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Assessment of Occupational Exposure to Manganese and Other Metals in Welding Fumes by Portable X-ray Fluorescence Spectrometer

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Abstract

Elemental analysis of welding fume samples can be done using several laboratory-based techniques. However, portable measurement techniques could offer several advantages. In this study, we sought to determine whether the portable X-ray fluorescence spectrometer (XRF) is suitable for analysis of five metals (manganese, iron, zinc, copper, and chromium) on 37-mm polytetrafluoroethylene filters. Using this filter fitted on a cyclone in line with a personal pump, gravimetric samples were collected from a group of boilermakers exposed to welding fumes. We assessed the assumption of uniform deposition of these metals on the filters, and the relationships between measurement results of each metal obtained from traditional laboratory-based XRF and the portable XRF. For all five metals of interest, repeated measurements with the portable XRF at the same filter area showed good consistency (reliability ratios are equal or close to 1.0 for almost all metals). The portable XRF readings taken from three different areas of each filter were not significantly different (p-values = 0.77 to 0.98). This suggested that the metal rich PM_{2.5} deposits uniformly on the samples collected using this gravimetric method. For comparison of the two XRFs, the results from the portable XRF were well correlated and highly predictive of those from the laboratory XRF. The Spearman correlation coefficients were from 0.325 for chromium, to 0.995 for manganese and 0.998 for iron. The mean differences as a percent of the mean laboratory XRF readings were also small (<5%) for manganese, iron, and copper. The differences were greater for zinc and chromium, which were present at very low amounts in our samples and below the limits of detection of the portable XRF for many of the samples. These five metals were moderately to strongly correlated with the total fine particle fraction on filters (Spearman ρ = 0.41 for zinc to 0.97 for iron). Such strong correlations and comparable results suggested that the portable XRF could be used as an effective and reliable tool for exposure assessment in many studies.

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AUTHORS' CONTRIBUTIONS

Author WL contributed to study design, samples collection and analysis, data analysis, interpretation of the results, and manuscript preparation. JMC and SCF contributed to the data collection and critical review of the manuscript. XL contributed to study design, statistical analyses, and critical review of the manuscript. DCC contributed to data collection and review of the manuscript. RFH and MGW contributed to study design, data analysis, interpretation of the results, and critical review of the manuscript. All authors read and approved the final manuscript.

Keywords

elemental analysis; manganese exposure assessment; Niton XL3t; portable XRF; welding fumes; X-ray fluorescence spectrometer

INTRODUCTION

Welding is a common industrial process worldwide. In the United States, a survey of employment indicated that about 466,400 workers were employed as welders, solderers, and brazers in 2008.⁽¹⁾ Some studies suggest that occupational exposures to welding fumes may pose the risk of serious respiratory, neurological, and reproductive effects.^(2–6) Welding fumes are complex mixtures of gases and small particles of metal oxides. The latter are generated by the vaporization and the oxidation of metals during the welding process.⁽⁷⁾ The majority of all welding is performed using mild steel or carbon and low alloy steels. These steel electrodes are composed of mostly iron (Fe) with varying amounts of manganese (Mn), whereas stainless steel electrodes contain chromium (Cr) and nickel (Ni) in addition to iron and manganese. Other metals such as copper (Cu) and zinc (Zn) from mild steel are also commonly detected in welding fume.^(2,8)

It is estimated that over 80% of the mass from welding emissions is in particles smaller than 1 μm .⁽²⁾ Analyses using electron microscopy have indicated that primary particles generated during welding are in the nano-size range (0.01–0.10 μm). However, these particles quickly agglomerate together in the air to form larger particles that usually have mean aerodynamic diameters in the range of 0.1–0.6 μm .⁽²⁾ Particles in these small sizes can reach the gas exchange region in the lung and then be absorbed into the blood, leading to adverse health effects.

