

# Portable XRF analysis of occupational air filter samples from different workplaces using different samplers: final results, summary and conclusions†

Martin Harper,<sup>a</sup> Bruce Pacolay,<sup>a</sup> Patrick Hintz,<sup>b</sup> David L. Bartley,<sup>c</sup>  
James E. Slaven<sup>d</sup> and Michael E. Andrew<sup>d</sup>

This paper concludes a five year program on research into the use of a portable X ray fluorescence (XRF) analyzer for analyzing lead in air sampling filters from different industrial environments, including mining, manufacturing and recycling. The results from four of these environments have already been reported. The results from two additional metal processes are presented here. At both of these sites, lead was a minor component of the total airborne metals and interferences from other elements were minimal. Nevertheless, only results from the three sites where lead was the most abundant metal were used in the overall calculation of method accuracy. The XRF analyzer was used to interrogate the filters, which were then subjected to acid digestion and analysis by inductively coupled plasma optical emission spectroscopy (ICP OES). The filter samples were collected using different filter holders or “samplers” where the size (diameter), depth and homogeneity of aerosol deposit varied from sampler to sampler. The aerosol collection efficiencies of the samplers were expected to differ, especially for larger particles. The distribution of particles once having entered the sampler was also expected to differ between samplers. Samplers were paired to allow the between sampler variability to be addressed, and, in some cases, internal sampler wall deposits were evaluated and compared to the filter catch. It was found, rather surprisingly, that analysis of the filter deposits (by ICP OES) of all the samplers gave equivalent results. It was also found that deposits on some of the sampler walls, which in some protocols are considered part of the sample, could be significant in comparison to the filter deposit. If it is concluded that wall deposits should be analyzed, then XRF analysis of the filter can only give a minimum estimate of the concentration. Techniques for the statistical analysis of field data were also developed as part of this program and have been reported elsewhere. The results, based on data from the three workplaces where lead was the major element present in the samples, are summarized here. A limit of detection and a limit of quantitation are provided. Analysis of some samples using a second analyzer with a different X ray source technology indicated reasonable agreement for some metals (but this was not evaluated for lead). Provided it is only necessary to analyze the filters, most personal samplers will provide acceptable results when used with portable XRF analysis for lead around applicable limit values.

---

<sup>a</sup> *Exposure Assessment Branch, Health Effects Laboratory Division, National Institute for Occupational Safety and Health, 1095 Willowdale Rd., MS 3030, Morgantown, WV 26505, USA*

<sup>b</sup> *Spokane Research Laboratory, National Institute for Occupational Safety and Health, 315 E. Montgomery Ave., Spokane, WA 99207, USA*

<sup>c</sup> *Guest Researcher, National Institute for Occupational Safety and Health, 4676 Columbia Parkway, Cincinnati, OH 45226, USA*

<sup>d</sup> *Biostatistics and Epidemiology Branch, Health Effects Laboratory Division, National Institute for Occupational Safety and Health, 1095 Willowdale Rd., MS 4020, Morgantown, WV 26505, USA*

† For the first three parts of the study see ref. 4, 5 and 6.

## Introduction

A useful goal of research into novel exposure measurement techniques is to develop methods that provide instantaneous feed back of results. This allows a clearer link to be made between changes in work process or practice, as well as faster interventions when exposures are deemed unacceptable. Where such direct reading instruments are not available, a secondary goal is to turn around the analytical results as quickly as possible. Portable X ray fluorescence (XRF) technology promises the possibility of analytical results within minutes of the end of sample collection. Bench top XRF analyzers have been used for determining lead on air filters for many years in the UK.<sup>1</sup> However, although there has been some effort in evaluating portable XRF methodologies from

the US National Institute for Occupational Safety and Health (NIOSH) and Occupational Safety and Health Administration (OSHA), these have not generally been considered sufficiently accurate by those agencies for use as anything other than screening tools, and there has been some question as to their ability to be used to support citations based on compliance with legally enforceable limit values.<sup>2,3</sup>

