PAPER

A comparison of X-ray fluorescence and wet chemical analysis for lead on air filters from different personal samplers used in a bronze foundry†

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Portable X-ray fluorescence (XRF) technology may provide faster turn-around without compromising accuracy when assessing personal exposures to metals such as lead, but it has only been tested in limited field environments. This study is part of a series, where different sampler types are used to collect airborne lead in different environments for presentation to a portable XRF analyzer. In this case personal samples were taken at a bronze foundry where lead is added to an alloy of copper, zinc and iron to improve casting, using the closed-face 37 mm cassette, the 37 mm GSP or "cone" sampler, the 25 mm Institute of Occupational Medicine (IOM) inhalable sampler, the 25 mm Button sampler, and the open-face 25 mm cassette. Mixed cellulose-ester filters were used in all samplers. Following XRF analysis the samples were extracted with acid and analyzed by inductively coupled plasma optical emission spectroscopy (ICP). For lead, all five samplers gave correlations (r^2) greater than 0.9 between the two analytical methods over the entire range of found lead mass, which encompassed both the action level and the permissible exposure limit enforced in the USA by the Occupational Safety and Health Administration (OSHA). However, a correction was required to adjust linear regression trendlines to give a 1 : 1 correlation for the average of three readings across the GSP sampler, and a similar correction was required for the single readings from the IOM sampler and the 25 mm filter cassette. The bias possibly is due to interference from other metals, possibly copper which can absorb the fluorescent radiation of lead. In the case of the Button sampler, the bias is larger, indicating a further source of error, perhaps due to the thickness of the deposit. However, in all cases, correction of the lead results did not greatly affect the overall percentage of samples where the XRF result was within 25% of the ICP result, although it did improve the overall accuracy of the results. The GSP, IOM and Button samplers are suitable candidates for further evaluation as compatible with on-site XRF analysis for lead and other metals. It is important to check carefully factory pre-set instrument calibrations, as a bias in the calibration for copper was observed.

Introduction

This study is part of an ongoing large-scale investigation into the use of portable X-ray fluorescence (XRF) analyzers for on-site evaluation of airborne lead samples in the workplace. Many current protocols require off-site analysis in a laboratory, which may take several days, even weeks. A more rapid response is preferred, especially by health and safety compliance officers who may be under regulatory deadlines. Health and safety managers faced with rapidly changing conditions, such as in the construction industries, or where process changes are being evaluated, would also benefit from a speedier analytical process. Anodic stripping voltammetry has been advocated as an on-site analytical technique for lead, but requires some chemical work-up of the sample.[1] X-Ray fluorescence (XRF) technology promises the possibility of analytical results within minutes of the end of sample collection without additional chemical steps. Bench-top XRF analyzers have been used for determining lead on air filters for many years in the UK.[2] However, although currently published portable XRF methodologies from US National Institute for Occupational Safety and Health (NIOSH) and Occupational Safety and Health Administration (OSHA) are generally considered sufficiently accurate for use as screening tools, there is some question as to their ability to be used to support citations based on compliance with legally enforceable limit values.[3,4] The accuracy requirements for airborne lead determinations to be used for regulatory compliance purposes in the USA are 95% confidence that the result is within ±20% of the true value (OSHA General Industry standard)[5] and 95% confidence that the result is within ±25% of the true value (OSHA Construction standard).[6] The EU requires sampling and analytical methods to have a 95% confidence that the result is within ±30% of the true value at concentrations close to limit values.[7] For a screening method, for example to determine when it may be necessary to take samples according to an accepted compliance method, a lower level of accuracy may be appropriate, such as 90% confidence that the result is within ±25% of the true value. The ability of portable analyzers to be used for compliance monitoring may be improved by presenting the sample in a different manner to the XRF analyzer, through the use of samplers which provide more uniform sample deposits, and this is the focus of the current investigation.

