PAPER

A comparison of X-ray fluorescence and wet chemical analysis of air filter samples from a scrap lead smelting operation

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Personal and area air samples were taken at a scrap lead smelter operation in a bullet manufacturing facility. Samples were taken using the 37-mm styrene–acrylonitrile closed-face filter cassette (CFC, the current US standard device for lead sampling), the 37-mm GSP or "cone" sampler, the 25-mm Institute of Occupational Medicine (IOM) inhalable sampler, and the 25-mm Button sampler (developed at the University of Cincinnati). Polyvinylchloride filters were used for sampling. The filters were pre- and post-weighed, and analyzed for lead content using a field-portable X-ray fluorescence (XRF) analyzer. The filters were then extracted with dilute nitric acid in an ultrasonic extraction bath and the solutions were analyzed by inductively coupled plasma optical emission spectroscopy. The 25-mm filters were analyzed using a single XRF reading, while three readings on different parts of the filter were taken from the 37-mm filters. The single reading from the 25-mm filters was adjusted for the nominal area of the filter to obtain the mass loading, while the three readings from the 37-mm filters were inserted into two different algorithms for calculating the mass loadings, and the algorithms were compared. The IOM sampler was designed for material collected in the body of the sampler to be part of the collected sample as well as that on the filter. Therefore, the IOM sampler cassettes were rinsed separately to determine if wall-loss corrections were necessary. All four samplers gave very good correlations between the two analytical methods above the limit of detection of the XRF procedure. The limit of detection for the 25-mm filters (5 μg) was lower than for the 37-mm filters (10 μg). The percentage of XRF results that were within 25% of the corresponding ICP results was evaluated. In addition, the bias from linear regression was estimated. Linear regression for the Button sampler and the IOM sampler using single readings and the GSP using all tested techniques for total filter loading gave acceptable XRF readings at loadings equivalent to sampling at the OSHA 8-hour Action Level and Permissible Exposure Limit. However, the CFC only had acceptable results when the center reading corrected for filter area was used, which was surprising, and may be a result of a limited data set. In addition to linear regression, simple estimation of bias indicated reasonable agreements between XRF and ICP results for single XRF readings on the Button sampler filters, (82% of the individual results within criterion), and on the IOM sampler filters (77% or 61%—see text), and on the GSP sampler filters using the OSHA algorithm (78%). As a result of this pilot project, all three samplers were considered suitable for inclusion in further field research studies.

Introduction

It is estimated that more than one million workers in the USA are exposed to lead in greater than 100 occupations.[1] The clinical effects of industrial lead poisoning include colic, anemia, peripheral neuropathy, encephalopathy, renal impairment, hypertension, and reproductive disability. In addition, other adverse effects, such as slowed nerve conduction, impaired synthesis of heme, and altered secretion of uric acid, occur at levels of exposure insufficient to produce overt signs and symptoms.[2–5] Inhalation of airborne lead fume and larger particles is a major contribution to the overall dose of lead to the body. Exposure limit standards therefore include a provision for monitoring lead in air. In the UK, the Health and Safety Executive has a maximum exposure limit for airborne lead[6] of 0.15 mg m^{-3}, while in the USA, the National Institute for Occupational Safety and Health (NIOSH) has a Recom-

mended Exposure Limit (REL)[7] of 0.1 mg m^{-3}. The American Conference of Governmental Industrial Hygienists (ACGIH) has a time-weighted average threshold limit value (TWA-TLV)[8] 0.05 mg m^{-3} for an 8-hour work shift, and the Occupational Safety and Health Administration (OSHA) has a Permissible Exposure Limit (PEL)[9] for airborne lead set at 0.05 mg m^{-3} for an 8-hour TWA (and an action level set at 0.03 mg m^{-3}). Measurements for comparison to exposure limit values in the USA generally are expressed as lead in "total" dust as sampled by the standard sampling methods in use for Particulates Not Otherwise Regulated (PNOR) in the USA (see below).

Recognizing that airborne lead is a major contributor to overall exposure (as it is supposed that 100% of fine particulate lead is absorbed versus 15–30% of ingested lead), airborne lead measurements are used to indicate where biological measurements may be necessary. For example, United States Code of Federal Regulations 29 CFR 1910.1025(j)(1)(i) requires employers to institute a medical surveillance program for all employees who are or may be exposed above the (OSHA)

action level for more than 30 days per year.[9] Blood-lead measurements are considered the best predictor of disease from exposure to lead, so that biological monitoring is the gold standard for assessing and controlling exposure. However, biological measurements are invasive and therefore it is preferable to restrict this requirement to situations where the likelihood of exposure is high. Airborne lead measurements are used to assess the potential for high exposure. However, the preamble to the OSHA standard documents criticism that the relationship between air lead levels and blood-lead measurements is poor.[10] If it is assumed that exposure measurement techniques accurately reflect airborne dose, then the poor correlation may be due to dose contributions from other sources of exposure, for example, hand-to-mouth transfer where personal hygiene is poor. An alternative hypothesis is that the airborne lead measurement techniques do not accurately predict airborne exposures. This may be the case, for example, where measurements of particulates containing lead do not reflect the same particle size distribution that enters the mouth and nose of the breathing worker.

