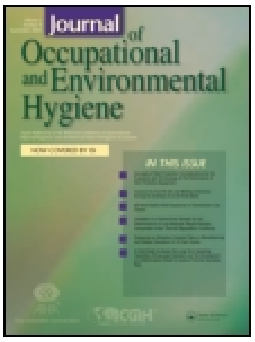

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Laboratory Evaluation of a Field-Portable Sealed Source X-Ray Fluorescence Spectrometer for Determination of Metals in Air Filter Samples

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Recent advances in field-portable X-ray fluorescence (FP XRF) spectrometer technology have made it a potentially valuable screening tool for the industrial hygienist to estimate worker exposures to airborne metals. Although recent studies have shown that FP XRF technology may be better suited for qualitative or semiquantitative analysis of airborne lead in the workplace, these studies have not extensively addressed its ability to measure other elements. This study involved a laboratory-based evaluation of a representative model FP XRF spectrometer to measure elements commonly encountered in workplace settings that may be collected on air sample filter media, including chromium, copper, iron, manganese, nickel, lead, and zinc. The evaluation included assessments of (1) response intensity with respect to location on the probe window, (2) limits of detection for five different filter media, (3) limits of detection as a function of analysis time, and (4) bias, precision, and accuracy estimates. Teflon, polyvinyl chloride, polypropylene, and mixed cellulose ester filter media all had similarly low limits of detection for the set of elements examined. Limits of detection, bias, and precision generally improved with increasing analysis time. Bias, precision, and accuracy estimates generally improved with increasing element concentration. Accuracy estimates met the National Institute for Occupational Safety and Health criterion for nearly all the element and concentration combinations. Based on these results, FP XRF spectrometry shows potential to be useful in the assessment of worker inhalation exposures to other metals in addition to lead.

Keywords accuracy, bias, metalworking, precision, welding

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INTRODUCTION

More than 6 million workers in the United States are employed in metalworking occupations, including welding, construction, and refining.(1) Many of these processes generate dusts and fumes that contain an array of toxic chemicals and metals. The combination and concentration of these hazardous agents depend on the process, materials used, environmental conditions, and contaminants that may be present, such as oils, lacquers, or paints.(2−4) Welding, for instance, is frequently carried out in closed or confined environments where ventilation and/or respiratory protection may be inadequate,(5) thereby increasing the potential for overexposure.

Chronic exposures to welding fumes have been associated with bronchitis, occupational asthma, pneumoconiosis, functional abnormalities of the respiratory system, neurotoxic effects, and diminished reproductive capacity in males.(6,7) Acute exposures have been associated with metal fume fever and pneumonitis.(8−12) Although a convincing link between carcinogenesis and welding has not been established, known carcinogens such as hexavalent chromium and nickel are typically present in stainless steel welding fumes(13,14)

The procedure typically used to determine the extent of exposure to welding fumes involves collecting air samples on filters and sending them to an analytical laboratory for analysis. These laboratory-based analytical methods involve instrumental analytical techniques, such as inductively coupled plasma-atomic emission spectroscopy (ICP-AES),(15) atomic absorption spectroscopy,(16) neutron activation analysis,(17) particle induced X-ray emission,(18) X-ray diffraction,(19) and energy dispersive X-ray analysis in conjunction with scanning electron microscopy(16) or transmission electron microscopy(20) for chemical bulk analyses. Of all these methods, ICP-AES, recommended in method 7300 of the *NIOSH Manual of Analytical Methods (NMAM)*,(15) has gained broad acceptance for analyzing the wide array of elements encountered in welding fumes.

Laboratory-based methods have good resolution power and low detection limits. However, weeks or even months may pass from when a sample is sent to an outside laboratory for analysis to the date that analytical results are ultimately received. Such delays are unacceptable in workplaces where there is a need for on-site screening techniques to measure airborne metal concentrations with near real-time (end of shift) speed. These on-site techniques can quickly locate sources of excessive airborne metal concentrations or determine the effectiveness of environmental controls and personal protective devices, and should complement existing laboratory-based methods, thereby increasing the amount of information on which to base decisions to protect the health of workers.

Field-portable X-ray fluorescence (FP XRF) spectrometry is a technology that could meet these time-dependent analytical needs. FP XRF spectrometry was originally developed for the identification, characterization, and measurement of trace lead concentrations in stack emissions and soil samples at Superfund and other remedial sites.(21–23) The continued refinement of FP XRF technology made on-site screening of metals in a variety of matrices possible. Some examples include the measurement of lead in painted surfaces;(24,25) lead dust in carpeting;(26) arsenic contamination on industrial building surfaces;(27) lead, zinc, and copper in soil;(28,29) barium and antimony in gunshot residue collected on wipe samples at crime scenes;(30) surface lead dust collected on wipe samples at manufacturing facilities;(31,32) airborne metals at metalworking plants;(33,34) airborne lead at various mining, manufacturing, and recycling operations;(35–38) and lead in airborne dust at lead abatement operations.(39) The latter study established method 7702 in the *NIOSH Manual of Analytical Methods (NMAM)*(40) as a screening method for airborne lead.

Innovations in FP XRF technology have resulted in the development of instruments that are considerably smaller, lighter, and more versatile than their predecessors that first appeared on the market more than three decades ago. These features have made FP XRF a very tempting option for industrial hygienists and occupational safety professionals in workplaces where routine monitoring of airborne metals is needed. The goal of this study was to evaluate one of the first FP XRF instruments in widespread use that was capable of measuring airborne metals of health concern (e.g., iron, manganese, nickel, chromium, lead, zinc, and copper).(41)

Parameters were examined that may directly or indirectly impact the concentrations reported by the FP XRF, including (1) response intensity with probe window location, (2) limits of detection (LOD) for various filter media, (3) LOD as a function of analysis time, and (4) bias, precision, and accuracy.(42–44) LOD, bias, precision, and accuracy were also examined to determine whether the technology met criteria for NIOSH method development protocols.(42)

MATERIALS

XRF Spectrometer

The NITON XL-701 (NITON Corp., Billerica, Mass.) was selected for this study from the field of commercially available FP XRF instruments. Although other manufacturers produce competing FP XRF instruments, and NITON is now marketing an updated version of these instruments, the XL-701 was used to establish NMAM method 7702(40) and was therefore selected for the sake of data comparison and continuity. The instrument is a self-contained rectangular unit weighing approximately 1.1 kg, and contains a single ^{109}Cd sealed radioisotope source with an activity of 10mCi. The encapsulated source satisfies the safety requirements of ANSI Standard N542 (Classification of Sealed Radioactive Sources), which consists of temperature, pressure, impact, vibration, and puncture tests. The probe also contains a high-resolution silicon detector. The vast majority of X-rays emitted by the ^{109}Cd sealed source are at energies of 22 and 25 keV, which can generate fluorescence in elements of atomic numbers 22 through 44 (titanium through ruthenium) by K-shell excitation, and elements of atomic numbers 67 through 94 (holmium through plutonium) by L-shell excitation. A small percentage of the X-rays (3.8%) are emitted at 88 keV, which generate fluorescence in elements through atomic number 82 (lead) by K shell excitation.