The results of a pilot project in a small lead scrap smelter and wire-drawing operation have already been published; the re-

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sults allowed ranking of the samplers, but the sample numbers were small, and not really sufficient for a full evaluation of accuracy.[8] Clinical effects of industrial lead poisoning were referenced, along with a discussion of the various applicable exposure limit values and sampling equipment and the relationship between air and blood measurements. Measurements for comparison to exposure limit values in the USA generally are expressed as lead in "total" dust[9] as sampled by the standard sampling method in use for Particulates Not Otherwise Regulated (PNOR) as described below.[10] In recent years, there has been a move towards using samplers that operate in accordance with the International Organization for Standardization (ISO) inhalable convention, especially for substances like metals, that may cause systemic toxicity from absorption in any part of the respiratory system. The 37 mm styrene/acrylonitrile filter cassette with a 4 mm entry inlet (CFC), which is the current US standard method for PNOR sampling, was not designed *a priori* to meet this convention. The Institute of Occupational Medicine (IOM) sampler, which, like the CFC, operates at 2 L min^{-1}, is the only sampler designed specifically to meet the inhalable convention.[11,12] The German GSP or "cone" sampler is another sampler of interest, which performed relatively well in tests of inhalability carried out in Europe.[13] A 9 mm conical entry inlet opens to a 37 mm filter and the sampler operates at a flow-rate of 3.5 L min^{-1}. The Button sampler from the University of Cincinnati was developed[14] to be independent of wind speed and direction because of a porous, curved inlet. Based on laboratory results, the performance of the sampler seemed likely to be close to the inhalable convention.[15] The Button sampler uses a 25 mm filter and is operated at 4 L min^{-1}. The pilot study concluded that the two 25 mm filter samplers could have significant advantage for on-filter analysis, since only a single reading was required, provided the dust sample was deposited in a uniform manner across the exposed filter area.[8] Therefore, a 25 mm version of the CFC (which has the advantage of being inexpensive and disposable) was also used in this study. This sampler was operated in the "open-face" mode since open-faced sampling results in a more even distribution of particles over the filter. However, it did not meet performance criteria for an inhalable sampler in tests.[13] At 2 L min^{-1}, this sampler is used as a standard sampling method in Sweden.

In the manufacturing plant participating in this study, lead is encountered as a trace contaminant in bronze, added to improve the casting. Lead does not dissolve in the bronze alloy, but forms discrete globules which are easily liberated during processing. Working of bronze with added lead has probably contributed to metalworkers exposure since prehistoric times.[16] Exposures in this specific industrial situation are found in both the melting and casting of the bronze (occupation designated as "metal pourer"), and in the removal of foundry sand from around the cast (occupation designated as "shake-out"). In addition to lead, the foundry dust contains large quantities of iron, copper and zinc from the bronze alloy used, and these metals could also be determined by the analytical techniques described. Since this alloy does not contain tin, a more descriptive term might be "ferruginous brass", rather than bronze. Metal pourers are exposed to fume from the molten bronze. Volatile elements such as lead and zinc might be expected to be concentrated in the fume. The shake-out operation exposes workers to silica dust contaminated with metals, but likely without an enhanced concentration of the volatile metals in these dusts. The workers in these occupations at this facility are in a substance-specific OSHA regulatory standard program, which includes routine blood lead monitoring and the use of powered air-purifying respirators at all times. Personal samples were taken at the height of the shirt collar, outside of the respirator.

Experimental

Personal samples were collected from both metal pourers and shake-out workers using the samplers under study. Samples were taken for approximately 4–6 hours. The numbers of useable samples from each sampler type collected were: 31 CFC, 31 GSP, 33 IOM, 30 Button and 31 25 mm open-face cassettes. Only one sample (from a 25 mm open-face cassette) was below the limits of detection of the portable XRF for lead as determined in the pilot project (5 μg per filter for the 25 mm filters and 10 μg per filter for the 37 mm filters).[8] These limits of detection correspond to the following concentrations according to sampler: CFC 10 μg m^{-3}, GSP 6 μg m^{-3}, IOM and 25 mm open-face cassette 5 μg m^{-3}, Button 3 μg m^{-3}.