Assessing the total dose from airborne particles requires a sampler that mimics the inhalation efficiency of the human nose and mouth.[11] The 37-mm styrene–acrylonitrile closed-face filter cassette (CFC), which is the current US standard device for PNOR sampling, was not designed *a priori* to have these characteristics. In the 1990s the concept of the "inhalable" sampling convention was borne out of experiments on the aspiration efficiency of the nose and mouth.[12] The inhalable convention includes particles with aerodynamic diameters ranging up to 100 μm. Many studies have shown that the

CFC may seriously underestimate the quantity of large (>40 μm aerodynamic diameter) particles that may be inhaled, where present in the air. Although these large particles may be expectorated, swallowed and ingested, so that a smaller portion of their lead content may be absorbed, their mass is significant and their contribution to the overall dose should not be ignored. The American Society for Testing and Materials (ASTM) published a standard[13] for determining lead exposures and a similar standard has been published by the International Organization for Standardization (ISO).[14] The ASTM standard uses the existing air sampling methodology for PNOR, but also recommends the evaluation of other sampling techniques that might more closely represent the true exposure, and, therefore, may be a better predictor of dose. The ISO Standard recommends sampling in accordance with the ISO inhalable convention, described below. The standard NIOSH PNOR sampling method (0500)[15] does not currently include samplers for the inhalable convention, although the situation may be under review in the near future. Recommendations for the selection and use of inhalable samplers have been published.[16] One relatively recent NIOSH method for sampling formaldehyde on textile or wood dust (5700) recommended an inhalable sampler.[17] The OSHA regulations do not mention the concept of inhalability, or samplers that meet the inhalable convention. The samplers used in this study are shown in Fig. 1.

The Institute of Occupational Medicine (IOM) sampler is the only sampler designed specifically to meet the inhalable convention.[11,18] Many hygienists and researchers object to the IOM sampler because the wide open inlet (15 mm), facing outwards from the body, is prone to collect large particles.
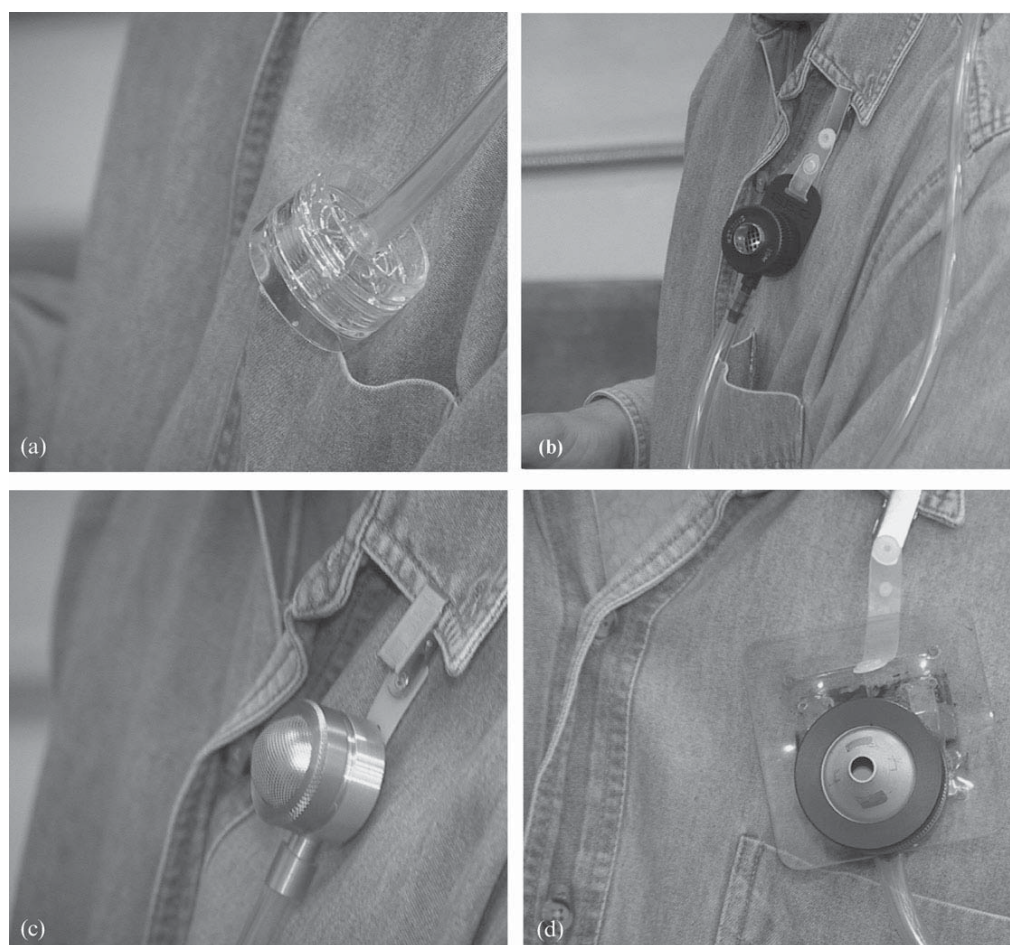

Fig. 1 Samplers used in this study. (a) CFC, (b) IOM, (c) Button, (d) GSP (note that the tape on the sampler was not used in practice). Photographs courtesy of A. J. Bird.