Elements with fluorescence energies at or very close to that of the incident X-rays, such as cadmium and silver, cannot be detected when using ^{109}Cd as the sole excitation source. The analytical application program was designed to reliably identify and quantify a set of elements that are of the greatest interest to potential users, including chromium, manganese, iron, cobalt, nickel, copper, zinc, arsenic, strontium, lead, mercury, rubidium, zirconium, and molybdenum.

The analyzer unit that controls the probe consists of a user interface keypad, LCD display, 4096-channel analyzer, data storage memory, and an RS232 communication port. The analyzer uses an internal calibration derived from theoretical considerations of XRF intensities for elements in the sample, and is claimed by the manufacturer to account for excitation conditions, source-analyzer geometry, and the absorption and enhancement of X-rays by other elements that may be present in the sample.

37-mm Sample Filters

The sample filters selected were in common use to collect airborne metals in workplace air for subsequent analysis. These included: Metricel mixed cellulose ester (MCE), 0.8 μm pore diameter (Pall Corp., East Hills, N.Y.); glass fiber (GF/A binder free), 260 μm typical thickness (Whatman, Piscataway, N.J.); polytetrafluoroethylene (PTFE, also known by the trade names Teflo or Teflon) filters, 0.8 μm pore diameter (Pall Corp.); polyvinylchloride (PVC) filters, 0.8 μm pore diameter (SKC, Eighty Four, Pa.); and polypropylene (PPE) filters, 5.0 μm pore diameter (Millipore, Billerica, Mass.). The 37-mm-diameter filter size is presently the most common size used

TABLE I. Thin Film Elemental Standard Concentrations and Corresponding Concentration Level Numbers Used in Subsequent Text, Tables, and Figures

Element	Standard Concentration (μg/cm^2)^A			
Chromium (Cr)^B	14.0	51.3	104.2	—
Copper (Cu)	15.2	48.7	99.1	150.9
Iron (Fe)	15.6	30.1	96.7	148.1
Manganese (Mn)^B	16.3	33.1	52.8	—
Nickel (Ni)^B	15.8	30.4	50.7	—
Lead (Pb)	16.1	26.9	42.4	161.0
Zinc (Zn)	5.4	9.3	17.4	32.6
Level #	1	2	3	4

[A] All standards had certified accurate and uniform deposits within ±5%.

[B] Three thin film standards in comparatively lower concentration ranges were used forchromium, manganese, and nickel, in keeping with the airborne concentrations anticipated at welding and metalworking operations.

for air sampling, and was the filter diameter used in NIOSH method 7702.(40)

Thin Film Reference Standards

Certified single-element thin film reference standards were obtained from Micromatter Corporation (Deer Harbor, Wash.). A standard diameter of 37 mm was selected to match the size of the filters recommended by the manufacturer of the XRF spectrometer. The standards had certified accurate and uniform deposits (±5%). A minimum of three concentration levels were acquired and measured for each element. Ideally, technology evaluation as a potential NIOSH method involves the estimation of accuracy over a concentration range from 0.1 to 2.0 times the exposure limit for the moiety, element or contaminant of interest.

The actual concentration range was limited by the mass of each metal that could be uniformly deposited on the sampling medium. Consequently, the minimum concentration selected for each element was between 10 and 15 μg/cm^2, with a minimum of two standards at higher concentrations to evenly span the concentrations anticipated in air samples collected at welding and metalworking operations. For most metals evaluated in this study, maximum concentrations were 5 to 15 times the lowest concentration (i.e., up to about 150 μg/cm^2). Maximum concentrations were limited to the greatest mass that could be deposited on the Mylar medium while maintaining deposit uniformity. The elements and concentrations used in this study are listed in Table I.

Elemental Foils

Iron, nickel, copper, and lead foils of 0.127 mm thickness and 99.8% purity or greater (metals basis) were obtained (Alfa Aesar, Ward Hill, Mass.). A 2-mm square was cut from the foils for the evaluation of K-shell signal intensities at various locations across the probe window of the instrument.

37-mm Filter Holders

Filter holders are cardboard forms with circular openings designed to encase a 37-mm filter between two 6.0-μm Mylar sheets that are attached to the filter holder with a pressure-sensitive adhesive (NITON). The filter holders control analytical variability by (1) preventing sample loss, and (2) allowing precise placement of the sample on the probe window for analysis.

METHODS

Response Across Probe Window

An experimental method was adapted from Dost(45) to evaluate the uniformity of response to selected elements across the surface of the instrument's 10 × 20 mm probe window using 2-mm square pieces of lead, copper, nickel, and iron elemental foils (Alfa-Aesar). The elemental foils represented metals commonly seen in construction, mining, and metalworking operations. Each elemental foil square was placed in a separate filter holder and was analyzed at a series of fixed positions on the probe window. Analysis positions were determined using a grid that divided the probe window into 50 squares measuring 2 mm on a side (Figure 1). Analysis time at each grid position was 60 source seconds. K-line signal intensity at each location was measured and plotted as a percentage of the maximum intensity observed for that element.

Note that a source second is the sample exposure time to the radioactive sealed source that is equivalent to one real-time second when the sealed source was new. The duration of the source second increases as the source decays, reaching two real-time seconds when the source is at its half-life. When sample exposure times are measured in source seconds, the total number of radioactive emissions, on average, should be identical. The instrument's application program contained an algorithm that continuously updated the real-time analysis duration based on source age.