Mixed cellulose-ester filters are normally prescribed for the metals digestion procedure, and were used in this study. This represents a variation from the pilot project, where polyvinyl chloride (PVC) filters were used. The XRF analyzer used (Model XL 701i, NITON Corp., Billerica, MA, USA) was of the same type (Cd^{109} excitation source, producing intense silver K X-rays at 22.1 keV), and is considered by the manufacturer to be an improvement over the model previously evaluated for the method published in the NIOSH Manual of Analytical Methods as method number 7702,[3] and used in the pilot project for this study.[8] Note that method 7702 does not specify a particular detector, but only one instrument was evaluated in the development of the method. Other instruments are under evaluation. The instrument used in this study uses the Lβ emission line to measure lead, as the emission energy from the cadmium decay radiation is not sufficient to excite Kα emission, and arsenic interferes with lead Lα.

The analytical window for this device is 2 cm × 1 cm. The instrument used gives readings in μg cm^{-2}, when set to Standard Filter mode under the Thin Sample mode. Method 7702 as written using the CFC and 37 mm filters requires taking three readings (in μg cm^{-2}) at different locations across the filter, in order to account for non-uniform sample distribution, and the three readings are combined according to a formula given in the method to give the total mass in μg per filter. The formula is based on field calibration in a specific industry (construction), and for the NIOSH method[3] is:

Total mass = 2 × Middle reading + 3.8 × Top reading + 3.8 × Bottom reading.

A similar OSHA method[4] incorporates both the filter and the support pad in the XRF analysis and has a different algorithm, also developed from the analysis of construction field samples, which is:

Total mass = 1.8 × Middle reading + 3.3 × Top reading + 3.3 × Bottom reading.

The OSHA method attributes the difference in their algorithm to the possible presence of the support pad, but no evidence for this is provided. Support pads were not included in the analysis of filters in this study. Careful handling is required to remove the filter from the support pad without disturbing the dust deposit on the filter, so keeping the filter and pad together is an attractive option. However, the Mylar film will not in that case sit smoothly over the filter because the filter holder is not deep enough to accommodate the pad. NIOSH and OSHA algorithm procedures were used for determining the lead present on the samplers (GSP and CFC) that use 37 mm filters by means of an Excel spreadsheet. For samplers using 25 mm filters (Button, IOM and 25 mm open-face cassette), homogenous deposition was assumed and the results from analyzing the central portion only were corrected by the ratio of the XRF window reading in μg cm^{-2} to the nominal area of the filter covered by the dust deposit, which was measured as 3.46 cm^2 for the Button sampler, and 3.80 cm^2 for the 25 mm cassette. The central grid area of the IOM sampler has a thick deposit of area 2.84 cm^2, and this was assumed to be the area of interest in the pilot project.[8] Good

results were obtained in that study, but results were not as good in this study when 2.84 cm^2 was used. On examination of filters from another field study (publication in preparation) a further faint halo of dust was observed to extend the deposit area to 3.46 cm^2. Therefore, both possible dimensions were used in the analysis. Calculations of filter loading were also made from the central reading only on the 37 mm filters (CFC and GSP), as well as using a mean, un-weighted average of the three readings, again with correction for the ratio of the XRF window reading in μg cm^{-2} to the sample deposit area of the filter (9.08 cm^2 for the 37 mm cassette and 7.55 cm^2 for the GSP).

All measurements involved counts accumulated for 240 nominal seconds. This time period is considered the best trade-off between accuracy and speed of analysis. The filters were removed from the samplers and placed in filter holders obtained from the instrument manufacturer. The filter holders were made of cardboard, with openings of either 25 mm or 37 mm diameter, and removable Mylar film covering both sides, including the filter area. The cardboard holders were placed on a test stage provided by the manufacturer, so that the filter holder could be placed in the same position(s) each time under the analyzer's X-ray beam. The XRF analyzer has a factory pre-set calibration which, in the version of software currently loaded, cannot be altered except by the manufacturer. As a part of this calibration, all of the elements that form the analytical suite that can be analyzed by the instrument are assessed, and an inverse matrix is produced. The matrix is used to perform a complete spectrum deconvolution, thus taking care of overlapping lines. The calibration for lead and other metals was checked against thin film standards from Micromatter Company (Deer Harbor, WA), and also with calibration standards provided by the Health and Safety Laboratory as part of their proficiency test program. Since copper, zinc and iron form part of the aerosol, their quantitation was important in determining possible matrix effects. A possible problem related to the calibration of copper was identified, and is described below.