Such particles may be larger than the 100 μm limit of the inhalable convention.[19] The IOM sampler also is prone to collect large particles which sediment into the orifice.[20] Early recommendations for using the IOM sampler involved a plastic cassette that had issues of weight stability caused by water uptake by the polymer,[21] so that an alternative stainless steel cassette is now preferred. This is not an issue with lead dust, as the filter is analyzed chemically rather than gravimetrically. However, for an analytical method that measures only the material collected on the filter, the IOM still may not be useful if a significant fraction of the sampled dust is caught on the walls of the cassette, as this is considered to be part of the sample. For wet chemical analysis these particles can be washed out and added to the filter extract, but it would not be possible to include them easily in procedures using direct on-filter analysis. (Note: similar wall-losses are not always included in samples collected using the CFC in the USA, but they are included in such samples taken in France.[22]) The IOM sampler may not be as well-suited for assessing concentrations much below the OSHA PEL as the flow rate of the IOM cannot be raised above 2.0 L min^{-1} without altering its sampling efficiency performance.

The German GSP or "cone" sampler is another sampler of interest. This sampler performed relatively well in tests of inhalability carried out in Europe.[23] A 7-mm sharp-edged conical entry inlet opens to a 37-mm filter. The sampler operates at a flowrate of 3.5 L min^{-1}. Although there is a potential for sampled material to be caught on the inside walls of the cone, the cone is not washed out for analysis.

The Button sampler from the University of Cincinnati was developed to be independent of wind speed and direction because of a porous, curved inlet.[24] Based on laboratory results, the performance of the sampler seemed likely to be close to the inhalable convention.[25] Field studies have shown the distribution of dust over the filter used in the Button sampler to be more even than that from the CFC, which is an important characteristic in this study.[26] A recent study has confirmed the absence of wall-losses in the Button sampler.[27] The Button sampler is operated at 4 L min^{-1}.

Samplers are usually returned to the laboratory for chemical analysis. However, on-site analysis often is preferred over waiting for analytical results from a laboratory, since it allows action to be taken immediately after assessment, and may encourage worker participation in the health and safety management process. On-site analysis may also result in lowering analytical costs. On-site analysis for metals is available using a range of methodologies, including portable X-ray fluorescence (XRF) technologies. XRF analysis consists of irradiating a target, in this case the filter sample, with high-energy X-rays that interact with electrons in the K and L shells near the atomic nucleus of elements in the target. The interaction causes the electrons to be expelled and then replaced by electrons from higher orbitals. The decrease in electron orbital energy is accompanied by release of an X-ray with a characteristic wavelength that is detected by an analyzer. Portable XRF spectrometers typically use radioactive sources for excitation of X-rays, although some models use relatively low power-consumption mini-X-ray tubes. The NIOSH has previously evaluated a radioactive (Cd^{109}) source XRF analyzer for lead on filters from CFC samples from construction sites,[28] and published the results in the Manual of Analytical Methods in the back-up report in Method 7702.[29] The field samples also were analyzed by graphite-furnace atomic absorption and gave results between 0.1 and 1514 μg per filter. The limit of detection of the XRF detector using these samples was estimated to be 6 μg per filter. The reported precision of the method was 0.054 with a bias of 0.069, leading to an overall method accuracy of 16%. At the upper 90% confidence limit the method accuracy was 27%, slightly greater than the limit of 25%, leading to an inconclusive statement as to whether the method meets the

required accuracy criterion[30] for a compliance method. However, there is some question as to the most appropriate statistical methodology to be used in determining precision using field data sets, where multiple replicates at specific concentrations do not exist, and this is discussed in more detail later.

The objective of this study is to examine several other samplers described above for use in Method 7702 in a specific field situation involving a lead smelter. A similar model of XRF analyzer to that used to provide the initial data for the NIOSH Method therefore was preferred, although this may not be the only analyzer of its type that could be used. The results of the XRF measurements were compared with the inductively coupled plasma–optical emission spectroscopic (ICP-OES) technique for metals. Since the analyzer is capable of irradiating and, therefore, exciting fluorescence from only a limited portion of the filter in a single measurement (a 2 cm by 1 cm window), the evaluation of techniques to optimize the estimation of the total mass of lead on the filter was a primary goal of this study. For example, the current PNOR sampling procedure provides a mass loading of only 28.8 μg of lead for an 8-hour sample at the OSHA Action Level, which is not very much higher than the limit of detection found in Method 7702. This study examines increasing sensitivity by reducing the filter area from around 1 000 mm^2 (CFC, GSP: 37-mm filter) to around 500 mm^2 (Button, IOM: 25-mm filter), increasing sensitivity with increased flow-rate (GSP: 3.5 L min^{-1}, Button: 4.0 L min^{-1}), and possibly increasing sensitivity with better sample distribution on the filter (Button), or combinations of the above.