Limits of Detection (LODs) and Limits of Quantitation (LOQs)

The study that established the NIOSH method for portable XRF to measure airborne lead collected on filter media used an analysis duration of 60 source seconds, which was recommended by the manufacturer.(39) LODs and LOQs were determined at 60 source seconds by analyzing 10 new, clean MCE filters. Reported concentrations were processed according to recommendations by the Royal Society of Chemistry and procedures specified in Section II of Standard Operating Procedure (SOP) 18 of the *NIOSH Guidelines for Air Sampling and Analytical Method Development and Evaluation*, which define the LOD and LOQ as the elemental mass at 3 and 10 standard deviations above the mean blank signal, respectively.(42,43) Because the uncertainty of mass reported by XRF decreases as analysis time increases,(21) the impact of sample duration on LODs and LOQs were determined by analyzing the filters at 60, 120, 180, and 240

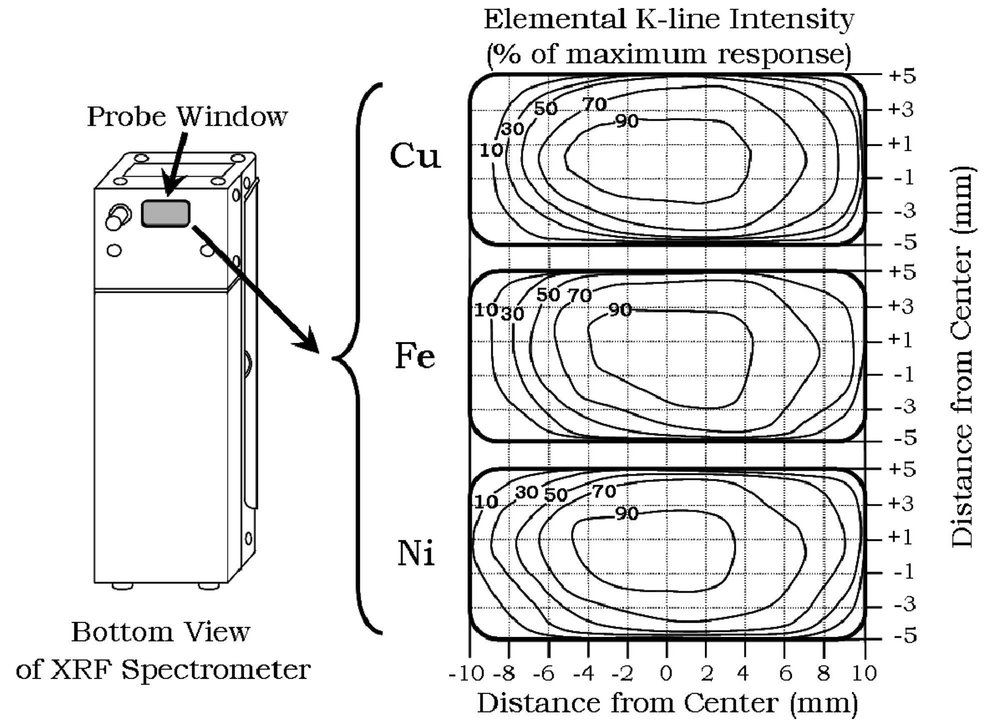

FIGURE 1. K-line intensity relative to maximum response for elemental copper, iron, and nickel foils. A 2 mm square of foil was presented to the probe window and analyzed for 60 source seconds at each of 50 locations. The analysis locations correspond to the squares formed by the dotted reference lines on the plot. The percentage of maximum response was determined for each point, and lines of equal response were drawn at 10, 30, 50, 70, and 90% of maximum.

source seconds. LODs were determined for molybdenum, lead, cobalt, nickel, iron, arsenic, copper, manganese, chromium, and zinc, which are of potential health concern in construction, manufacturing, and mining operations.

Although MCE has long been the filter medium of choice for airborne metal collection and subsequent XRF analysis, and the XRF used in this study is tuned to use MCE, early characterization studies of full-size laboratory-based XRF instruments have demonstrated that other media may also be used.(21) To date, little information has appeared in the scientific literature on the LODs for various filter media on portable XRF spectrometers. The LODs for the 10 elements that were determined on MCE (see previous paragraph) were also determined for PPE, PVC, PTFE, and GF/A media. The shortest analysis time to give the lowest LODs for the majority of elements measured on MCE was used as the analysis time for all experiments in this study.

An instrument designed to measure airborne metals collected on filters should be capable of reporting their concentrations as far below the current occupational exposure limit (OEL) as possible.(41,46) In this study, the OEL was defined as the lowest concentration among the latest ACGIH® threshold limit value (TLV®), Occupational Safety and Health Administration (OSHA) permissible exposure level (PEL), and NIOSH recommended exposure level (REL). The recommended analytical sensitivity for a method specified by NIOSH is one-tenth the OEL for the contaminant of interest.(42)

The OEL values shown in Table II assume an air sample collected on a 37 mm diameter filter in a closed-face cassette (effective deposit diameter = 33 mm, deposit area = 8.55 cm^2) at a sample flow rate of 2 L/min for 8 hr, yielding a total sample volume of 0.96 m^3. Columns showing multiples of the OEL on a filter (0.1 or 1.0 × OEL), refer to the elemental masses collected using the same flow rate and deposit area. For the elements collected under these conditions, 0.1 × OEL is considered to be the ideal analytical sensitivity.

Accuracy

Accuracy is a measure of method performance. In this study, accuracy estimates for each element measured by the portable XRF spectrometer were determined using the NIOSH guidelines for method development:(40)

(1) Estimate bias and precision (or relative standard deviation [RSD]) for each group of observations within each time and concentration stratum.
(2) Determine homogeneity of bias and RSD for each group.
(3) Correct observations within groups for apparent bias where necessary.
(4) Pool groups by analysis time and concentration where possible.
(5) Calculate method accuracy estimates for these groups.

TABLE II. OELs of Elements Found in Welding Fume and Concentrations on Filter Needed for Recommended Analytical Sensitivity

Element^A	OEL in Air (μg/m^3)	0.1 x OEL on Filter (μg/cm^2)	1.0 x OEL on Filter (μg/cm^2)	2.0 x OEL on Filter (μg/cm^2)
Arsenic (As)	10	0.11	1.1	2.2
Copper (Cu)	100	1.1	11	22
Manganese (Mn)	200	2.3	23	46
Chromium (Cr)^B	1.0	0.01	0.11	0.22
Zinc (Zn)^C	2000	23	230	460
Molybdenum (Mo)	500	5.6	56	110
Lead (Pb)	50	0.56	5.6	11
Cobalt (Co)	20	0.23	2.3	4.6
Nickel (Ni)	15	0.17	1.7	3.4
Iron (Fe)	230	2.6	26	52

Notes: The OEL is defined as the lowest concentration among the latest ACGIH TLV, OSHA PEL, and NIOSH REL values. Figures in this table are based on a 37-mm closed-face cassette filter with a 33 mm effective deposit diameter at a flow rate of 2 L/min flow rate for a sample duration of 8 hr (except where noted), yielding a total sample volume of 0.96 m^3.

^{A}Elemental standards for As, Mo, and Co were not available at the time of this study.

^{B}Values in this row are based on 10-hr sample duration.

^{C}Values indicated for zinc oxide (ZnO).