All samples were analyzed at a laboratory accredited by the American Industrial Hygiene Association (AIHA). NIOSH Method 7300 (metals by ICP[17]) was modified to include extraction of the Mylar film covering the filters. The Mylar film in contact with both sides of the filter was carefully removed using extreme care, as some sample often attaches to the Mylar film and could come loose. The filter and Mylar film were placed in a clean 50 mL centrifuge tube. A 10 mL aliquot of 1 : 1 (v/v) purified (American Society for Testing and Materials Type II) water : nitric acid was added and the sample was digested for 60 minutes in a hot-block type digester at 110 °C. When cool, the sample was diluted to 25 mL with purified water, and the tube was sealed and shaken, and then analyzed. Three filters from previous AIHA proficiency test rounds were incorporated into the ICP analytical run as blind quality checks and all three results were in range. Media blanks and field blanks were also included.

Statistical analysis was performed in accordance with the rationale and protocol provided in the pilot project paper.[8] Linear regression is used to ascertain the extent of possible bias, but it is not used as a measure of accuracy. A robust measure of accuracy is obtained by comparing each XRF result with its corresponding ICP value and accepting or rejecting it based on a pre-determined cut-off (*e.g.* ±20%, ±25%, ±30%). This leads to an "error rate", and samplers can be ranked accordingly or classified according to specific acceptance criteria (*e.g.* 90%, 95%). This measure is conservative in that the uncertainty attached to the reference method (ICP) is included in the calculation. Although there does appear to be some log-normality associated with the data, no transformation was used in the development of linear correlations A few data points, where the XRF value had a difference of 31% or more from the ICP value, were removed from the regression as it was suspected that these points might cause the trendlines not to give the best estimate of bias. Since only points wildly deviant from the trendline were excluded, and, since the linear regression was not being used to test for accuracy, an outlier test was not considered necessary. These points were still included in the figured plots unless they represented very high values, in which case their inclusion would reduce the clarity of the plots by compression.

Results and discussion

During the course of this study a proficiency test program for metals on filters by XRF analysis was started by the HSL. These samples consisted of aerosol from various metal mixes created in a standardized chamber and deposited on filters. Results from our participation in this study were able to resolve several important questions. The program round consisted of a number of filters containing different elements, together with standards for calibration purposes. As the software generation installed in the portable unit under test cannot accommodate user calibration, these standards were analyzed and the results compared to their certified values. Examination of those results indicated a possible calibration bias for copper, but not for other elements, including lead. An approximately 10% calibration bias for copper was confirmed on evaluation of the proficiency samples, and this observation appears to be further confirmed by the field sample results in this study. No bias was observed with the proficiency test standards and samples for zinc and iron, and no bias was observed in our samples for those metals. No bias was observed for the proficiency test standards and samples for lead, but there appeared to be a small bias on analysis of the field samples from the bronze-casting facility, as described below.

The majority of samples collected in this study contained less than 100 μg lead. Field blank filters all registered below our pre-selected XRF reporting limit of 0.5 μg cm^{-2} for all metals tested. More sensitive analysis by ICP confirmed this observation. All of the sample filter results for lead based on the ICP analysis were above the values considered to be limits of detection for the XRF analysis found in the pilot study[8] (5 μg per filter for 25 mm filters, and 10 μg per filter for 37 mm filters), except in the case of one 25 mm open-face cassette result which was excluded from the statistical analysis. In the pilot study good results were obtained after culling samples with ICP values below the limit of detection values, even where these showed a signal for lead on the XRF analyzer. This raised the possibility that these values may be limits of quantitation for the XRF technique, rather than limits of detection. In this study, the presence of useable results near the limits of detection provides further confirmation that these may be limits of quantitation, but no conclusion will be presented on this point until further data have been gathered. Zinc, copper and iron were also detected by the XRF analyzer and analyzed by ICP. Spearman's non-parametric rank correlations were highly significant ($p < 0.01$) between all the metals. Pearson's correlations were also significant ($p < 0.01$) between lead and each of the other elements. Results for the other metals varied from near the detection limit to approximately 700 μg zinc per filter, 250 μg copper per filter, and 200 μg iron per filter, varying somewhat according to sampler type. The geometric mean concentrations of metals found by each sampler type (ICP analysis), divided according to job type (metal pourer and shake-out operator) are given in Table 1. The particle size distributions of aerosol in metal pouring (metal in fume) and shake-out (metal associated with molding sand dust) ought to be rather different, but the general similarity between the concentration results for the different samplers indicates there might not be gross size-selective differences in sampler collection efficiency for the size ranges of these aerosols. The major difference is with zinc, the most volatile metal.