Investigation was also made of different protocols for estimating the mass of lead deposit on 37 mm filters. Three readings taken at different distances along a diameter of the filter (top, middle and bottom) are combined according to a formula to take into account both inhomogeneity in the aerosol deposit on the filter and the unsampled area of the filter. For the NIOSH method the algorithm is incorporated into the microprocessor programming of the instrument by the manufacturer and was that used in the original field study to validate the method.[28] The XRF calculates raw readings in terms of μg cm^{-2}, and the values are combined according to the following formula:

$$2 \times \text{Middle reading} + 3.8 \times \text{Top reading} + 3.8 \times \text{Bottom reading}$$

The OSHA method[31] incorporates both the filter and the support pad in the sample holder for XRF analysis of CFC samples, and has a different algorithm (which can also be programmed into the instrument software), based on the analysis of field samples, which is:

$$1.8 \times \text{Middle reading} + 3.3 \times \text{Top reading} + 3.3 \times \text{Bottom reading}$$

In the OSHA method documentation, the difference between the algorithms is ascribed to the presence of the support pad, but without experimental verification. In both cases, the differential weightings given to different parts of the CFC filter are a result of non-uniform filter deposition, which is a well-known characteristic of the CFC.[32] Using multiple readings in this way is time-consuming, and does not easily allow the flexibility of adjusting the reading time according to the lead loading. A uniform deposit of aerosol would be preferred.

As noted, the results of XRF measurements of lead are compared with those obtained using traditional ICP-OES analysis. Extraction of the analyte from the filter sample must first be performed so that the analyte in solution can be nebulized into the ICP-OES instrument. The current NIOSH method for the analysis of lead by ICP-OES utilizes either

hotplate or microwave digestion sample extraction techniques.[33] These methods involve the use of elevated temperatures and strong acids, and the sample preparation step is usually the most time-consuming step in the sample analysis. In order to shorten the sample analysis and eliminate the analyst's exposure to the concentrated acids and high temperatures, researchers have explored ultrasonic extraction of samples for lead and have developed an American Society of Testing Materials method (ASTM E-1979–98) for the ultrasonic extraction of lead samples.[34,35] This technique has been incorporated into a field method for lead analysis by anodic stripping voltammetry.[36] The ultrasonic technique has the added advantage of allowing the use of polvinylchloride (PVC) filters in place of mixed cellulose-ester filters, since complete filter digestion is not required. PVC filters allow more accurate gravimetric analysis than MCE filters.[37]

Experimental

The manufacturing plant participating in this study used lead in the production of bullets. In the process at the time of sampling, scrap lead from sources such as tyre weights was melted in a small furnace and pumped into a cast to form a billet. Antimony was added in small proportion to the melt to adjust the properties of the cast lead. Lead melted from scrap included other ingredients, which, on occasion, caused the pot to foam, a condition which tended to result in higher exposures to the furnace operator. As a result of this observation, virgin lead is now used in place of scrap. The cast billets were heated until the lead became ductile, and then were drawn into a wire to meet the diameter specifications of the bullet to be made. The wire was then run through another machine to be cut to the desired length.

Personal and area samples were collected around the furnace and wire-drawing areas using the samplers under study. All of the CFC and IOM samples were personal samples, while the majority of the GSP and Button samples were area samples. This was not an ideal distribution as it may add an additional source of variation in the analysis, but it was dictated by very practical considerations: the larger pumps required for the higher flows for the GSP and Button samplers are heavy, and user comfort turned out to be an important factor in recruiting volunteers. Samples were taken for approximately 4 hours in the morning or approximately 3 hours in the afternoon. After allowance for pump faults and sample losses during analysis, and samples below the limit of detection of the portable XRF, the remaining samples used in the analysis were from 14 CFC, 9 GSP, 12 Button and 17 IOM samples. Pure, homopolymer, PVC filters were pre- and post-weighed to allow the determination of total dust mass as well as lead content. This is important as samples that have high dust loading (e.g., >0.5 mg per 25 mm filter) may also exhibit matrix effects in the XRF metal determination through absorption of X-rays.[38]

The XRF analyzer (NITON XL 701) was similar to the model evaluated in NIOSH Method 7702 (XL 700), although there have been improvements to the instrument over time (e.g. in the detector and electronics). All XRF measurements involved counts accumulated for 60 nominal seconds. The filter samples were removed from the filter holders (samplers) and placed in a 25-mm or 37-mm filter holder, depending on filter size. The filter holders were made of cardboard, with Mylar film over the filter area. Since neither of the Button, IOM and GSP samplers use a thick back-up pad like the CFC, only their filters were analyzed. For consistency, the back-up pad of the CFC also was not included in the analysis, as per the NIOSH method, even though the addition of the back-up pad is a feature of the OSHA method.[31] The cardboard holders were placed on a test stage provided by the manufacturer of the XRF instrument, so that the filter holder could be placed under the analyzer's X-ray beam. The XRF analyzer's calibration

was checked with thin film standards from Micromatter Company (Deer Harbor, WA). These standards consisted of Nucleopore® polycarbonate membranes coated with specified metals, and were designed for use in the calibration of XRF equipment. The thin film standard (serial number 13099) had a diameter of 23 mm and a lead concentration of 58.7 μg cm^{-2} with a relative error of ± 5%. The thin film standard (serial number 13100) had a diameter of 32 mm and a lead concentration of 59.4 μg cm^{-2} with a relative error of ± 5%. Both experimenters in this study had participated in the company-sponsored instrument use and safety training program.