Bias Estimates

Each individual reference standard (Table I) was analyzed 10 times at 60, 120, 180, and 240 source seconds. All analyses consisted of a single reading at the center of the reference standard. A one-way analysis of variance procedure (ANOVA, $p = 0.05$, response and analysis time set as the dependent and independent variables for the analysis, respectively) was applied to the data to determine whether any significant differences existed between the observed concentrations at the different analysis times. If no significant differences were found, the analysis times were pooled for the remaining calculations.

Because XRF is a nondestructive analytical technology, and sample position for analysis on the instrument used in this study was very precise (the reference standards were certified to be of uniform thickness (±5%) and were encased in sample holders that allow the same region of the sample to be presented to the instrument's probe window for repeated analyses), it would be reasonable to expect that the observed concentrations (those reported by the XRF) would be in close agreement with the certified reference standard concentrations. Bias is the deviation of an observed (experimentally measured) concentration from its standard (certified, known, actual, or verified by accepted protocol) concentration. Therefore, the bias for each individual reference standard would be the difference between the certified reference standard concentration (C_{std}) and the group mean of the observed concentrations ($\overline{X_{C_{obs}}}$), with the result divided by the reference standard concentration, or:

$$bias = \frac{\overline{X_{C_{obs}}} - C_{std}}{C_{std}}. \quad \textbf{(1)}$$

The observed concentrations (C_{obs}) were plotted against the reference standard concentrations (C_{std}) for each element, and a regression line of best fit for the data was determined, where model response was related to the y-intercept (I_y), standard concentration and slope (m) assuming linear response:

$$model\ response = (m \times C_{std}) + I_y. \quad \textbf{(2)}$$

The observed concentrations were corrected for any apparent bias in the data (provided the bias is homogeneous, see below). The adjusted concentrations for any given sample (C_{adj}) were then determined by a simple algebraic rearrangement of Formula 2, solving for the reference standard concentration, and setting it equal to the adjusted concentration:

$$C_{std} = C_{adj} = (C_{obs} - I_y)/m \quad \textbf{(3)}$$

The corresponding 95% confidence interval (CI) for all bias estimates in this study were also determined per NIOSH guidelines.(42)

RSD Estimates

RSD (relative standard deviation, or precision [P]), is a measure of reproducibility, or how closely a group of observations are grouped or clustered. In this study, RSD estimates for a group of observed concentrations of a given elemental standard were made by dividing the standard deviation of the observed concentrations ($\sigma_{C_{obs}}$) by the group mean:

$$P = RSD = \frac{\sigma_{C_{obs}}}{\overline{\overline{X_{C_{obs}}}}} \quad \textbf{(4)}$$

As was the case for bias, the 95% CI values for each RSD estimate were determined per NIOSH method development guidelines.(42)

Two-way ANOVA ($p = 0.05$) with an interaction term (analysis times∗concentration levels) was applied to bias data for each element to determine whether any significant differences in bias were being driven by certain combinations (interactions) of analysis times and concentration levels. If no significant differences could be found between concentration levels for a term, the concentration levels for that element were pooled, resulting in a single bias value for that element. This pooled term for bias was used in subsequent accuracy estimate calculations. The 95% confidence intervals (CIs) were then recalculated for the pooled groups as appropriate. If any part of the CI for bias was within 10% of the expected bias value, the bias was considered to be homogeneous for that concentration level or element.(42)

Homogeneity of RSD was evaluated using Bartlett's test.(47) Elements where bias and/or RSD were found to be homogeneous were combined for the accuracy estimate calculations.

Accuracy Estimates

In this study, accuracy estimates were used to evaluate the ability of the method to measure a given element over the observed concentration range and analysis times. The accuracy estimates and corresponding confidence intervals were calculated from the true relative standard deviation and the estimates of *bias* and *RSD* (Eqs. 1 and 4, respectively).(44)

For elements where it was not possible to pool bias and RSD across concentration levels, separate accuracy estimates were made for each concentration level. For elements where bias and RSD could be pooled across the concentration levels, a single accuracy estimate was made using the pooled data.

The resulting accuracy estimates were compared with the NIOSH accuracy criterion, the accuracy estimates of other concentration levels within the element where available, and accuracy estimates from previous studies using similar technology and calculation methods.(39,40)