Table 1 Geometric mean concentrations of metals found by each sampler type (ICP analysis), divided according to job type. 90% of geometric standard deviations are between 2.05 and 4.96 (metal pourers) and between 1.74 and 7.76 (shake-out). There is no pattern to the standard deviations other than for copper in shake-out operations, where some considerably high values increase the standard deviations (range: 6.49–21.05). Only the difference in zinc concentrations between the job types is significant

	Metal pourer concentrations/μg m^{-3}				Shake-out concentrations/μg m^{-3}			
Sampler	Pb	Fe	Cu	Zn	Pb	Fe	Cu	Zn
CFC	68.4	78.7	108	461	41.5	62.2	105	132
GSP	63.0	86.9	117	406	44.1	69.4	83.4	158
25 mm	65.5	79.2	111	442	43.3	73.2	132	123
Button	58.8	73.3	124	365	42.1	71.1	149	122
IOM	49.9	63.2	86.4	334	50.3	101	154	170

The values for the mass of lead collected by each sampler appeared to be relatively evenly spread over the range, and so linear regression for a comparison of XRF and ICP analysis to detect any systematic bias was performed on the untransformed data. The trendlines were forced through the origin. Data points representing outliers, that is with XRF values >31% different from ICP values (2 GSP, 6 CFC (NIOSH), 2 CFC (OSHA), 1 IOM, 3 Button and 4 25 mm open-face samples) were not included in the calculation of trendlines, but were included in the calculation of accuracy. Minus the outliers noted above, all five samplers gave very good correlations (r^2 = 0.92–0.99) between the two analytical methods over the entire range of found lead mass, which encompassed the mass expected from 8 h time-weighted average samples at both the action level (30 μg m^{-3}) and the permissible exposure limit (50 μg m^{-3}) enforced in the USA by the OSHA. However, the slopes of the linear regression lines did not always fall close to the 1 : 1 value expected for an unbiased method. In particular, the average value of three readings from the GSP sampler, and the single readings from the IOM sampler, the Button sampler, and the 25 mm filter cassette all needed a positive correction to the XRF results in order to minimize the overall mean differences between the two analytical methods. However, correcting the data in this way did not greatly affect the number of results where the XRF value fell within ±25% of the corresponding ICP value. Data points in the figures have not been corrected for bias. There was no trend of increasing or decreasing accuracy with increasing lead values, and no trend of diminishing XRF response with increasing lead values in any of these results.

GSP

The single reading from the center of the GSP filters correlates remarkably well with the ICP results. However, using an average of three readings across the filter gives results with an approximately 10% negative bias. Both data sets are plotted in Fig. 1. The difference in the slopes indicates an uneven distribution of lead across the filter, with a larger proportion on the center. This is confirmed by careful visual observation of the samples, and overestimation of other metals such as zinc occurs if the central reading only is used. Therefore, it may be considered that the average results are a more accurate reflection of the true measurement, and this is evidence for an approximately 10% negative bias in the XRF analysis. The GSP sampler filter analyses met the criterion of XRF value within ±25% of the ICP value in 93.5% of the samples when using either the middle reading only or the average of all three readings, and also met this criterion in 90.3% of the samples using the OSHA algorithm, all without needing further correction. Correcting the averaged results for a 10% bias actually lowered the number of samples meeting the 25% criterion to 90.0%.

CFC

The CFC is known to have an uneven dust deposition and attempts have been made to account for this in methods published by NIOSH and OSHA. The different algorithms developed by these agencies were applied to the results from this study and may be compared graphically in Fig. 2. The NIOSH algorithm is seen to have a positive bias, in line with previous studies.[8,18] The OSHA algorithm provides results closer to a 1 : 1 correlation. 87.1% of the 37 mm cassette XRF analyses were within 25% of the ICP analyses with the OSHA algorithm, but only 64.5% of samples met this criterion using the NIOSH algorithm.