The algorithmic procedure described above was used for determining the lead present on both samplers (GSP and CFC) that use 37-mm filters. For samplers using 25-mm filters (Button and IOM), homogenous deposition was assumed and the results from analyzing the central portion only were corrected by multiplying the XRF result in μg cm^{-2} by the nominal area of the filter covered by the dust deposit. For the Button sampler that was easily measured to be 3.46 cm^2. However, for the IOM sampler it becomes rather more difficult to determine. In some recent samples, when the area of the obvious grid pattern is measured, the result is 2.84 cm^2, but there is a faint halo of deposit on all samples which might be interpreted as a value of 3.46 cm^2 for the deposit area for this sampler too. This variable deposit phenomenon may be a function of particle size, and the ability of particles to deviate from a direct path from the inlet to the filter. The central reading only on the 37-mm filters, and also a mean, non-weighted average of the three readings, were also recorded and the raw XRF data were adjusted for the effective area of the filter (GSP 7.55 cm^2, CFC 9.08 cm^2). It should be noted that the mass collected per unit area of filter over similar sampling periods varies by a factor of 5 between the extremes of the Button sampler operated at 4 L min^{-1} and the CFC operated at 2 L min^{-1}. The Button sampler would therefore be most affected by layer depth or matrix effects.

The PVC filters and 10% (v/v) nitric acid were placed in 50 mL centrifuge tubes in a Branson 3510 ultrasonic bath for 30 minutes. Analysis was carried out at DHL Laboratory (Birmingham, AL) using an ICP-OES, measuring at a wavelength of 220.4 nm. The NIOSH Method 7300 procedure was followed for the analysis of extracted samples for lead.[33] Each centrifuge tube from the extraction step was uncapped and the sample was diluted to 50 mL with distilled, deionized water. The tubes were then capped, shaken for five to ten seconds, and the sample allowed to settle. In addition to the filter extractions, the interior of each IOM cassette was rinsed with the 10% (v/v) nitric acid to evaluate sample losses to the sampler interior wall, as, when the analysis is gravimetric, particles collected here are intended to be part of the sample catch. The rinse solution was diluted to 10 mL for analysis. The ICP-OES was calibrated according to the manufacturers' recommendations. Calibration standards were analyzed each day of analysis in the range of 0.8 μg mL^{-1} to 20 μg mL^{-1}. Derived calibrations showed correlation coefficients greater than 0.999. Samples over this range were diluted and run again. A check standard was run every ten samples, and recoveries were checked with at least two spiked media blanks per ten samples. During the period of this study the laboratory, while not accredited by the American Industrial Hygiene Association, participated in their on-going Proficiency Analytical Testing programs for metals and was rated proficient.

Bias, as defined by the NIOSH Guidelines for Air Sampling and Analytical Method Development and Evaluation,[30] is as follows:

$$B = [(\mu/T) - 1] \qquad (1)$$

where μ is defined to be the population mean of measurements of a known concentration T. The above definition is typically used where there are several laboratory measurements at the

given concentration T so that estimates of μ are available across a range of concentrations. This definition does not accommodate field situations where there may be only one measurement each at several concentrations.

This definition can be modified to accommodate field data where there are several pairs of measurements over a range of concentrations as described in the following. Given that one measurement (x) is the reference result for concentration and the second measurement in the pair (y) is based on a new measurement method, then the bias ($B_{y/x}$) can be defined as:

$$B_{y/x} = [(\mu_{y/x}/x) - 1] \qquad (2)$$

where $\mu_{y/x}$ is defined to be the conditional mean of the data from the new measurement method that produces the random variable (y) given that the true concentration value (x) from the reference method is known. The quantity $\mu_{y/x}$ can be estimated using linear least squares regression. Regression methods can be used to obtain confidence intervals for $\mu_{y/x}$. This allows for assessment of acceptability of the measurement method based on a predetermined minimal level of acceptable bias.

For this application it was necessary to perform the regression analysis and estimation procedures outlined above using the log-transformed concentrations in order to have approximately normal regression errors. When this is the case it is simple to modify this estimation method by transforming the upper and lower limits back out of the log scale and calculating the estimate of bias directly as follows: using a modified definition of bias appropriate for a lognormal distribution as given by eqn. 3, the bias can then be estimated by eqn. 4, which represents the estimated regression for a given value of log concentration transformed back out of the log scale.

The definition of bias is given by

$$B_{y/x} = (\text{median concentration}/\exp{(x)}) - 1 \qquad (3)$$

and the estimate for bias ($\hat{B}_{y/x}$) is then obtained as:

$$\hat{B}_{y/x} = \exp((\hat{\beta}_{o} + \hat{\beta}_1 x)/\exp(x)) - 1 \qquad (4)$$

where $\hat{\beta}_{o}$ and $\hat{\beta}_1$ represent the estimates of slope and intercept from the linear least squares regression of log XRF on log ICP, for any known concentration $\exp(x)$ or log concentration x. This estimate of the bias has a different interpretation from that in eqn. 2 in that, assuming the log-transformed concentrations have a normal distribution, this approach gives approximate estimates based on the invariance of percentiles to the log transform. Estimates of the mean value of a distribution are not invariant to the log transform, so the definition for bias in eqn. 2 no longer holds when transforming the estimates out of the log scale. However, if the assumption of normality for the log-transformed concentrations holds, then the log transformed probability limits will also be consistent with the definition of the bias estimate and will be an approximation of eqn. 3. This is based on the assumption that for the log-transformed concentrations the theoretical mean and median are identical. Hence the estimated mean in the log scale will provide an approximate estimate of the median in the log scale, as well as the original concentration scale, since the probabilities associated with percentiles are invariant to the log transform.

