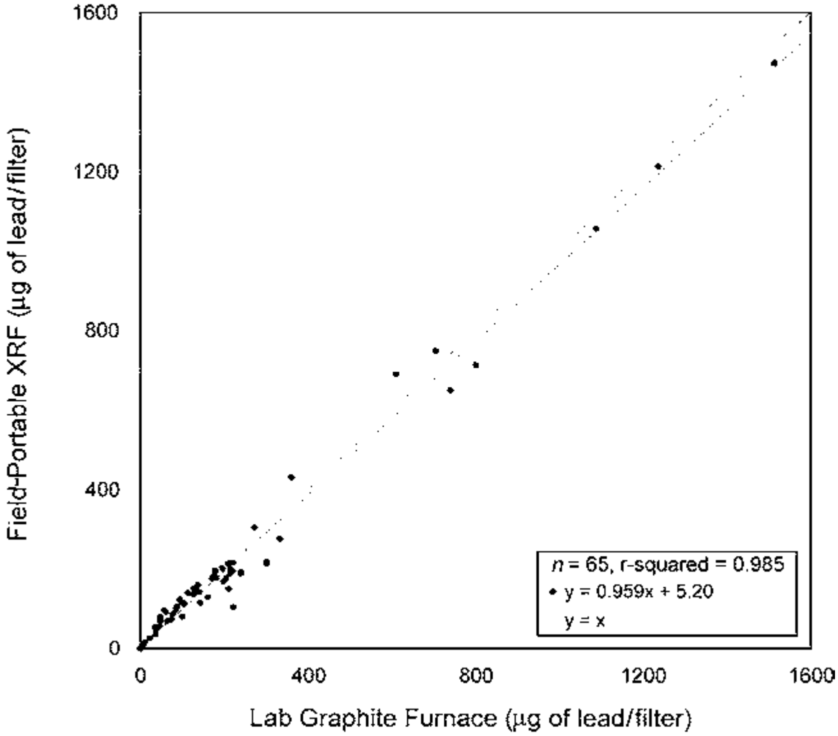

FIGURE 4

Plot of results for field-portable XRF vs. laboratory Graphite Furnace AA over the range of 0.1–1514.6 μg of lead/sample.

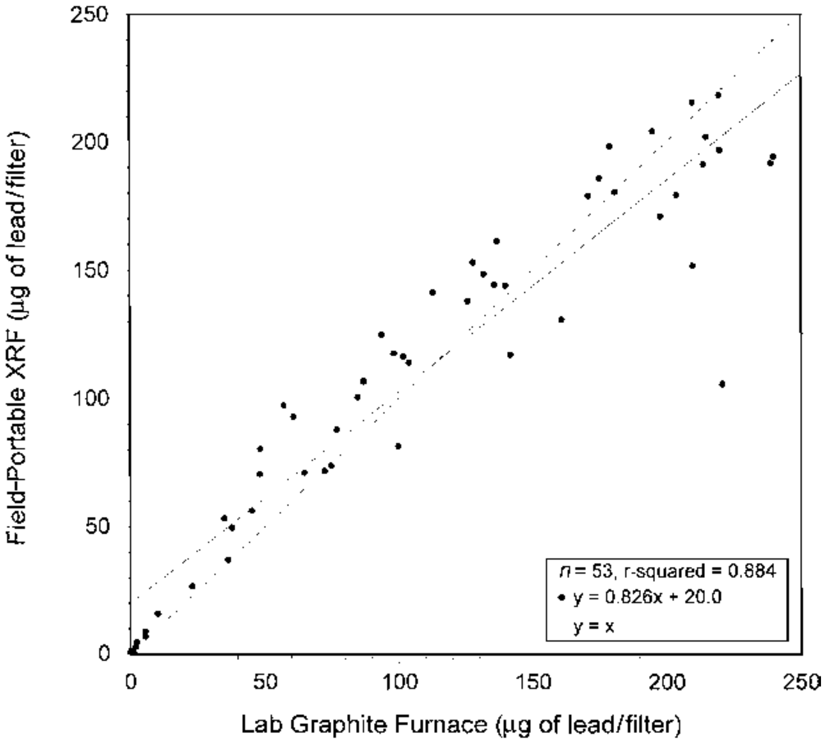

FIGURE 5

Plot of results for field-portable XRF vs. laboratory Graphite Furnace AA over the range of 0.1–240 μg of lead/sample.