In 1989, the Occupational Safety and Health Administration (OSHA) set a permissible exposure limit (PEL) for total welding fume at 5 mg/m^3 as an 8-hr time-weighted average (TWA). However, the OSHA PEL was eventually rescinded, and no new PEL for welding fumes has since been established.⁽⁹⁾ NIOSH has established a recommended exposure limit (REL) for welding fumes (and total particulates) of the lowest feasible concentration.^(3,6) Before 2005, the ACGIH[®] threshold limit value time-weighted average (TLV[®] -TWA) was 5 mg/m^3 total fume concentration in the breathing zone of the worker during the welding of iron, mild steel, and aluminum. However, ACGIH retracted the TLV for welding fume in 2004 without giving an explanation for the change. There has been no specific TLV for welding fume since then.⁽¹⁰⁾

In recent years, there has been increased interest in the health effects of welding fume and more epidemiologic studies investigating various effects of exposure to welding fume. Usually, the assessment of worker's exposure to welding fumes is conducted by collecting personal air samples for laboratory analysis of specific elements.^(11–12) Fume sample (metal rich particulates) is collected on a membrane filter, which is fitted in a particle size selector and connected to a personal sampling pump. After the gravimetric analysis for total particulates on the filter, elemental analysis can also be done.

X-ray fluorescence (XRF) spectrometry is one of several analytical methods that have been applied to elemental analysis of air samples, including instrumental neutron activation analysis (NAA), atomic absorption spectrophotometry (AAS), and inductively coupled plasma-atomic emission spectroscopy (ICP-AES). XRF is a preferred method in many cases because it obtains many elemental concentrations with minimal labor, low detection limits,

high sensitivity for a number of elements, good accuracy for particles $<10\ \mu\text{m}$ in size, and it is a nondestructive analysis.⁽¹³⁾

The common type of XRF analysis is based on energy dispersive X-ray fluorescence of elemental components in a thin film sample. Emissions of X-ray photons from the sample are integrated over time and yield quantitative measurements of elements ranging from aluminum (Al) through uranium (U) and semi-quantitative measurements of sodium (Na) and magnesium (Mg). A spectrum of X-ray counts vs. photon energy is acquired and displayed during the analysis, with individual peak energies corresponding to each element and peak area corresponding to elemental concentrations.^(14,15) Although laboratory-based XRF instruments have good resolution power and low detection limits, use of this method can have turnarounds of weeks or even months if samples are sent to an outside laboratory for analysis.

Recent advances in portable X-ray fluorescence analyzer technology have made it a potentially valuable tool for rapid and reliable assessments of worker exposures to airborne metals.⁽¹⁶⁾ The National Institute for Occupational Safety and Health (NIOSH) has developed a standard analytical method for determination of lead on air sample filters using portable XRF technology,⁽¹⁷⁾ and several studies suggest that this technique can provide faster turnaround without compromising accuracy when assessing personal exposures to metals such as lead.^(18–22) However, the suitability of portable XRF for analysis of other airborne metals of health concern, particularly, manganese, iron, zinc, copper, and chromium has not been fully evaluated.⁽²³⁾

To determine whether the portable XRF is suitable for analysis of metals (Mn, Cu, Cr, Fe, and Zn) on air samples collected in an occupational setting, we compared the analysis of these metals by portable XRF with those made with traditional laboratory XRF. We also sought to verify the assumption of uniform deposition of materials on these welding fume samples and to assess the correlations of each of these metals with the fine particle fraction ($\text{PM}_{2.5}$).

MATERIALS AND METHODS

Study Population

Between 2003 and 2008, participants were recruited while training at the International Brotherhood of Boilermakers—Local #29, Quincy, Massachusetts. Most participants had <1 to 3 years of welding experience and spent substantial time welding. Self-administered questionnaires were used to obtain personal and work history information. Each participant also completed a work log and an exposure diary to assess the number of hours welded, type of welding done, and use of protective equipment and ventilation. The study was approved by the Institutional Review Board of the Harvard School of Public Health, and written informed consent was obtained from all study participants.