IOM

There is an issue with the appropriate multiplier for the effective area of the IOM sampler. The deposit normally seen on the filter is a checkerboard pattern following the grid pattern of the filter support structure. Any estimate of the area from the diameter of this deposit is actually an overestimate, because of the absence of a deposit over the grid. However, if it is assumed that the XRF window samples a representative area of this pattern then the diameter of the grid area is probably an appropriate dimension. In a previous study, the diameter had been measured at 2.84 cm^2 and this became the default value for this study. However, using 2.84 cm^2 in this study created an excessive bias between the IOM XRF results and ICP results. Although the samples were consumed in the chemical analysis and so the sample deposit area could not be re-measured, samples collected from another workplace were available. When these additional samples were scrutinized closely, a less dense halo of deposit could be seen extending further out to give an area of 3.46 cm^2. This factor provides results that are much more consistent with other results in this study, and so has been used, although the variation in density of the deposit suggests the correct answer may be between the two values. Once this factor is used, the IOM XRF results are biased approximately 10% lower than the chemical analysis, in line with those from the single reading of the 25 mm open-face

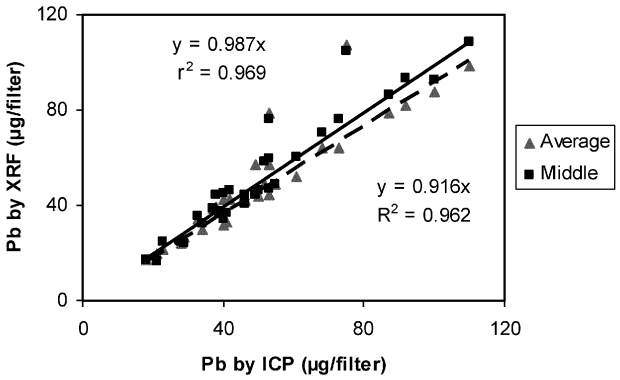

Fig. 1 Plot of XRF lead values *vs.* ICP lead values for GSP samples. Values for the central reading only (solid line) and for the average of readings at three positions (dashed line) are shown. Two outliers in the plot were not used in calculating the trendline.

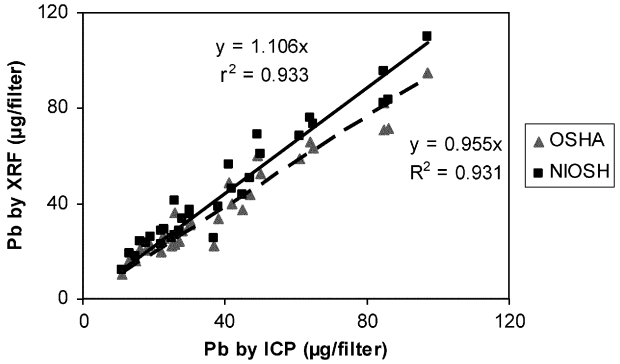

Fig. 2 Plot of XRF values *vs.* ICP lead values for CFC samples. Values calculated by the NIOSH 7702 (solid line) and OSHA OSA1 (dashed line) algorithms are shown. Six outliers in the plot for the NIOSH algorithm and two values in the plot for the OSHA algorithm were not used in calculating the trendlines.

filters, and the GSP 3-reading averages. These data are shown graphically in Fig. 3 for the 3.46 cm^2 area, without correction. 93.9% of the IOM sampler XRF results using a filter deposit area of 3.46 cm^2 were within 25% of the corresponding ICP results before correction, and this increased to 97.0% after correction. However, only 57.6% of results using the 2.84 cm^2 deposit area met the criterion before correction.

Button

The Button sampler results exhibit the largest negative bias (approx. 20%) between the XRF results and the ICP results for lead, significantly larger than either that of the IOM, the 25 mm open-face cassette, or the GSP average values. Thus it is possible that an additional factor is affecting the Button sampler results (see below). The Button sampler data is provided graphically in Fig. 4. The Button sampler analyses met the criterion of XRF results within 25% of ICP results in 90.0% of the samples both with and without correction for bias.