Typically, estimation of accuracy requires the assumption of a normal distribution of errors. For the data in this study, the situation is not as clear cut. Since the regression analysis provides evidence that the errors in the XRF (relative to the ICP-OES result) are apparently lognormal, then existing methods based on the assumption of normality for calculating accuracy do not readily apply. Therefore, a useful nonparametric method for quantifying accuracy and ranking samplers

by accuracy is as follows:

$$\Pr\left(\left|\frac{Y}{T} - 1\right| < A\right) = q \qquad (5)$$

where A is the accuracy, $Y = $ XRF and $T = $ ICP, and q is the confidence. In general one can either fix A and estimate q or fix q and estimate A. The NIOSH standard accuracy criterion requires $A = 0.25$ or less with $q = 0.95$. It is also possible to get a simple characterization of accuracy by fixing A and calculating q. This can be accomplished for pairs of field samples, by calculating:

$$\hat{a} = \frac{Y}{T} - 1 \qquad (6)$$

and computing the proportion of values of the quantity $\hat{a}$ that fall within the limits $(-A, A)$ where A is a pre-specified accuracy level. For this study we set $A = 0.25$, consistent with the NIOSH standard accuracy criterion.

Results and discussion

The rinse solutions from the IOM cassette walls contained non-detectable or insignificant quantities of lead. Other workers have confirmed the observation that the IOM cassette walls collect insignificant quantities of metals.[39] Therefore, none of the IOM filter samples required corrections for wall losses. The filter results varied from non-detectable to 1330 µg lead based on the ICP analysis, with most samples being under 100 µg. The CFC samples had the smallest range (up to 57 µg per filter) while the GSP had the highest value. Although several samples exceeded a recommended maximum 500 µg total dust loading, they were not voided as they did not adversely affect the correlation, and the recommendation was based on theoretical calculations rather than experimental verification.[38] In addition, the dust collected was thought to be almost entirely lead or lead compounds, and the XRF analyzer has been shown to provide a linear response up to about 1500 µg lead. For each sampler, the bias of individual XRF results from their corresponding ICP values was plotted in rank order of increasing ICP result and no trends were observed. An approximate field limit of detection for the XRF technique could be identified from examination of this data-set, as the point below which variation around the regression line became noticeably extreme, as 5 µg per filter for the 25-mm filters, and 10 µg per filter for the 37-mm filters. Due to the small sample size, this is
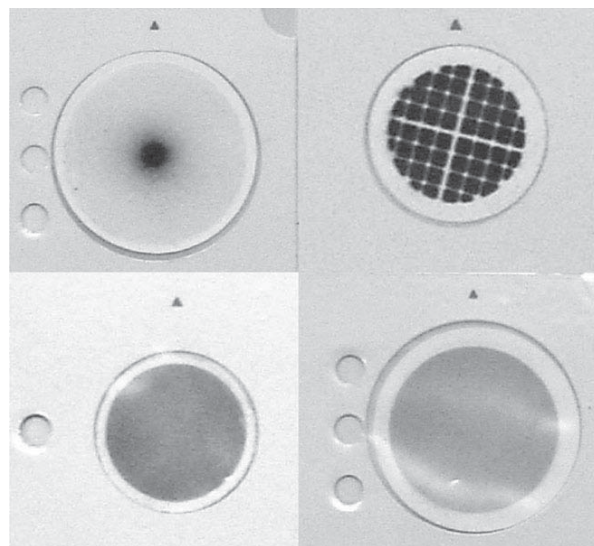

Fig. 2 Typical dust depositions on filters (samples taken from a different location). Clockwise from top left: (a) CFC, (b) IOM, (c) GSP, (d) Button.

Table 1 Bias from linear regression at the OSHA Action Level loading for an 8-h TWA sample

Sampler	Algorithm	Slope	R^2	OSHA AL loading/ICP µg	XRF reading/µg	Bias (%)	OSHA PEL loading/ICP µg	XRF reading/µg	Bias (%)
CFC	NIOSH	1.128	0.898	28.8	44.3	53.8	48	78.8	64.2
	OSHA	1.083	0.920	28.8	38.1	32.3	48	66.2	37.9
	Average	1.159	0.823	28.8	49.1	70.5	48	88.8	85.0
	Center	1.015	0.839	28.8	30.3	5.2	48	50.9	6.0
GSP	NIOSH	1.011	0.971	50.4	52.6	4.4	84	88.2	5.0
	OSHA	0.980	0.968	50.4	49.4	−2.0	84	76.9	−8.5
	Average	0.963	0.970	50.4	43.6	−13.5	84	71.3	−15.1
	Center	0.949	0.929	50.4	41.3	−18.1	84	67.0	−20.2
IOM	2.84	1.029	0.923	28.8	31.7	10.2	48	53.7	11.9
	3.46	0.978	0.938	28.8	26.7	−7.3	48	44.1	−8.1
Button		0.989	0.951	57.6	55.1	−5.3	96	91.3	−4.9

not a statistically rigorous value, but for the 37-mm filters it is consistent with the reported LODs from the NIOSH method (6 µg) and the OSHA method (7.5 µg). Typical dust deposition patterns on the filters are shown in Fig. 2. Statistical analysis was performed on samples above the LOD as described above.