TABLE II

Instrumental LOD and LOQ determination

Control ID	M (middle) (μg of lead/cm^2)	B (bottom) (μg of lead/cm^2)	T (top) (μg of lead/cm^2)	XRF result (μg of lead/sample)
Field blank	0.19	-0.07	0.15	0.684
Field blank	0.37	0.37	0.45	3.856
Blank	-0.2	-0.09	-0.04	-0.894
Blank	0.29	-0.08	0.24	1.188
Blank	0.72	0.48	-0.15	2.694
Blank	1.08	0.4	0.85	6.91
Blank	0.01	0.28	0.34	2.376
Blank	0.34	0.03	0.41	2.352
Blank	0.2	0.09	0.16	1.35
Blank	0.55	-0.23	-0.06	-0.002
Blank	-0.13	0.25	0.36	2.058
Blank	0.13	0.51	-0.03	2.084
Blank	-0.07	-0.13	0.29	0.468
Blank	0.15	0.31	0.07	1.744
Blank	-0.04	0.09	0.37	1.668
Blank	0.61	0.06	0.1	1.828
Blank	0.16	-0.09	0.57	2.144
Blank	0.62	-0.18	-0.3	-0.584
Blank	0.08	0.31	-0.04	1.186
Blank	0.23	-0.02	-0.35	-0.946
Field blank	-0.46	0.69	-0.08	1.398
Field blank	-0.26	0.07	0.74	2.558
Blank	0.17	0.37	0.22	2.582
Blank	0.47	-0.24	0.65	2.498
Blank	0.44	0.16	-0.29	0.386
Blank	0.11	0.54	0.01	2.31
Blank	-0.03	0.01	0.04	0.13
Blank	-0.05	-0.08	0.29	0.698
Blank	-0.08	0.09	0.19	0.904

not detected (ND). The remaining data set contained 58 data points ranging from 10.3 to 1514.6 μg of lead/sample (GFAA value). The total bias of the data set was determined by taking the mean of the point bias estimates. The total bias of the data set was 0.069 ± 0.063 (95% confidence interval). The 95 percent confidence interval for bias includes the NIOSH bias criteria of less than ± 0.10; therefore, the XRF method meets the NIOSH bias criterion for an approved analytical method.

The XRF method precision was estimated by performing three repeat analyses of fourteen 37-mm closed-faced filter samples ranging from 10.3 to 612 μg of lead/sample. The mean and standard deviation were calculated for the three repeat analytical results for each sample. The standard deviation of the three readings was divided by the mean to yield a point precision estimate for each sample. The mean of the point precision estimates defined the XRF method precision as 0.054 ± 0.019 (95 percent confidence interval). The point precision estimate around 30 μg of lead/sample was 0.0352 (3.52 percent) at 34.1 μg. The point precision estimate around 50 μg of lead/sample was 0.0385 (3.85 percent) at 48.4 μg.

The accuracy of the XRF method was estimated using the Nomogram Relating Accuracy to Precision and Bias.(6) The nomogram was used to identify the single value estimate of accuracy and the 90 percent confidence interval for accuracy using the Bonferroni procedure. The single value estimate of accuracy was 16.4 percent. The 95 percent confidence statistic for accuracy was 27 percent. This was obtained by using the 97.5 percent confidence statistic for the bias (0.132) and the 97.5 percent confidence statistic for the precision (0.073). The 5 percent confidence statistic for accuracy was 7.1 percent. This was obtained by using the 2.5 percent confidence statistic for the bias (0.006) and the 2.5 percent confidence statistic for the precision (0.035). The 90 percent confidence interval for accuracy (7.1% to 27%) includes the 25 percent accuracy criterion.

DISCUSSION

The results of this study indicate that for the determination of lead in workplace air samples, there is no statistically significant difference between the field-portable X-ray fluorescence method using the NITON 700 XRF and the laboratory-based NIOSH Method 7105 "Lead by HGAAS." The algorithm identified by this study as defining the most statistically significant results when sampling with 37-mm closed-faced cassettes uses three analytical measurements and is $2*M + 3.8*(T + B)$. This algorithm is consistent with the algorithm used by the manufacturer to develop the instrument software.