The objective of this study was to evaluate a portable XRF analyzer for airborne lead, and the study concentrated on one particular analyzer as representative. A secondary objective was to determine the appropriate sampler to use with portable XRF analysis. Airborne lead is collected on filters housed in filter holders or “samplers”. The filter is presented to the XRF analyzer. Different samplers produce different patterns of dust deposit on the filter. Two issues are of importance for surface analysis: spatial homogeneity and thickness. The optimum sample would be homogenous across the filter, with a precisely known outer boundary, and minimal thickness. When the sample is thick, the excitation X rays can be absorbed before reaching the element of concern, or the generated fluorescence X rays can be absorbed before reaching the detector. Given the lower energy of the fluorescence X rays, the latter is the greater concern. The most serious absorption, however, will occur when the fluorescence X rays can themselves excite other elements in the sample, and this is the case for the lead  $L\beta$  radiation, which is of high enough energy to excite other elements. The different samplers, therefore, were used to collect samples in different environments, which presented different mixtures of metals. Lead may be used in industrial processes or encountered as a by product. At a lead mine concentrator mill,<sup>4</sup> lead is found as the sulfide, in association with lesser amounts of iron and zinc. At a lead acid battery recycler,<sup>4</sup> lead was predominant, with much less antimony and tin. At a solder manufacturer,<sup>5</sup> only tin approached the airborne lead levels. At a bronze foundry,<sup>6</sup> copper, iron and zinc were present at concentrations approximately equal to, or greater than, the lead, and at a nickel chromium recycler plant (reported here), many other metals were present at levels equal to or greater than lead. Finally, at a primary copper smelter (also reported here), lead was only a minor component of the aerosol, which was dominated by copper and iron. To account for possible elemental interferences, factory calibration of the XRF analyzer uses a multi element inverse matrix. Since evaluation of lead analysis by portable XRF was the primary aim of this study, the analysis of other metals was secondary insofar as it might explain anomalies in the lead results. Throughout the study, XRF results were compared to inductively coupled plasma optical emission spectroscopy (ICP OES) measurements from the same samples after digestion of the filters.

The nickel chromium recycling facility for which data are reported in this manuscript operates a secondary submerged arc smelting furnace dedicated to recovery of nickel, chromium, and iron. The process starts by feeding waste solids, *via* a screw conveyor, to a pelletizing disk using either water or liquid wastes. Pellets are transferred to a rotary hearth furnace operating at 1260 °C (2300 °F) for the reduction of oxidized metal species to their metallic form. Reduced pellets are fed to the main furnace where they are smelted for extraction of

metal components. The molten metal is cast into approximately 24 pound (10 kg) “pigs” which are used for the manufacture of stainless steel. The process is recognized by the US Environmental Protection Agency as a best demonstrated available technology (BDAT) for metals reclamation of stainless steel waste and nickel cadmium batteries (cadmium is recovered in a separate distillation process). The original scope of the waste stream entering the facility has grown over the past 20 years and now includes, in addition to the above, metal bearing waste from nickel and chrome plating, nickel metal hydride batteries, waste magnesium, and spent nickel and chrome catalysts. About 60 000 tons of material annually are recovered that would otherwise be disposed of in a landfill. Areas sampled included around the thermal oxidizer, the blending conveyor belt, the pelletizing disk, the electric arc and rotary hearth furnaces (particularly around the feed areas), and in casting. These areas were selected to give a range of lead concentrations and do not represent personnel exposures. No personal samples were taken in this facility. By virtue of its volatility, zinc is one of the most abundant airborne metals, with levels approaching those of iron, the metal found in the highest concentrations. After these two metals likely comes chromium, but due to matrix dissolution problems, as described below, ICP OES analysis may have underestimated the total. Magnesium is next highest, along with likely similar concentrations of nickel and manganese, but again the ICP OES analysis of the latter metals is problematic. Cadmium and lead are present at roughly similar levels, about one sixth the concentrations of zinc and iron and about one half the likely concentrations of nickel and manganese. The sources of lead include the terminals of batteries and solder on printed circuit boards.