Work monitoring occurred at the union welding school. The welding school has a large, temperature-controlled room outfitted with 10 workstations with local exhaust ventilation where apprentice welders receive instruction and practice on welding, cutting, and grinding techniques. Apprentice welders primarily performed shielded metal arc welding (SMAW, or STICK) and gas metal arc welding (GMAW, or MIG), most commonly using base metals of mild steel and stainless steel (manganese, chromium, and nickel alloys) with electrodes composed of mainly iron with variable amounts of manganese (1–5%). Plasma arc or acetylene torch cutting and grinding also occurred at the work site. Some participants were also monitored over a day when they were not welding, grinding, or cutting. On these days,

participants were asked to stay mainly in the hall or within the school area without significant exposure to welding fume.

Gravimetric Sampling Method

Personal, integrated gravimetric samples were collected over the duration of the work shift. We used KTL cyclones (GK2.05SH; BGI Incorporated, Waltham, Mass.) with aerodynamic diameter cutpoint of $2.5\ \mu\text{m}$, in line with personal sampling pumps (Apex/Vortex; Casella CEL, UK) drawing 3.5 L/min of air. The cyclone was secured to the participant's shoulder in the breathing zone area, and the pump was placed in a padded pouch that was carried by the participant for the entire workday. Each cyclone was fitted with a cassette holding a 37-mm polytetrafluoroethylene (PTFE) membrane filter (Pall Gelman Laboratories, Ann Arbor, Mich.). These filters are suggested for elemental analysis using XRF because they are analytically clean, are thin to reduce scattering, and have known pore size and particle collection efficiencies.^(13,14)

Before and after sampling, the filters were weighed in a temperature- and humidity-controlled room using a standard protocol on an MT5 micro-balance (Mettler-Toledo Inc., Columbus, Ohio). We divided the blank corrected mass of each sample by the sample air volume to calculate the $\text{PM}_{2.5}$ concentration. This gravimetric method has been found to be accurate, sensitive, and robust.⁽²⁴⁾

In addition to the gravimetric method, on a subset of participants, we continuously monitored personal, cross-shift, $\text{PM}_{2.5}$ exposures using the light-scattering technology of a DustTrak Aerosol Monitor (TSI Inc., St. Paul, Minn.) fitted with a $\text{PM}_{2.5}$ inlet impactor. The monitor was placed in a padded pouch, with the inlet tubing secured to the participant's shoulder in the breathing zone area. The monitor took $\text{PM}_{2.5}$ concentration readings every 10 sec and recorded 1-min averages. Then, 8-hr TWA $\text{PM}_{2.5}$ exposures were calculated. A previous study of welding fume exposures validated the use of the DustTrak to capture welding fume exposures.⁽²⁴⁾ The results from this instrument were, in general, well correlated and highly predictive of those from a filter-based, gravimetric sampling method.

Laboratory XRF Analysis

The filters from the cyclone samples collected before 2007 were sent to an accredited laboratory for analyses of elemental components using the PANalytical Epsilon 5 Energy Dispersive XRF analyzer (Almelo, The Netherlands), with standard operating procedures including quality control and assurance measures.⁽¹⁴⁾ For this XRF, the measurement was focused on an area of $\sim 2\ \text{cm}^2$ at the center of the filter, which was assumed to be representative of the entire deposit. Each element and the corresponding limit of detection (LOD) were reported as μg of element per filter.

After the laboratory XRF analyses, each filter was placed in its original petri dish. These filters were returned to us and then stored in a freezer at -20°C .

Portable XRF Analysis

All filters were analyzed for elemental components using a NITON Portable XRF model XL3t series 600 (ThermoFisher, Billerica, Mass.) and its test stand with 37-mm filter mounting. We adopted NIOSH analytical method 7702⁽¹⁷⁾ procedures for our filter analyses. To ensure that we were measuring and comparing the same things as done previously by the laboratory, DRI standard operating procedures⁽¹⁴⁾ and other standard operating procedures for XRF analysis of air samples^(25–28) were also used as references.