The slope and correlation co-efficients for linear regression of the log(base 10)-transformed filter analysis data (trendline forced through the origin)are given in Table 1, alongside the mean bias for different values of sample loading around "critical" loadings at the 8-hour time-weighted average (TWA) permissible exposure limit (PEL) and action level as given by the regression equation (which is equivalent to eqn. 4). The percentage of samples that meet the criterion of eqn. 6 is
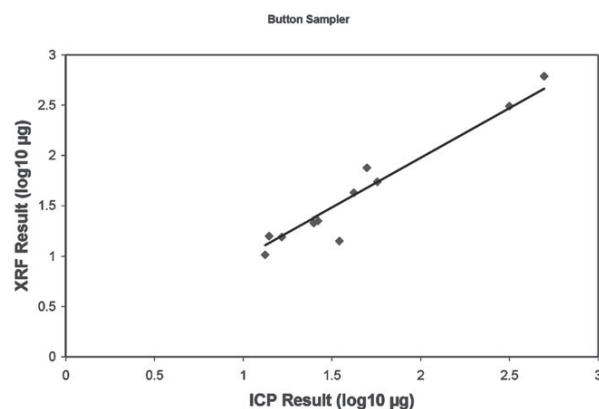
Fig. 3 Correlation of XRF and ICP results for the Button sampler.
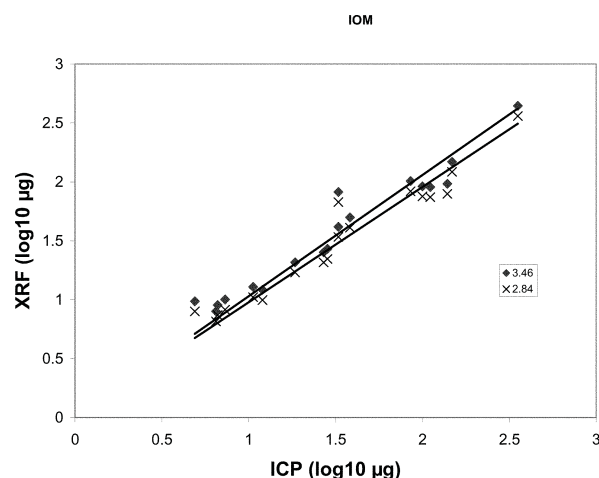
Fig. 4 Correlation of XRF and ICP results for the IOM sampler (based on both area calculations).

discussed below. It should be noted that the CFC results cover a smaller range of filter loadings than is found with the other samplers, and this may have a bearing on the relatively poor performance of the CFC. Using the NIOSH algorithm on the CFC results, only 7.1% of the actual XRF readings were within 25% of the corresponding ICP values, and the mean bias of the XRF reading from the ICP values from the linear regression (expressed as the deviation of the regression line slope from unity) was greater than 25% over the range which includes the "critical" values mentioned above (Table 1). The OSHA algorithm gives slightly better results, where 14.3% of the actual XRF readings were within 25% of the corresponding ICP values. However, the bias was still greater than 25% over the critical range. Use of the center reading only gave surprisingly good results with a bias from linear regression within 25% for the critical range, and 71.4% of samples within 25% of the corresponding ICP values. This should be contrasted with using the unweighted average of three readings where the bias from linear regression was outside of the criterion over the critical range and where none of the individual XRF values was within 25% of the corresponding ICP values.

The mean bias from linear regression for the GSP sampler over the critical range was within 25% using all calculation methods, with both NIOSH and OSHA algorithms performing well. However, a greater proportion of the individual XRF results (77.8%) were within 25% of the corresponding ICP values when using the OSHA algorithm vs. the other methods (55.6% for all three).

The mean bias from linear regression for the IOM sampler over the critical range was within 25% using the single reading method, and 77.8% of the actual XRF readings were within 25% of the corresponding ICP values when the value of 2.84 cm^2 is used for the deposit area. When the value of 3.46 cm^2 is used, this is reduced to 61.1%. Results are given in Table 1 using both values, as more recent data suggests that the latter value might be the most appropriate. The mean bias from linear regression for the Button sampler over the critical range was also within 25%, and 81.8% of the actual XRF readings were within 25% of the corresponding ICP values. Given the practical advantages of these two 25 mm samplers, and their relatively good performance, the actual regression curves are provided in Figs. 3 and 4.

Conclusions

In this study, the standard US sampler (CFC) using either the NIOSH or the OSHA algorithm did not perform within the required accuracy criterion over a range of concentrations either side of a critical loading value. This may be due to the small range of lead loading collected by these samplers, although, in comparison, the NIOSH Method 7702 also reports accuracy exceeding the NIOSH criterion. The results

using the center reading only (adjusted for the ratio of the XRF window to the total effective filtration area of the filter) gives results equivalent to those found with the IOM and Button samplers, although this conclusion runs counter to the results from using an average of all three readings, and also to the experience of prior studies.

These results can be considered in the light of prior studies using the XRF on-filter methodology. One difference between the study of Morley et al.[28] and the present study is the use of PVC filters in this study in place of MCE filters. Even though the surface of PVC filters has more three-dimensional relief than that of MCE filters, any loss in signal from particles embedded deeper in the filter would cause a negative XRF bias, and this was not noted. It may also be possible that the extraction of particles in the digestion step of ICP-OES analysis was less than 100%, which would cause a positive bias in the XRF reading, but this has not been observed in other studies of lead fume. The major difference between the two studies is in the industry where the tests were carried out, which undoubtedly resulted in different chemistry and particle size distribution of the resulting aerosols. For example, it may be possible that particle size distribution affected the homogeneity of aerosol deposition on the filter. The issue will be examined in the continuation of this study.