Data are also presented for samples from a copper smelter. The primary products are 99% pure copper cast anodes, which are eventually sold to a refinery for further processing, and sulfur dioxide gas, which is captured and processed at the company’s acid plant. The smelting process begins by loading a stock material containing a mixture of recycled, copper containing material from various sources together with mine ore concentrates into an Isa vessel at a rate of 100–110 tons per hour using a conveyor belt. The Isa vessel is a vertical heating chamber containing a gas lance which burns a mixture of natural gas, oxygen, and blast air to melt the stock material at 1200 °C (2200 °F). The molten stock material is then tapped from the bottom of the Isa vessel and poured into the main electric furnace. Here the stock material continues to be heated between 1200 °C and 1260 °C (2300 °F) until a separation of slag and matte occurs. The slag is tapped and discarded while the remaining matte is tapped and collected into large ladles which feed converters. Silica is added as a fluxing agent, and arsenic is added for refining purposes. Oxygen is injected from the bottom and the ensuing reaction further separates the molten charge material to purify the copper. The slag material from the converter contains between 5–50% copper, so it is returned to the main furnace to re enter the process. The smelter contains four converters, of which two to three are always operating while one is maintained on a regular rotating cycle. Air samples contain mostly copper with some iron and arsenic. Lead, zinc and molybdenum are present in the ore and

form minor components of the air samples. Again, no personal samples were taken in this facility. Samplers were located at various locations along the process, focusing on decks above the converters and the main furnace from which metal fume rises. Samplers were also placed in the matte tapping room which taps matte from the main furnace into the converter ladles and the upper deck where stock material is loaded into the Isa vessel.

The US OSHA enforces an airborne permissible exposure limit (PEL) of  $50 \mu\text{g m}^{-3}$  for personal samples and also an action level of  $30 \mu\text{g m}^{-3}$ , which requires employers to institute aspects of a lead control program. The US Mine Safety and Health Administration (MSHA) enforces an airborne PEL of  $150 \mu\text{g m}^{-3}$  for personal samples. Appropriate personal protective equipment may be used where concentrations are above these levels. When all six industrial locations are combined, we have concentration values extending from near the limit of detection to around  $5000 \mu\text{g m}^{-3}$ .

## Experimental

Samples were taken for approximately 4–6 hours. The samplers used in this study have been described extensively and include: the 37 mm styrene/acrylonitrile filter cassette (Omega Specialty Instruments, MA, (now SKC South, TX), USA), operated in the “closed face” mode and referred to as the CFC, the Institute of Occupational Medicine (IOM; SKC Ltd, UK) sampler, the German GSP (Gesamtstaubprobenahme; GSM NEUSS GmbH, Germany) or “cone” sampler, the Button sampler from the University of Cincinnati (SKC, Inc., PA, USA), and a 25 mm styrene/acrylonitrile filter cassette (Omega Specialty Instruments, MA, USA), operated in the “open face” mode. Samples collected from the nickel chromium recycler were: 44 GSP; 53 CFC (24 analyzed by XRF without their support pads as had been done in the past, and 29 analyzed with the support pad under the filter); 46 IOM; 43 Button; and 49 25 mm open face cassettes, for a total of 249. Samples collected from the copper smelter were 18 CFC; and 18 IOM. Mixed cellulose ester filters were used for all samples. After returning samples to the laboratory, wipe samples were taken from the interiors of the CFC and 25 mm open faced samplers from the nickel chromium recycler and from the interiors of the IOM and CFC samplers from the copper smelter. These wipes were submitted for analysis by ICP OES. A radioactive source XRF unit ( $^{109}\text{Cd}$  excitation source, main emission at 22.1 keV, Si PIN detector, Model XL701, THERMO NITON Corporation, Billerica, MA, USA) was used to analyze all samples as previously described.<sup>4–6</sup> The analytical window is a 2 cm  $\times$  4 cm rectangle. This instrument has been evaluated for precision of replicate analyses, and coefficients of variation are low and similar to those of the reference ICP OES analysis.<sup>7</sup> A second portable XRF instrument, which uses a different X ray generation technology was used to analyze samples from the nickel chromium recycler. The model XT 240 (Innov X Systems, Inc. Woburn, MA, USA) is a tube type energy dispersive instrument with a silver anode that can generate X rays in the energy range 10 to 35 keV. It is cradled in a bench top docking station. The 1.4 cm diameter circular probe window

( $1.54 \text{ cm}^2$  area) is flush with the upper stand in the docking station and also houses a Si PIN detector.