Calibrations were performed before the first and after the last use of the portable XRF for sample analysis each day. We used Micromatter XRF calibration standards obtained from Advanced Applied Solutions, Inc., Vancouver, Canada. These single-element calibration standards were in 37-mm filter form and mounted in the filter sleeves for use with the NITON XL3t Portable XRF. They were prepared by vacuum deposition, resulting in highly uniform deposits (in $\mu\text{g}/\text{cm}^2$) and had certified accuracy ($\pm 5\%$). We used a set of standards for each of the elements of interest (Mn, Fe, Zn, Cu, and Cr), within the anticipated range of depositions of the samples.

All readings of standard reference materials were within 5% of their respective certified values. Averages of absolute difference in reading (based on certified value) were 1.83%, 2.38%, 1.80%, 1.72%, and 2.77% for Mn, Fe, Zn, Cu, and Cr, respectively. XRF readings of samples were adjusted based on averaged calibration results. Blank samples were also analyzed to verify that the XRF was not registering false positive results for the elements of concern.

For this portable XRF analysis, we used standard filter mode to measure three areas of each filter, with two readings per area. The XRF was run for 90–120 seconds per reading. With respect to NIOSH analytical method 7702⁽¹⁷⁾ and the design of the test stand, XRF windows were identified as top (T), middle (M), and bottom (B) (each an area of $\sim 2 \text{ cm}^2$, as shown in Figure 1).

Data Analysis

Initially, the distributions of the measurement data for $\text{PM}_{2.5}$ and five metals of interest were explored with smooth histograms. Because our exposure data were not normally distributed, we used non-parametric analysis methods to compare levels of different measurements from the portable XRF and to investigate the agreement between pairs of results from the portable and the laboratory XRFs.

To examine whether the depositions of each of these five metals on the three areas of a filter were uniform, we used the Wilcoxon signed-rank test to compare the portable XRF measurement results within the same filter area, and non-parametric one-way analysis of variance (ANOVA) to compare the XRF measurement results simultaneously across all three filter areas. The reliability ratio was also calculated for each metal to assess the consistency of the portable XRF repeated measurement results.

The reliability ratio (λ) is defined as the ratio of the variance of the unobserved true measurement (σ_x^2) divided by the variance of the observed error-prone measurement, which is the sum of the variance of the true measurement and the variance of the measurement error (σ_u^2). Note that λ will range between 0 and 1 and the reliability is considered perfect when $\lambda = 1$.⁽²⁹⁾

$$\text{Reliability Ratio } (\lambda) = \frac{\sigma_x^2}{\sigma_x^2 + \sigma_u^2}$$

Since the true measurement result cannot be actually obtained from any instrument, the reliability ratio is, in practice, estimated from the observed replications of the error-prone measurements, using the following equation:

$$\text{Estimated Reliability Ratio } (\lambda) = \frac{\text{Var}_{\bar{x}} - 0.25 \text{Var}_{\Delta}}{\text{Var}_{\bar{x}} + 0.25 \text{Var}_{\Delta}}$$

where

$\text{Var}_{\bar{x}}$ = Variance of the averaged readings

Var_{Δ} = Variance of the difference in repeated readings

Spearman coefficients were calculated to determine the correlation between measurement results from the portable and the laboratory XRF for each of the five metals, between the gravimetric PM_{2.5} concentrations and each of the metals, as well as the intercorrelations of the metals.

Statistical analyses were performed using SAS 9.1.3 (SAS Institute Inc., N.C.). The level of statistical significance for all analyses was set at $\alpha = 0.05$.