Another study of note is that of Drake, et al.,[40] which examined samples from lead ore milling operations. Their results did not agree with those of Morley et al., with XRF results 26.5% higher on average than the wet chemical analysis. The reason proposed was that the XRF was measuring a form of lead (e.g. silicate) that was not digestible by the wet chemical extraction technique, although the samples were not tested for the presence of such materials. In fact, lead does not readily enter into combination with silica in nature, because of its chalcophilic nature. The few discrete lead minerals that have been described are very rare, and lead does not commonly replace ions in other silicate minerals. Therefore, it is highly possible that the bias found in that study, which is similar to the bias seen here, reflects a problem with the algorithm used to calculate the lead loading on the filter.

The OSHA algorithm gave better results than the NIOSH algorithm for the CFC, but the results are still not appropriate to a fully quantitative method. However, there were differences between the protocol used in the OSHA method and that employed here. A single reading adjusted for the effective filter area gave the best results, but this is contrary to other studies that suggested the use of an algorithm. It is possible that dust on these filters was more evenly distributed than commonly observed on CFC samplers, due to the fine particle size from the smelting fume, but the result also may be just a fortuitous combination of dust loading and matrix effect. A further factor affecting the CFC results is the potential for material to be deposited on the cassette walls. Traditionally, NIOSH has not considered this part of the sample, so that there is no bias if it is not measured in the field. However, OSHA does consider this to be part of the sample, which is why they wipe the interior. Unfortunately, portable XRF analysis of wipes is not considered fully quantitative.[41]

The GSP sampler had good bias using both the NIOSH and OSHA algorithms, although the number of samples within 25% of the ICP values was better for the OSHA than for the NIOSH algorithm. There is no obvious reason why either algorithm would be applicable to the GSP filters, given that they were not determined using this sampler type. Reasonable results were also obtained from an average of all three readings, adjusted for filter area, which is plausible if the dust is evenly deposited on these filters. However, results using the center reading only were not quite as good.

The results from the 25-mm samplers (IOM and Button) using a single reading adjusted for the effective filter area appear very promising. These results may be caused by the uniform distribution of the sample across these filters, as has been observed visually in a number of studies, and investigated experimentally in the case of the Button sampler.[24] The Button sampler, the IOM sampler and the GSP sampler have been shown to have negligible wall deposition.[27] This is in contrast to the CFC sampler where a very large proportion of the sample can be on the walls.[22] The OSHA method, which was not available at the time the samples were taken in this study, takes account of this by requiring the inner walls of the CFC to be wiped, and the wipe analyzed,[31] although this is an additional analytical burden.

A LOD of 5 μg per filter for an IOM sampler is equivalent to an air concentration of 5.2 μg m^{-3} (for an 8-h TWA sample) while the same calculation for the Button sampler gives a minimum air concentration of 2.6 μg m^{-3} (although the increased load on the pump from the higher flow-rate may not allow sampling for the full 8-h period). Both of these are achievable with a single XRF analyzer reading, with acceptable bias at the target concentrations from linear regression. Fewer readings represent an advantage, since a 60-second nominal count reading (which has been extended to 180 nominal seconds in current protocols) can stretch to many minutes as the source of X-rays decays over time. The corresponding LOD's for the 37-mm filter samplers are 10.4 μg m^{-3} for the CFC and 6.0 μg m^{-3} for the GSP. Of the four samplers used in this study, the Button sampler has the best combination of: least bias from linear regression (approximately 5%), most sample results by XRF within 25% of the ICP values (80.2%), highest sensitivity in terms of LOD, little or no wall losses, and requires only a single reading. Therefore, the Button sampler may be preferred on analytical grounds, although the sampling efficiency for different particle size distributions is also an important consideration factoring into sampler selection.[42] The IOM sampler had acceptable bias from linear regression (approximately 11%), a high percentage of XRF results within 25% of ICP values (78 or 61%), higher sensitivity than the CFC, little or no wall losses, and requires only a single reading. Thus the IOM may also be a preferred sampler, particularly if it is desired to have the most accurate assessment of the inhalable fraction of the aerosol. However, the difficulty of defining the actual sample deposit area for the IOM filters may be a drawback for accurate determinations.

All of these samplers, in addition to the open-faced 25-mm styrene–acrylonitrile cassette, are currently being used in similar studies in other workplaces where lead is encountered in different matrices, and with other metals, and where it is evolved through different processes. There are two reasons for this. Firstly, it is important to account for any particle size and matrix effects on the XRF analysis. Since lead has a high mass absorption and relatively low wavelength X-ray fluorescence it is particularly vulnerable to particle size effects. Secondly, it has been strongly recommended that any change in exposure assessment methodology, such as moving from a standard based on "total" dust sampling to one based on "inhalable" dust sampling, should be assessed by field comparisons between the existing and proposed methods, especially when it may be accompanied by a corresponding change in the numeric exposure limit value.[43–46] In order to carry out such studies with confidence, the accuracy associated with the sampling and analytical methodologies should be well established. Although the number of samples evaluated was not large, this study provides an empirical ranking of analytical performance for the samplers used in this field analysis method. Further studies are underway to support these results.

Acknowledgements

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