The analytical window for these analyzers is less than the deposit area for the filters in the samplers under test. In bench top instruments analytical windows may be large enough to cover the entire filter area, and samples may also be able to be rotated to account for non uniform deposition, but this feature is not available with the portable units. Two different algorithms have been used for combining three readings from different parts of the filters from CFC samplers.<sup>2,3</sup> These have been reviewed previously.

The OSHA method ascribes the difference to the fact that their protocol calls for the support pad to be included under the filter in the analysis. Although no proof was offered, the supposition could be reasonable as this would place the filter slightly closer to the analyzer. However, the thickness of the cardboard filter holders (see below) is not optimal for enclosing both the filter and support pad. In order to determine whether the presence of the back up pad really did affect the analysis of the CFC, two sets of CFC samples were taken at the nickel chromium recycler; one set was analyzed with the support pad in place and one set without.

The filters 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 are made of cardboard, with Mylar film over the filter area. For the THERMO NITON instrument, the cardboard holders were placed on the manufacturer's provided test stage, so that the filter holder could be placed under the analyzers X ray beam in appropriate positions. For the Innov X instrument, the samples in their Mylar holders were placed on top of the probe window at locations expected to duplicate the “top”, “center” and “bottom” positions of the filter as with the THERMO NITON holder. Data handling for the filters from the different samplers has been described previously.<sup>4–6</sup>

Both XRF analyzers report readings in  $\mu\text{g cm}^{-2}$ . For the Innov X tube type instrument, each individual reading involved collecting the fluorescence radiation for 240 seconds. For the THERMO NITON source instrument the analysis time is extended as the radiation source decays. Counts were recorded for 240 nominal seconds, the actual time taken being that for the number of decays equivalent to that occurring in 240 seconds when the source was initially calibrated. This time period is considered the best trade off between accuracy and speed of analysis. The THERMO NITON analyzer was set up in “thin film” mode. The internal calibration of both analyzers was checked with thin film standards from Micro matter Company (Deer Harbor, WA, USA) each day before sample filters were analyzed. Each Innov X reading was taken in triplicate and the average was used.

After XRF analysis, the samples (filters plus Mylar film) from the nickel chromium recycler were extracted by sonication with 50% nitric acid and analyzed by NIOSH Method 7300 (metals by ICP).<sup>8</sup> This concentration of acid normally is sufficient to dissolve lead unless particularly difficult species such as lead sulfate ( $\text{PbSO}_4$ ) or lead dioxide ( $\text{PbO}_2$ ) are present, and good results were achieved in the prior studies with this procedure. However, in this study it was noted that 50% nitric acid was not sufficient to dissolve several other

metals present in the nickel chromium recycler samples, and so following this experience the samples from the copper smelter were extracted with *aqua regia* on a hot block (95 °C). Note that neither procedure actually dissolves the Mylar film. Because of the large discrepancy noted between XRF analysis of chromium and the ICP OES results, four spare samples from the nickel chromium recycler, were analyzed using the THERMO NITON instrument but then submitted to neutron activation analysis (NAA) at a commercial facility (General Activation Analysis, Inc., Encinitas, CA, USA). The samples plus comparator standards were irradiated in a TRIGA Mark I nuclear reactor at a flux of  $1.8 \times 10^{12}$  neutrons  $\text{cm}^{-2} \text{s}^{-1}$ . The elements Cr, Fe, Mn and Ni produce the isotopes  $^{51}\text{Cr}$ ,  $^{59}\text{Fe}$ ,  $^{56}\text{Mn}$  and  $^{65}\text{Ni}$  ( $^{58}\text{Co}$ ) with half lives of 28 days, 45 days, 2.5 hours and 2.5 hours (71 days), respectively. Emissions from the irradiated samples were counted after decay periods of one hour, one day, one week and two weeks to obtain total mass results.