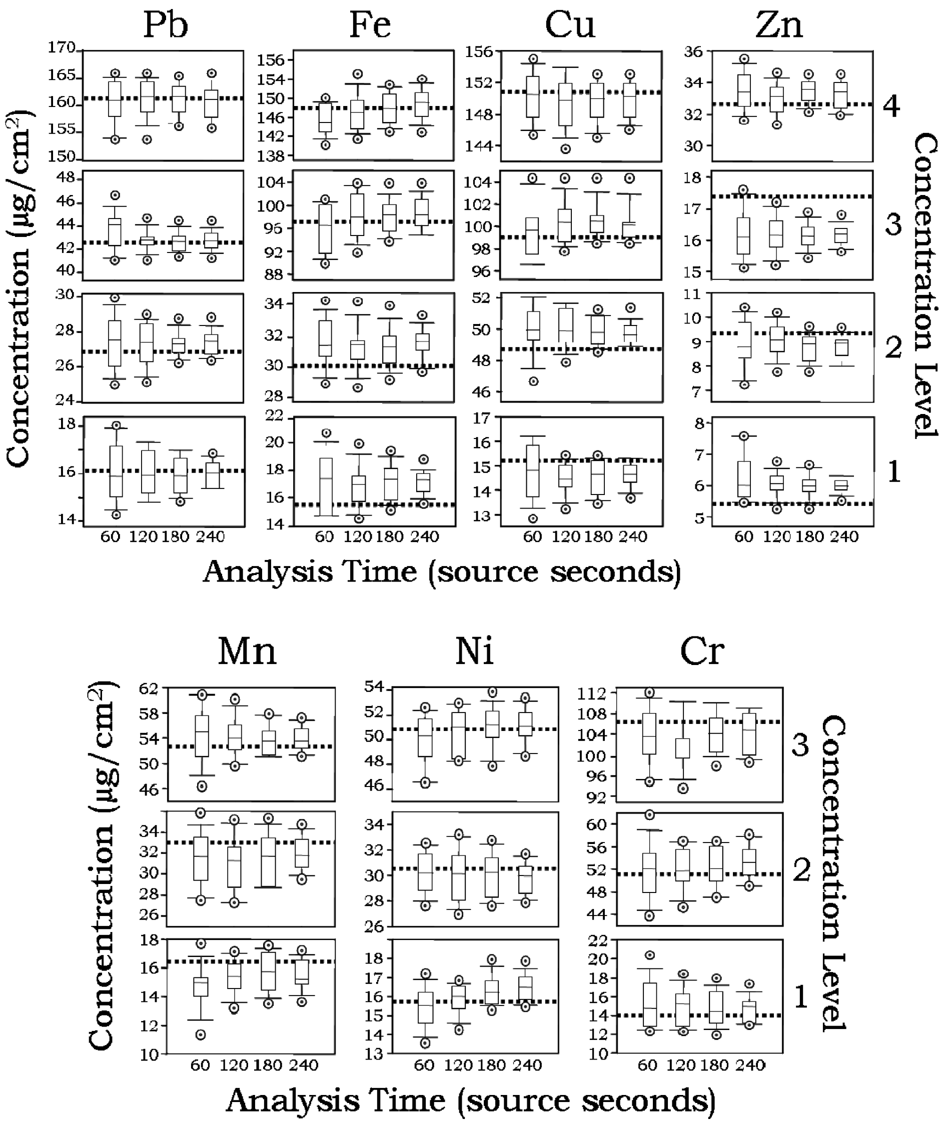

FIGURE 2. Box plots of repeated measurement (N = 10) of certified calibration standards by analysis time, relative to the actual standard concentrations (shown as a dashed line in each individual graph). Data for all elements except zinc were adjusted for apparent bias (see text). The line in each box plot indicates the 50*th* percentile (median), while the bottom and top ends indicate the 25th and 75th percentiles, respectively. The ends of the lower and upper error bars indicate the 10*th* and 90*th* percentiles, respectively. Circular symbols below and/or above the ends of the error bars indicate the minimum and maximum concentrations observed, respectively. In cases where observations were very tightly clustered, some features have been omitted for clarity.

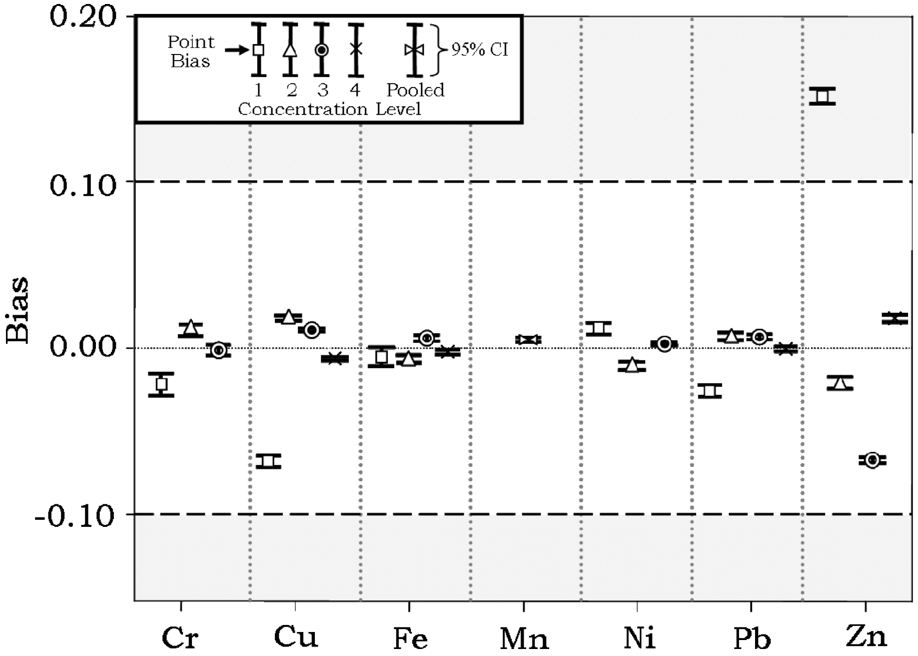

FIGURE 3. Bias estimates of adjusted data with corresponding 95% confidence intervals. For all elements except nickel, estimates are displayed by concentration level with all analysis times combined. For nickel, the estimate for pooled analysis times and concentration levels is shown. The thick dashed horizontal lines indicate bias values of ±0.10. The NIOSH criterion for bias is met when any part of the 95% confidence interval includes bias values less than ±0.10.(42)

RESULTS AND DISCUSSION

Response Across Probe Window

Copper K-line intensities at or exceeding 90% of maximum occurred in an irregularly shaped elliptical area of approximately 8 mm^2 (Figure 1). This area was roughly centered in the probe window, with a slight bias toward the left side (viewing the underside of the instrument with the battery pack facing down). Nickel and iron showed similar response patterns. The distribution of nickel intensities was most symmetrical at the extreme left and right sides of the probe window. The overall response patterns were similar to those reported in a previous study on a portable XRF instrument by another manufacturer.(45) Because the sealed source and detector are in fixed geometric positions relative to the sample, the response patterns for other metals should not differ much from those discussed here.

In XRF spectrometry, the observed concentration of an element is a function of the intensity of its characteristic fluorescence energy. Hence, the intensity plots of Figure 1 could be considered as relative concentrations normalized to the area of greatest response. The instrument must use an

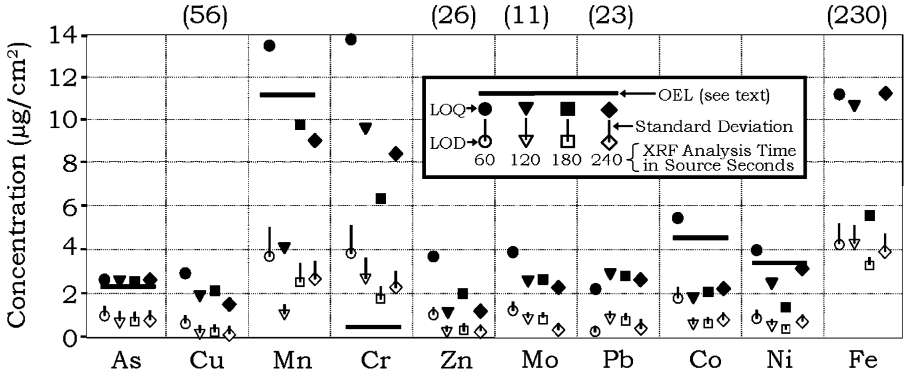

FIGURE 4. LODs and LOQs by element and analysis time for mixed cellulose ester (MCE) filter medium. The thick lines on the graph denote concentrations corresponding to 1.0×OEL on a 37-mm filter for that element (see text and Table II for additional details). Parenthetical numbers above each plot denote the 1.0×OEL concentrations that are beyond the range of the graph for the respective element.