25 mm open-face filter

The single filter readings from this sampler, multiplied by the effective area of the filter from direct measurements of the deposit were used for the XRF values in Fig. 5, and the correlation with the ICP result is very good (minus the outliers noted above). However, there is a consistent negative bias of approximately 10%, in line with the GSP average filter results (above) and the IOM results (below). The 25 mm cassette analyses met the criterion of XRF results within 25% of ICP results in 86.7% of samples, with or without correction.

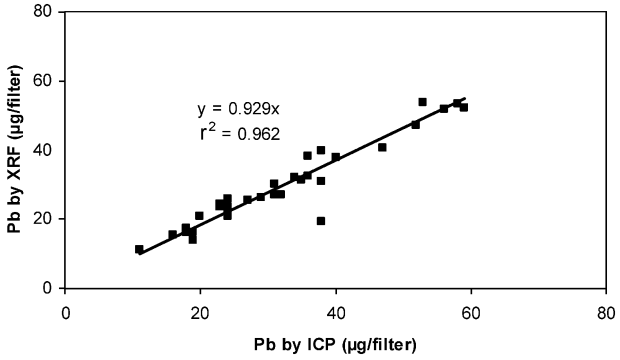

Fig. 3 Plot of XRF values *vs.* ICP lead values for IOM samples using 3.46 cm^2 as the nominal filter deposit area. One outlier in the plot was not used in calculating the trendline.

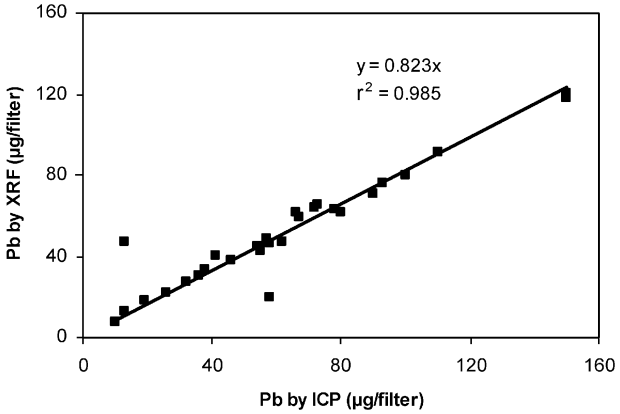

Fig. 4 Plot of XRF values *vs.* ICP lead values for Button samples. Three outliers in the plot were not used in calculating the trendline.

Interferences

There are two possible types of interferences. A commonly encountered interference is from the presence of atoms absorbing the fluorescent response from the atoms of interest. For example the Lβ emission line of lead is of high enough energy to excite Kα emissions from copper, iron and zinc, and therefore lead emission could be absorbed, and the signal reduced, by large quantities of these other elements. The internal calibration algorithm for the instrument under test is supposed to correct for the effects of other elements. Matrix effects can also result simply from the thickness of the sample causing excessive absorption or scatter of the X-ray beam, so that either not all atoms at depth are excited, or the emission from excited atoms at depth is absorbed or scattered before reaching the detector. In order to investigate the cause of noted interferences further, the Button sampler data was divided into the different work environments sampled. The ICP/XRF trendline slopes for lead did not differ between metal pourers and shake-out operators, even though metal pourers operate in an atmosphere containing substantially more of the most volatile element, zinc, than do the shake-out personnel (but approximately equal amounts of copper and iron). Therefore any possible interference cannot be from zinc as the very different concentrations of zinc in the two workplaces should have resulted in substantially different slopes in the lead results between the two work divisions. Of the other two metals suspected to be culprits, copper is the most likely. A negative bias for the analysis of copper was noted for proficiency and field samples. Because the copper presence is underestimated, the effect of copper on lead may not properly be taken into account by the instruments internal calibration algorithm. It is very possible that this effect is the cause of the 10% biases observed with the GSP average, the IOM and the 25 mm open-