RESULTS

A total of 133 air samples were analyzed for this study. Based on gravimetric analysis of these filters, the welders' median exposure to PM_{2.5} on welding days ($n = 102$) was 0.679 mg/m³ (25th–75th percentiles: [0.404 to 1.459]), and 0.106 mg/m³ (25th–75th percentiles: [0.043 to 0.143]) on non-welding days ($n = 20$). For some of these gravimetric samples ($n = 19$), we also ran DustTrak in parallel. The PM_{2.5} concentrations that we obtained from gravimetric method and from the DustTrak were strongly correlated (Spearman $\rho = 0.91$), consistent with the finding from a previous study in this same setting.⁽²⁴⁾

Assessment of Sample Distribution on Filters

Because the laboratory XRF analysis focuses on only the 2-cm² center area of the filters, we examined whether the deposition on this center area was representative of the deposition on the remaining area of the filter using the portable XRF. Two readings were taken at each of three areas on the filter: the top (T), middle (M), and bottom (B) areas. Any portable XRF reading that was below the limit of detection (LOD) was not included in the data analysis. The LODs of the portable XRF for the five metals of interest were approximately 0.2 µg/cm². Thus, for some filters, the amount of a metal at a given area was based on a single available reading from that area. The numbers (percent) of samples for which all six readings were below LODs were 12 (9.0%), 4 (3.0%), 44 (33.1%), 58 (43.6%), and 86 (64.7%) for Mn, Fe, Zn, Cu, and Cr, respectively. Almost all of the samples were detectable by the laboratory XRF for these five metals (LODs of lab XRF are < 0.01 µg/m² for the five metals—only four samples were not detectable for Cr). The amounts of each metal at each filter area (either a single reading or average of two at same area) of the filters are shown in Table I.

The consistency of repeat measurements with the portable XRF at a given filter area for these metals was extremely good (reliability ratios are equal or close to 1.0) for almost all metals except for Cr measured at M area on filters. The differences in repeat measurements at the same filter area were all very small and far from significant. There was also little difference between readings at the different areas for any of the metals ($P\text{-value} > 0.77$) (Table II). When the amounts of metal on filter were determined from the middle area (M) only, the results were less than 5% different from the results determined by averaging across all three areas for all metals.

Comparison of Portable vs. Laboratory XRF Results

Of the 133 available samples, 97 had previously been analyzed by laboratory-based XRF (all collected from 2003 to 2006). Since the laboratory XRF measures only the center area of the filters, we compared these readings for each element to the measurement of the same center area using the portable XRF. Only Fe was found at amounts above the limit of detection using the portable XRF on all 97 filters with laboratory results. The comparisons of readings of other metals are based only on those filters with at least one reading at the M site above the limit of detection for the portable XRF. For all metals except Cr, the number of filters with only one portable XRF reading at the M site was small (< 5). For Cr, only two filters had both portable XRF readings at the M site above the limit of detection.

For Mn, Fe, Zn, and Cu, there were very strong correlations of measurement results from the two XRFs (Spearman $\rho = 0.936$ [Zn] to 0.998 [Fe]), as shown in Figure 2. The correlation of readings for Cr was much lower (Spearman $\rho = 0.325$). However, Cr was present at relatively low concentrations and was detectable by the portable XRF at the M area of the filter in only 14 samples. If samples with Cr readings only from other areas on the filter were included and averages of Cr were based on any available readings, the correlation of measurement results from the two XRFs improve moderately (Spearman $\rho = 0.485$, $n = 26$). The rank order of correlation coefficients for the different metals was the same as the rank order of the total amounts of the different metals on the filters.

On average, for most of these metals, the readings from portable XRF and laboratory XRF were comparable. As shown in Table III, the mean differences as a percentage of the mean laboratory XRF readings were 1% or less for Mn and Fe. However, the median portable XRF readings were greater than those of laboratory XRF readings for the other three metals. Amounts of Zn, Cu, and Cr on these samples were much lower (and below the portable XRF LODs in many samples) as compared with those of Mn and Fe.

The percent difference between portable and laboratory XRF measurements for the different metals by total sample mass on filter is shown in Figure 3. At low total sample mass, the percent differences were larger than at high total sample mass. For Mn and Fe, the differences of results from the two XRFs centered around zero and fell within $\pm 5\%$ when the sample mass rose above approximately 1.5 and 0.5 mg/filter, respectively. The differences between the two methods were more pronounced for Zn and Cr, which was related to the lower amounts of these metals on filters.