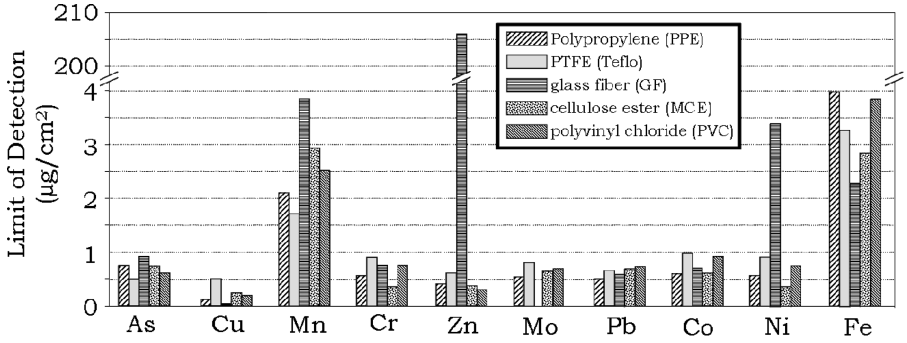

FIGURE 5. LODs by filter and element, based on 60 source second analyses of 10 clean blank filters of each medium.(42) The LOD was calculated per NIOSH SOP 18 as the mass 3 standard deviations above the mean blank signal. The LOQ (not shown) is the elemental mass 10 standard deviations above the mean blank signal.(42) Thus, in instances where the reported mean blank signal is zero, the LOQ is 3.33×LOD.

algorithm of this type when calculating the mass of metals present on a filter, and any deviation from this loading distribution would bias the observed concentrations reported by the instrument. This may explain the persistent bias in observed concentrations when single element standards of uniform loading (certified uniform thickness within ±5%) were measured on the portable XRF (Figures 2 and 3). This could also explain why the observed concentrations of lead in workplace air samples collected on filters in an earlier study were higher than expected in most instances when the samples had apparently uniform loadings from center to edge on the filter.(38) This may also explain why errors in observed concentrations occur in closed-face cassette samples with a large deposits at the center of the filter; the deposit peak breaks free when the filter is transferred to the sample holder, with that portion of the sample being lost or scattered across the face of the filter.

The instrument in this study also has an algorithm to estimate total elemental mass based on three readings taken at fixed locations on the filter. Because this algorithm is more heavily weighted for the top and bottom readings (relative to the center), this could result in overestimates in the concentrations reported on the portable XRF relative to laboratory methods that digest the entire filter and report concentrations based on a thoroughly mixed aliquot.(38,48)

If the response for lead with location on the probe window is the same as those seen for copper, iron, and nickel in this study, total lead concentrations would be overestimated relative to other methods where filters have more uniform deposits than those used to establish the XRF three-measurement technique. It is also expected that this error could be seen in single readings taken by the XRF at the center of filters where sample deposits are more uniform than those used to establish the instrument's calibration. This may also explain why the concentrations reported by the XRF for uniformly deposited standards tend to be higher than expected (Figure 4). Corrections in reported concentrations should be made based on the sample loading pattern on the filter prior to making estimates of bias, precision, and accuracy.

In addition to variations in filter sample deposits, other variables may affect the concentration reported by the XRF, such as particle size, elemental composition within the sample, the presence of elements known to interfere with the fluorescence energy of the element(s) of interest, and presence of elements with conflicting secondary fluorescence energies. The depth of deposit within the filter could also pose a matrix problem, especially with GF/A filters.

Although we are aware of other methods to determine LOD and LOQ using field samples developed by NIOSH and EPA, this study elected to use the mean blank signal method as defined by the Royal Society of Chemistry and in NIOSH SOP 18 (Section II, Part A) because it is the best way to compare these values using direct readings of 10 clean samples of each filter media evaluated in this study.(42,43)

LODs and LOQs

Figure 4 shows the LOD as a function of analysis time for MCE filter media. The LODs for all elements except lead were highest at 60 source seconds. LODs decreased (i.e., improved) with increasing analysis time through 180 source seconds for molybdenum, nickel, iron, and chromium. The lowest LOD values were reached at 120 source seconds for arsenic, manganese and cobalt, and at 60 source seconds for lead. Although LOD values for molybdenum, copper, and zinc were lowest at 240 source seconds, the differences were within one standard deviation of the observed values at 120 and 180 source seconds. Based on this information, an analysis time of 180 seconds is considered sufficient to ensure LODs are at their lowest levels possible.

With the exception of chromium, all LODs measured in this study at all analysis times were below their respective OELs. The LOQ values, calculated as 10 times the standard deviation above the mean blank signal, are usually expected to appear like an amplified version of the LODs. This did not always hold true, however. Arsenic was one such case where the LOQs appeared to be nearly identical across all analysis times. This was because the standard deviation was smaller at the 60 second analysis time relative to the longer analysis times. Other elements, such as iron, had elevated LODs and LOQs because of nonzero mean blank signal levels and the lack of a zero adjustment that can be set by the user.

Based on the above findings, an analysis time of 180 source seconds was used to determine the LODs for five commonly used filter media (Figure 5). For GF/A filters, the highest LODs were observed for nickel, arsenic, manganese, and zinc, while the lowest LODs were observed on this media for molybdenum, iron, and copper. The lowest LOD was observed for lead on PPE. Interestingly, for GF/A media, the mean blank signal level for molybdenum was below zero, so the 3 standard deviation value above the mean blank signal raised the LOD to zero.

However, the depth of any deposit on a GF/A filter could pose a matrix problem with the use of these filters, preventing complete analysis of the collected sample. The lowest LODs for cobalt and nickel were on MCE. PTFE and polyvinyl chloride had shown the most consistently low LODs, which were in the same range as those for MCE. Previous studies found MCE to be the best media for air sample collection and analysis by XRF spectrometry.(21) Because MCE is an inexpensive filter media and is widely available, it is generally preferred in most air sampling applications.

However, if factors such as pore size, flow resistance and efficiency (a function of pore size) are equal for all filter media, then PPE, polyvinyl chloride, and PTFE could be viable substitutes for MCE. These alternate media would also be useful for sampling corrosive atmospheres. Other sample collection and analysis factors may also influence the media type selected. For instance, polyvinyl chloride would be a good choice when sampling procedures call for gravimetric analysis.

Effect of Analysis Time on Reported Concentration

Box plots of repeated (sets of 10) concentration measurements by element, standard concentration levels, and analysis times are shown in Figure 2. The range of observed concentrations generally decreased as analysis times increased, with some minor exceptions (namely, the smallest range of observations occurred at 180 sec at concentration level 4 for iron and zinc, and levels 3 and 4 for lead). This trend was expected, since the measured concentrations at increasing analysis times were based on a proportionately larger number of photons reaching the instrument's detector from the sample following excitation of electrons by incident X-rays. Because no significant differences (one-way ANOVA, $p > 0.05$) were found among the measured concentrations for the four analysis times within any element and standard concentration combination, the measured concentrations for all analysis times were combined for the remaining calculations.