The interior surfaces of the CFC and 25 mm open face cassette samplers from the nickel chromium recycler and the CFC and IOM samplers from the copper smelter were wiped using a “ghost wipe” as described previously,<sup>4,6</sup> and the wipes were analyzed by ICP OES separately using the same digestion procedure as the respective filters.

Statistical analysis on the THERMO NITON XRF and ICP OES lead data for the nickel chromium recycler samples was performed in accordance with the rationale and protocol provided in the pilot project paper.<sup>9</sup> The robust measure of accuracy as described includes all data points. This method essentially compares each XRF value directly with its corresponding ICP OES reference value as to whether it meets or exceeds a pre determined measure of closeness to that value (e.g.  $\pm 20\%$ , 25% or 30%). The estimate is conservative in that the uncertainty in the reference method is not addressed. Samplers can be ranked in accordance with the percentage of values falling within the selected limit, and an acceptability criterion can be used (e.g. 90 or 95%) to classify samplers as appropriate for specific decision end points, such as compliance with limit values. However, alternative approaches are possible, once a larger data set is available. Two methodologies (known as the ISO GUM (Guide to Uncertainty in Measurement) approach and the Bootstrap approach) specific to this type of field evaluation of a non destructive method have been compared.<sup>10</sup> Data from some of the field studies in this program were used to evaluate differences between the two

approaches, and the results are summarized below. However, the data from the two studies reported here were not included in that analysis as noted below. The Innov X instrument was not evaluated for lead using these samples.

### Results from the nickel–chromium recycler

Most of the filter analyses (except from CFC samplers) for lead by ICP OES were above the values used in prior studies<sup>4–6</sup> to cull samples, *i.e.* 5  $\mu\text{g}$  per filter for 25 mm filters, 7  $\mu\text{g}$  per filter for the GSP sampler filters and 10  $\mu\text{g}$  per filter for the CFC sampler filters. Since the cull from the CFC samplers would have been excessive in this study, 7  $\mu\text{g}$  per filter was used for the CFC samples, otherwise filters below the values given above were excluded from the analysis. These values are under study as the limits of quantitation for the XRF technique, and this is discussed below.

Iron makes up the bulk of the metal recycled at this facility and so is present in the largest quantities on the filters. For the CFC samples, this represents iron concentration ranges of 47 to 1670  $\mu\text{g m}^{-3}$  (mean: 380  $\mu\text{g m}^{-3}$ , geometric mean: 300  $\mu\text{g m}^{-3}$ ). Zinc, being a very volatile metal, is also found at high concentrations, ranging from 52 to 4500  $\mu\text{g m}^{-3}$  (mean: 350  $\mu\text{g m}^{-3}$ , geometric mean: 190  $\mu\text{g m}^{-3}$ ). Several of the metals present at the next highest concentrations were not digested properly by the 50% nitric acid used, and so the ICP OES results are suspect. Chromium, nickel and manganese are in this group. Approximate arithmetic mean concentrations after adjustment for low ICP OES recovery are 230  $\mu\text{g m}^{-3}$ , 120  $\mu\text{g m}^{-3}$ , and 110  $\mu\text{g m}^{-3}$ , respectively. Magnesium is found at similar levels. Lead (9.9 to 450  $\mu\text{g m}^{-3}$ , mean: 54  $\mu\text{g m}^{-3}$ , geometric mean: 35  $\mu\text{g m}^{-3}$ ) and cadmium (16 to 420  $\mu\text{g m}^{-3}$ , mean: 64  $\mu\text{g m}^{-3}$ , geometric mean: 50  $\mu\text{g m}^{-3}$ ) are present in smaller quantities at approximately equal amounts. Concentrations of lead were relatively consistent from area to area within the facility, although, as might be expected, the casting area had generally the lowest results.