The results from portable XRF analyses suggested that, of the metals analyzed, these welders had the highest exposure to iron, with a median concentration of $192.82 \mu\text{g}/\text{m}^3$, followed by manganese at $18.71 \mu\text{g}/\text{m}^3$. Zinc and copper were present at detectable amounts in most samples. However, chromium was detected in only a small number of samples. In addition to these elements, XRF analysis also revealed the presence of other elements such as nickel in some samples.

Each metal exposure, based on the results from the portable XRF, was moderately to strongly correlated with total $\text{PM}_{2.5}$ (Table IV). Iron was most highly correlated with $\text{PM}_{2.5}$ (Spearman $\rho = 0.968$), followed by manganese (Spearman $\rho = 0.924$). Chromium, copper, and zinc were moderately correlated with $\text{PM}_{2.5}$ (Spearman $\rho = 0.408$ to 0.517). The correlations among the metals were also moderate to strong for most pairs of metals. The results were similar in direction and strength to those observed in a recent study at the same setting.⁽⁸⁾

DISCUSSION

Our results demonstrate extremely good correlation between portable XRF measurements of Mn, Fe, Zn, and Cu concentrations on air filters collected from welders and laboratory-based XRF analytic results. This was not the case for Cr, which was likely because Cr levels, when detectable by the portable XRF, were very close to the limit of detection. Furthermore, at the amounts found on our samples of welding fume, the sample distribution is uniform over the filter for all these five metals. Thus, analysis of the 2-cm² central area of the filter is a good representation of the whole filter.

For the five metals of interest in this study, the limits of detection were approximately 0.2 µg/cm². The portable XRF readings were biased positively as amounts of metal on filter approached the LOD because the portable XRF device does not display any readings below the LOD, thus; near the limit of detection only upward, not downward, random variation in readings are seen. In our findings this is most obvious for Cr for which only 14 of the 97 filters analyzed by laboratory XRF had measurement results from M area that exceeded the limit of detection for the portable XRF, and the average reading of Cr was closest of any of the metals to the portable XRF LOD. A similar effect could be seen for Zn and Cu at lower amounts of sample on filters. Overall, the bias at lower amounts of metals can be seen in our results in the parallel between the order of average readings and both the correlation with and the percent difference from laboratory XRF readings.

Gravimetric analysis of total sample mass (PM_{2.5}) could potentially be used as an indicator of the likely accuracy level of portable XRF readings. For our welding fume samples, our results suggest that accuracy within 5% of the laboratory XRF results can be achieved at total sample mass levels above approximately 1.5 mg/filter for Mn, 0.5 mg/filter for Fe, and 2–3 mg/filter or more for Zn, Cu, and Cr. These levels, however, are dependent on the correlation between each individual metal and PM_{2.5}, which may differ in different exposure settings.

The portable XRF has typically been used for the identification, characterization, and measurement of trace lead concentrations in stack emissions and soil samples. A NIOSH standard analytical method for lead on air samples using the Niton 700 series portable XRF has been developed and statistically evaluated.⁽¹⁷⁾ This method has been applied for exposure assessment in a few studies, all of which showed excellent correlation between the portable XRF measurement results and those of other techniques.^(18–21)

Our findings have confirmed that, for welding fume samples collected using this gravimetric method, the assumption of uniform deposition of these elements on the filter does hold. This also validated the exposure assessment in our previous studies in which samples were collected using the same technique but were analyzed focusing on the center area of those filters. In general, results from elemental analyses using the portable XRF were well correlated and highly predictive of those obtained from the laboratory-based XRF. For many of these metals, analysis using portable XRF indicated excellent agreement for samples with mass loadings well above the LOD; agreement was weaker at lower loadings on the filter. These were similar to the results from other studies. For example, the study of portable XRF for measurement of airborne lead levels in South Korean workplaces also found that measurement results from portable XRF are highly correlated with those from the laboratory-based ICP method.⁽²⁰⁾ In terms of repeatability of the portable XRF we used in this study, the calculated reliability ratios indicate that, in general, the results from the repeated measurements were highly consistent for all five metals of interest.