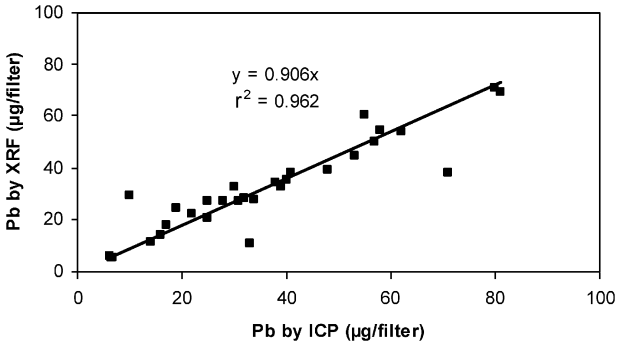

Fig. 5 Plot of XRF values *vs.* ICP lead values for 25 mm open-faced cassette samples. Four outliers in the plot were not used in calculating the trendline.

face cassette, although this should be proven by studies that are planned to take place in workplace with different ratios of lead and copper than those found here. However, there seems to be another factor affecting the Button sampler to cause the approximately 20% bias. Since the Button sampler combines the highest flow-rate and the smallest filter area to give the thickest sample per unit filter area, it is the sampler most prone to the matrix thickness effect. Therefore the bias in the Button sampler may be a result of a combination of elemental and matrix interferences. However, no trend of diminished lead response was observed with loading, which might be expected if thickness is the issue, and so this explanation may require data from other studies before confirmation.

Conclusions

The overall accuracy for the analysis of filter samples was reasonable in most cases and several samplers met a criterion of XRF value within ±25% of the ICP value in at least 90% of the samples over the range of concentrations encountered in this industry. Very little change in the percentage of results meeting the criterion was observed when the accuracy criterion was increased from ±25% to ±30%. Note that the variance of the ICP method has not been included, so that this is a conservative estimate of accuracy. The GSP sampler gave good results (90% or better within 25%) using an average of all three readings and the center reading only. As with the 25 mm samplers, fewer readings represent an advantage, since a 240 second nominal count reading can stretch out to many minutes as the sealed X-ray source decays over time. However, the excellent results for the central reading only may be fortuitous in that this might reflect the central region of the filter possibly having a greater relative proportion of the total filter deposit, compensating for any loss in lead response due to matrix effects. Thus the average reading actually may be the most accurate in the absence of matrix complications.

The standard US sampling method (CFC) using the NIOSH algorithm did not provide acceptable results, the XRF results being biased high, confirming the results of other studies.[8,18] It should be noted, however, that even in the original evaluation[19] used by NIOSH as the reference data for the method 7702, this algorithm was not thought to be the one of several considered that best fit the data, but, since it was based on geometric considerations and the inaccuracy involved was not considered excessive, it was the algorithm incorporated in the method. This is under review. The OSHA algorithm seems more applicable, and perhaps performance might have been even better had the OSHA procedure been carried out exactly, *i.e.* if the back-up pad had been included in the analysis, and this will be tested in a future study. In practice, it is advisable not to attempt to separate the filter and back-up pad. The pressure required during assembly to make an effective cassette seal tends to stick the outer edge of the filter to the pad, necessitating separation with a sharp knife using extraordinary care not to disturb the filter deposit. The central deposit often is so precariously balanced that just covering it with the Mylar film can disturb it.

Although correcting the IOM samples for bias gave the best results of all (within 25% for 97% of samples), there is some doubt as to which is the correct filter area to use. It is possible that this is a reflection of different particle sizes in different industries. A problem in defining the proper area of dust distribution would be a drawback to the use of this sampler for on-filter analysis. The Button sampler had the highest negative bias, and there currently is not a fully satisfactory explanation for this observation. A further drawback to the use of the Button sampler is the difficulty in pulling a flow-rate of 4 L min^{-1} through a 0.8 μm pore-size, 25 mm filter for extended periods of time in a dusty environment. Even with high-volume pumps from the same manufacturer, any sampling period greater than a few hours involved an excessive risk of pump failure.

All of these samplers are being used in similar studies in other workplaces where lead is encountered. It is highly likely that a definitive recommendation on sampler selection will be made at the conclusion of this work. The good results obtained in the HSL proficiency test program are an indication that portable XRF instruments can produce results equivalent to benchtop devices provided the most appropriate sampler is selected and matrix interferences are well-characterized. Analysis for all samplers was of the filter catch only and the extent of sample deposition on other parts of the sampler was not evaluated in this study. This issue will be addressed in future studies.

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