Data near the PEL are of particular concern as the bias appears to be greater in this region than over the entire range of data presented in this study (see Figure 4). The regression line for the entire data set is less than 1 yet the method bias is positive. The cause of this apparent inequity can be explained by comparing the regression line for the entire data set to the $y = x$ line. The axis of the two lines intersect at $x = 122$. Below 122 μg of lead/sample, the bias is positive, including a positive y-intercept. This indicates that the XRF analytical result is likely to be higher than the GFAA analytical result over the range of 0–122 μg of lead/sample. This is a protective factor for workers exposed to lead at and around the PEL. Above 122 μg of lead/sample, the bias is negative. An exaggerated version of this trend for the data set can be seen in Figure 5. The precision at and around the PEL is considered very good, 3.5 percent at 30 μg of lead/sample and 3.9 percent at 50 μg of lead/sample.

The estimated LOD using the NIOSH SOP 018 method was 6.22 μg of lead/sample. The estimated MDL using the EPA method was 6.18 μg of lead/sample. The average of these two estimates is 6.2 μg of lead/sample. The LOQ for the method is defined to two significant figures as 17 μg of lead/sample. Any instrument response below 6.2 μg of lead/sample should be reported as (ND). Any instrument signal between 6.2 and 17 μg of lead/sample should be reported to two significant figures and enclosed in parentheses to emphasize the imprecision of the result. The instrumental LOQ of 17 μg of lead/sample is sufficiently sensitive to quantitate lead exposures below the OSHA action level of 30 μg of lead/m^3. In our calculation of the LOD using NIOSH SOP 018, the assumption was made that the method has no bias. Actually, the XRF method has an overall positive bias, 0.069. This positive bias functions as a protective factor for workers up to two times the PEL, and meets the method bias parameters required by NIOSH for an approved analytical method.

The 16.4 percent (7.1 percent–27 percent, 90 percent confidence interval) accuracy statistics slightly exceed the NIOSH accuracy criterion of ± 25 percent. With the inclusion of additional data within the calculation of method accuracy, the true accuracy may be well within the NIOSH accuracy criterion. The samples used to develop this method were field samples. Field samples are subject to greater inherent variability than the lab-generated samples or reference materials that are used for traditional analytical method development. Lab-generated samples give uniform distribution and depth on a filter, field samples do not. Once an analytical method is established in a laboratory, it is tested in the field to evaluate sampler losses, field precision, field bias, and the utility of the method for personal sampling. Field evaluations test the ruggedness of an analytical method. Because this method was developed and tested in the field, the ruggedness of the method should be considered when evaluating the 95 percent confidence statistic for accuracy. The 50 percent confidence statistic for accuracy is 16.4 percent. This is well within the limits of the NIOSH accuracy criterion.

Further research is recommended to evaluate alternate XRF technologies whose radioactive sources excite L-shell X rays. One study has been published evaluating the X-MET 880 field portable XRF (Metorex Inc., Princeton, New Jersey) and the Spectrace 9000 field portable XRF (TN Technologies, Round Rock, Texas) for the evaluation of air filter samples for metals.(16) Both instruments use ^{109}Cd sources for the determination of lead in air filter samples.

CONCLUSION

The data presented in this study indicate that field-portable XRF can be used for the analysis of lead air filter samples over the range of 17 to 1500 μg of lead/sample. The practicing industrial hygienist can use field-portable XRF to produce a rapid, on-site determination of lead exposure that can immediately be communicated to workers and help identify appropriate levels of personal protection. As the method is non-destructive, samples can subsequently be sent to a laboratory for confirmation. Confirmation would be recommended when greater than 16.4 percent accuracy from an analytical method is required. This study provided data of suitable quality for the development of NIOSH Method 7702, "Lead by Field Portable XRF."

LIMITATIONS

A limitation of the method is that some of the lead-containing dust brought into the cassette while sampling can cling to the walls of the cassette. This method evaluated only the lead-containing dust that impacts the surface of the filter. The laboratory method can involve a thorough rinsing of the interior of the cassette, thereby removing any lead-containing dust from the sides of the cassette. The XRF method defined in this study cannot account for lead-containing dust that may cling to the inside of the cassette. Samples collected at and around the PEL should not be affected by this limitation.

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DISCLAIMER

Mention of company names does not constitute endorsement by the Cincinnati College of Medicine or the National Institute for Occupational Safety and Health.

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