Recently, NIOSH conducted a laboratory evaluation of the portable XRF for determination of some other metals in air filter samples.⁽³⁰⁾ They used the Niton model XL-701 as the

representative of portable XRF in that evaluation and found that bias, precision, and accuracy estimates generally improved with increasing element concentration. These are also suggested by the results from our study. Positive bias in the difference between portable and laboratory XRF results appeared to be greatest when the amounts of a given metal were close to the LOD. The Niton model XL3t we used is a newer portable XRF with upgraded hardware and application programs. As further improvements are made to these devices, the LODs should further decrease, thus expanding the range of concentrations for which the portable device will have excellent precision and accuracy.

Use of portable XRF for elemental analysis of air samples offers many advantages compared with the conventional laboratory methods that have historically been employed for the analysis of environmental samples. It is a viable cost- and time-effective analytical approach for analyzing a variety of elements, particularly for the analysis of initial exposure assessment samples or for applications where laboratory analysis is impractical.^(13,16)

Based on the results from the current and previous studies, this portable analytical method shows potential to be useful and applicable for assessment of exposure to a variety of metals. Our results also suggest that one measurement of a filter at the middle area provides nearly identical results to averaging over three areas—the approach described in the NIOSH method.⁽¹²⁾ The uniform deposition of these small particles, however, may well be dependent on sampler design. Furthermore, the deposition pattern may be different for larger particles. This portable XRF technique could be particularly advantageous when time is short or when analysis of a large number of filters is needed, such as in larger epidemiologic studies, at least in similar study settings to ours.

A limitation of XRF analysis, both portable and laboratory based, is that the technique is insensitive to the chemical species of the elements. It cannot discern metal oxidation states or identify metal complexes. While the welding fume metals are likely present as metal oxides, the solubility of each element, which may affect toxicity, remains unknown. Another disadvantage is the subjection of the sample to a vacuum, resulting in loss of some volatile species, such as hydrocarbons.⁽¹⁴⁾ This is also a limitation of both the laboratory and portable XRF techniques. In addition, XRF and many other analytical techniques do not measure particles adhering to the surface of inner walls of the samplers. However, wall losses have been shown to be low especially for these small particles.⁽¹⁸⁾

CONCLUSIONS

Results from elemental analyses of welding fume samples using the portable XRF were compared with those previously obtained by laboratory-based XRF. The correlations of measurement results for the five metals of interest were, overall, in very good agreement for the range of sample mass that was well over the LODs. Portable XRF analysis results from three areas on each of these filters also revealed that the readings were not different for all of these five metals. The findings suggest that for welding fume samples collected using this gravimetric method, the assumption of uniform deposition of these elements on the filter does hold, and that a single measurement of the central area of the filter is representative of the whole filter.

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FIGURE 1.
Portable XRF analysis of a 37-mm filter on 3 different areas (T = Top area, M = Middle area, B = Bottom area)

FIGURE 2.
Correlation of portable vs. laboratory XRF readings

FIGURE 3.
Magnitude of differences in reading from the two XRFs, by sample mass (total $PM_{2.5}$)

TABLE I

Portable XRF Readings for Each Metal on Three Areas of Filters

Median (25th–75th percentiles) of Readings, $\mu\text{g}/\text{cm}^2$			
	T	M	B
Mn	3.47 (1.53–6.20) n = 122	3.48 (1.47–6.39) n = 123	3.52 (1.39–6.21) n = 123
Fe	38.69 (15.43–79.26) n = 129	38.48 (14.95–79.39) n = 129	37.73 (15.38–74.00) n = 129
Zn	0.55 (0.38–1.18) n = 81	0.54 (0.38–1.22) n = 87	0.51 (0.37–1.09) n = 88
Cu	0.96 (0.61–1.57) n = 71	0.99 (0.66–1.53) n = 70	0.90 (0.61–1.48) n = 71
Cr	0.23 (0.20–0.25) n = 24	0.25 (0.22–0.39) n = 23	0.23 (0.20–0.31) n = 20

Notes: For each of the box plots, the bottom and top of the box are the 25th and 75th percentile of the readings, and the horizontal line through the middle of the box is the 50th percentile (median). The ends of each vertical line mark the adjacent values (defined as 1.5 times the interquartile range beyond the 25th and 75th percentiles). Dots above the line represent readings with values those are more extreme than the adjacent values. For each metal, a reading from the plot needs to be multiplied by the corresponding factor indicated above the boxplots for each metal to obtain the actual amount of that metal on the filter.