According to NIOSH guidelines, an experimental method is suitable for development if recoveries exceed 75% in the tested concentration range.(42) Although this is a preliminary laboratory based study that involved pure calibration standards, and not field samples with potential interfering elements and contaminants, the findings here indicate that portable XRF can meet NIOSH requirements for method development for all elements in the measured concentration ranges (Table I, Figure 2).

The correlation coefficients (R^2) for all elements in this study ranged from 0.97 to 0.99. Linear regression lines fit the data well, and the observed concentrations were adjusted by using the fitted lines (Eq. 3). The adjusted concentrations were then plotted by element and concentration level in Figure 2.

Bias Estimates

Bias estimates and their associated confidence intervals were determined for the adjusted data (Figure 3). With the exception of the lowest concentration of zinc, the XRF method met the NIOSH bias criterion (bias with 95% CI ≤ 0.1) for all concentration levels of the elements evaluated in this study. Bias was also well within the NIOSH bias criterion for manganese, the element where all concentrations were combined. Bias decreased with increasing concentration for chromium, copper, nickel, and lead. Although the bias values for iron did not show this trend with increasing concentration, they were considerably lower than any other element in the study where separate concentration levels were reported with no value greater than ±0.0094 at 95% CI.

Zinc showed considerable variability in bias among the lowest three concentration levels. It is not clear why this is occurring. This may be due to a lack of sensitivity in the detector array in this part of the energy spectrum. It is also possible that spectral interference effects may be occurring from other metals that may be present in the standard itself.

Precision (RSD) Estimates

The RSD estimates for all elements evaluated in this study were homogeneous across all analysis times. However, the RSD estimates were not homogeneous among the concentration levels for all elements except manganese. Therefore, the RSD estimates for all analysis times and concentration levels were pooled for manganese, and the RSD estimates for all analysis times only were pooled for the remaining elements. Figure 6 shows the RSD estimates and 95% CIs by concentration level for chromium, copper, iron, manganese, nickel, lead, and zinc. As was the case with bias, RSD (precision) generally improved with increasing concentration, as count rates increased with concentration. The trend was weaker in the lowest two concentrations of nickel and zinc.

Accuracy Estimates

The calculations of method accuracy estimates in this study were interpreted in accordance with the NIOSH guidelines for method development.(42) The calculations of method accuracy estimates used bias and RSD. The single value accuracy estimates used the median values of bias and RSD, and the upper and lower (two-sided) confidence interval (CI) were calculated from the corresponding CI values for precision and bias. The resulting accuracy estimates were then categorized in one of three ways: (1) acceptable, where the estimate and CI were entirely within the ±25% region; (2) inconclusive, where some part of the estimate and CI was within the ±25%

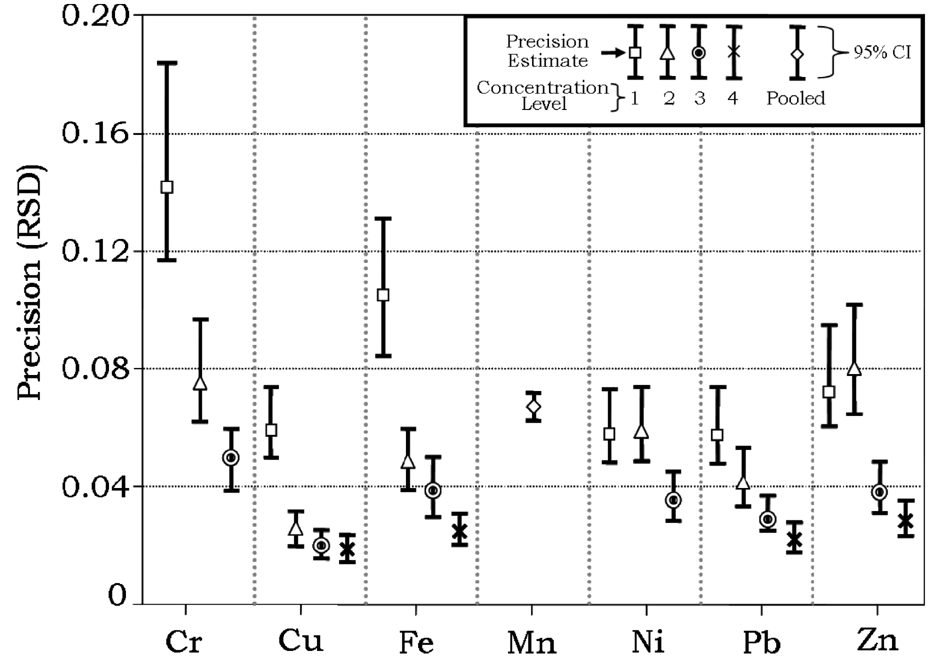

FIGURE 6. RSD estimates of adjusted data with associated 95% confidence intervals (CIs). For all elements except manganese, estimates are displayed by concentration level with all analysis times combined. For manganese, estimates are shown for all analysis times and concentration levels combined.

region; or (3) rejected, where no part of the estimate and CI was within the ±25% region.[42]

When the NIOSH 25% accuracy criterion was applied to the accuracy estimates using the adjusted data (Figure 7), it could be said that FP XRF is an acceptable method for all elements and concentration levels except of the lowest concentrations of chromium, where the method was inconclusive for chromium, and marginally rejected (0.26 at the lowest reach of the

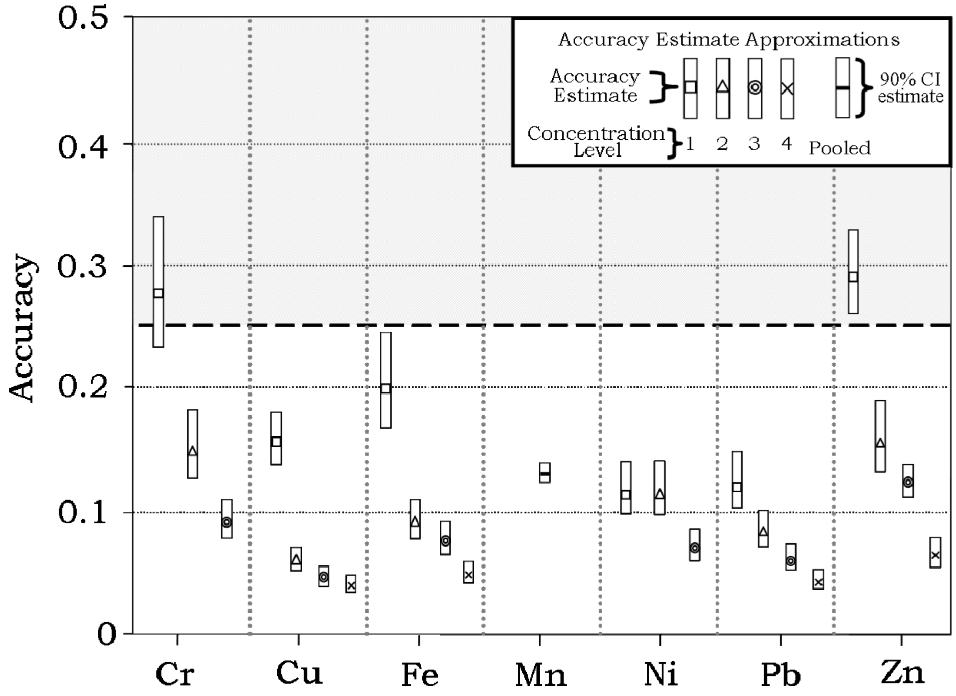

FIGURE 7. Accuracy estimates of adjusted data with the corresponding 90% confidence intervals (CIs). The thick dashed horizontal line on the graph denotes the NIOSH 25% accuracy criterion.[42]

CI range) for zinc. The trend toward decreasing accuracy with lower concentration is likely due to the nature of the technology, as comparatively high imprecision and bias are generally proportional to lower count rates.

ADDITIONAL COMMENTS

In recent years, it has become apparent that methods found to be inconclusive or rejected using the NIOSH accuracy criterion may actually still be fit-for-purpose. If such methods are simple, inexpensive, and provide results quickly, they may be quite useful as screening methods in the field, determining when samples should be sent for more quantitative analyses.

With the recent evolution of instruments that have user-adjustable calibration, further evaluation of these technologies is warranted using experimentally generated samples and workplace samples with confirmatory analysis by conventional laboratory methods.(15)

Some elements measured by FP XRF are known to have spectra that interfere with other elements, and some elements measured in workplaces by XRF are among those with potential interferences. For instance, chromium and iron, two elements that are encountered in stainless steel welding, absorb the same X-ray wavelength as emissions from the K_α orbital of manganese. Other elements known to fluoresce at wavelengths sufficiently close to cause concern include tungsten with nickel and zinc, vanadium with titanium, chromium with vanadium, and cadmium with silver and tin. Manufacturers of FP XRFs typically account for these interferences when designing the instrument's algorithm and factory calibration. Although this study evaluated XRF calibration using single element thin film standards in isolation, the algorithm for measuring these elements appeared to be satisfactory. The next logical step is to determine the performance of the FP XRF algorithm and calibration by analyzing samples from various workplaces and comparing the results against wet chemistry confirmatory analyses.

CONCLUSIONS

An evaluation study was conducted on one of the first widely used FP XRF instruments. LODs were determined for various analysis times and filter media. MCE was best suited for air sample collection and subsequent analysis on this technology. PPE, PVC, and PTFE filter media also had suitably low LODs. The LODs decreased with increasing analysis time, reaching a minimum at roughly 180 sec for most tested elements.

Apparent bias was identified and corrected where needed by using the appropriate correction factor in accordance with NIOSH method development guidelines.(42,49) In the case of the instrument examined in this study, corrections were necessary when bias was significant and the instrument had no provision for calibration adjustment. Instances where these corrections were applied must be interpreted with caution, however, since the instrument manufacturer may have designed the built-in calibration algorithm to account for interferences that occur when multiple elements and other potential contaminants may not be present in the samples being analyzed. Although no correction may be necessary when one set of workplace samples are measured by the portable XRF, it is entirely possible that samples from another workplace may have interfering elements or other contaminants that may require an adjustment for apparent bias and, quite possibly, one that is unique to that set of samples.

NIOSH method development guidelines call for the correction of the raw data for any apparent bias before reporting results and making any estimates of method accuracy.(42) On making these corrections, NIOSH criteria were met in nearly every case for bias, precision, and accuracy. It is hoped that newer versions of the portable XRF will not require such adjustments. The technology is now reaping the benefits of a series of rapid technological improvements, such as the ability of some instruments to compensate for decay of the sealed radioactive source calibration drift. This is being accomplished either automatically or through a user-accessible component in the application program.

A recent study(49) has demonstrated that air sampling technologies such as the IOM, GSP, and button samplers give sample deposits that are more uniform than those obtained from closed-face cassettes. When these observations are considered with those of the present study, it is apparent that a revision of analytical procedures and/or algorithms will be needed to account for the differences in sample deposits with location on the filter when these technologies are used to collect subsequently analyze and airborne metals collected on filters in the workplace.

This study was intended to be a preliminary assessment of XRF to correctly identify and quantify a suite of elements individually under highly controlled laboratory conditions. If the NIOSH accuracy criterion was applied to this study and used to define method acceptability at this stage, FP XRF spectrometry would be the acceptable method for the analysis of nickel, copper, manganese, iron, and lead, as measured in their respective concentration ranges. The method would also be acceptable for all except the lowest concentrations of chromium and zinc. In the case of chromium, the method would be considered inconclusive due to overlap of the 90% confidence interval with the NIOSH 25% accuracy criterion. For the lowest concentration level of zinc, the method would be narrowly rejected because the 90% CI was close to but did not touch the NIOSH 25% accuracy criterion.

Although this may appear to be discouraging at first glance, two things must be kept in mind: (1) Several aspects of FP XRF technology, such as detector and computing ability, have improved considerably since this model was tested. It is therefore not unreasonable to expect the performance parameters of the technology to improve. (2) The cases where the method was inconclusive and rejected must be considered in the proper context. They involved only the lowest of several concentration ranges for the element; the method was acceptable at the remaining higher concentrations. Therefore, it may be best to view the method for these elements as qualitative at the low concentrations and more quantitative at the higher concentrations.

The accuracy estimates made by Bartley are a refinement of the estimates made in NIOSH guidelines to fit the circumstances in this study.(42,44) Specifically, the accuracy estimates are made when the following information is known: (1) the concentrations reported by the FP XRF when analyzing (2) elements of known concentrations at (3) a specific number of concentration levels. NIOSH method development guidelines were used in this study because they are to be used "in the development of a sampling and analytical method," and was previously used to establish NMAM 7702.(39,40) Furthermore, and perhaps even more importantly, by obtaining these parameters under ideal conditions, those who use FP XRF technology will have a clearly defined baseline or "best possible" performance that can be expected when the instrument is used in the workplace.

Since the data in this study were collected, newer portable XRFs have been produced with upgraded hardware and application programs. Improvements such as these can be expected to reduce LODs and improve precision, accuracy, and bias estimates.

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