TABLE II

Difference in Repeated Readings, Within and Between Areas of Filter

	Within Area ^A			Between Areas ^B T vs. M vs. B
	T	M	B	
Mn				
N	120	121	121	121
Difference: Mean (SD)	0.01 (0.47)	−0.02 (0.38)	0.00 (0.41)	0.03 (0.20)
Reliability Ratio	0.99	1.00	1.00	N/A
P-value	0.66	0.60	0.55	0.98
Fe				
N	129	128	129	129
Difference: Mean (SD)	−0.02 (1.79)	0.13 (1.73)	0.05 (1.47)	1.12 (4.00)
Reliability Ratio	1.00	1.00	1.00	N/A
P-value	0.69	0.83	0.92	0.97
Zn				
N	65	66	70	79
Difference: Mean (SD)	−0.01 (0.13)	0.02 (0.15)	−0.01 (0.12)	0.01 (0.10)
Reliability Ratio	0.99	0.99	0.99	N/A
P-value	0.98	0.46	0.63	0.88
Cu				
N	59	65	58	64
Difference: Mean (SD)	0.01 (0.21)	−0.03 (0.21)	−0.01 (0.25)	0.02 (0.10)
Reliability Ratio	0.99	0.99	0.98	N/A
P-value	0.83	0.18	0.99	0.79
Cr				
N	7	9	6	9
Difference: Mean (SD)	−0.03 (0.07)	−0.05 (0.17)	0.01 (0.10)	0.04 (0.12)
Reliability Ratio	0.97	0.85	0.95	N/A
P-value	0.38	0.65	1.00	0.77

^AP-value for the comparison of two readings on each filter area using Wilcoxon signed-rank test (only cases in which both readings were above the limit of detection were included).

^BP-value for the comparison of readings from three filter areas using non-parametric one-way ANOVA; difference values for each filter were calculated as the difference in amount at each filter area from the mean of the three areas (only filters with at least one reading above the limit of detection from each area for a given metal were included. If there were two readings from a given filter area, these were averaged.).

TABLE III

XRF Results ($\mu\text{g}/\text{filter}$) and Differences Based on Laboratory XRF

	Mn	Fe	Zn	Cu	Cr
# Sample Pairs	94	97	68	48	14
Portable XRF, $\mu\text{g}/\text{filter}$ Median IQR ^A	29.7 (28.9)	307.6 (447.3)	2.9 (4.8)	5.7 (5.4)	1.4 (0.8)
Laboratory XRF, $\mu\text{g}/\text{filter}$ Median IQR ^A	30.1 (31.0)	310.8 (428.4)	2.3 (5.3)	6.0 (5.1)	0.3 (0.4)
Difference, $\mu\text{g}/\text{filter}$ Median IQR ^A	-0.3 (1.8)	1.5 (11.3)	0.8 (0.9)	0.3 (1.1)	1.0 (0.5)
Median difference as % of median lab XRF readings	1.0 %	0.5 %	34.5 %	5.1 %	362.1 %

^A IQR: Interquartile range.

TABLE IV
Spearman Correlation Coefficients Within and Between Metals and Total PM_{2.5} Exposures

	Mn	Fe	Zn	Cu	Cr
PM _{2.5}	0.92	0.97	0.41	0.52	0.46
Mn	1.00	0.87	0.41	0.30	0.41
Fe		1.00	0.40	0.60	0.46
Zn			1.00	0.26	0.17
Cu				1.00	0.64
Cr					1.00