Nearly all of 18 field blanks (37 mm and 25 mm filters) were either non detectable for lead on ICP OES analysis, or slightly negative after subtraction of media blanks, with one single high value of 5.1  $\mu\text{g}$  per filter. All wipe sample field blanks were below the ICP OES limit of detection. These results are in line with our other studies. Table 1 includes the numbers of samples taken, and the numbers of samples used in the analysis after subtraction of low values, the loading range

**Table 1** Summary statistics for portable XRF analysis for lead in comparison to ICP OES for different samplers used in the nickel chromium recycler (filter catch only). (*N*) *N* is the total number of samples collected, *N* is the number of samples used in the analysis after removing low sample results as per the text

Sampler	(N) <i>N</i>	Loading range ( $\mu\text{g}$ per filter)	Algorithm	Accuracy		
				20%	25%	30%
CFC without pad	(24) 21	<7 160	NIOSH	42.9	57.1	61.9
GSP	(44) 44	<7 250	OSHA	81.0	90.5	90.5
			Average	72.7	86.4	93.2
			Middle	61.4	65.9	70.5
IOM	(46) 39	<5 110	3.46	87.2	94.9	94.9
			2.84	74.4	87.2	94.9
Button 25 mm	(43) 40	<5 170		92.5	92.5	92.5
	(49) 46	<5 150		89.1	93.5	95.7

**Table 2** Comparison of fractional bias estimates between CFC samples from the nickel chromium recycler with and without the support pad

Algorithm	No support pad	Support pad	<i>p</i> value <sup>a</sup>
	Mean (95% CI) ( <i>N</i> = 24)	Mean (95% CI) ( <i>N</i> = 29)	
NIOSH	0.129 ( 0.01, 0.267)	0.534 (0.412, 0.656)	< .0001
OSHA	0.023 ( 0.142, 0.097)	0.329 (0.223, 0.436)	< .0001

<sup>a</sup> *p* value of the difference between bias estimates is from *t* statistic for two independent samples.

for lead and the percentage numbers of samples whose XRF values fell within  $\pm 20\%$ , 25% or 30% of the corresponding ICP OES values. No sampler met the criterion of 95% of samples with XRF values within  $\pm 25\%$  of the ICP OES values, although there did not appear to be a specific bias in the regression analysis. For the CFC analyses, Table 2 shows that the confidence interval of the bias with support pad using either the NIOSH or OSHA algorithm did not include zero. The confidence intervals for the bias without support pad do include zero, and thus it can be concluded that the data without support pad are closer to the ICP OES reference. This is in agreement with the similar experiment at the lead acid battery recycler, although in that case, only the confidence interval for the OSHA algorithm without support pad included zero.

Wipe samples were taken from the interior of CFC and 25 mm open faced cassettes, but almost every value for lead was below the ICP OES reporting limit. As this may be a result of the generally low lead loadings, zinc data were examined as a surrogate. Detectable zinc was found on the interior surfaces of approximately 60% of the 25 mm open faced cassettes, but in less than 25% of the CFCs. In no case did the percentage of sample found in the cassette exceed 28% of the total sample (filter plus cassette). Iron was also examined and has a similar distribution for CFC samples: 40% with deposits, maximum 29%, but nearly all 25 mm open faced samplers had detectable iron in the wipes with a maximum 62% of total sample. These differences may indicate an association of these metals with particles of different sizes.

### Comparison of XRF analyzers with each other and with ICP-OES and NAA

As noted, while lead data did not appear to show any specific bias between XRF and ICP OES analysis, a rather extreme bias was noted for chromium, and possibly also for nickel and manganese. For example, XRF analyses of the 25 mm open face cassette filters were higher than ICP OES results by approximately 850% for Cr, 20% for Ni, and 60% for Mn.

Thus the two XRF instruments, the THERMO NITON and Innov X, were compared for these metals and summary data are presented in Table 3. For chromium, the tube type XRF results were very close to those from the sealed source XRF, suggesting the ICP OES analysis was biased low due to the extraction technique. For manganese and nickel, the differences between XRF and ICP OES are less pronounced, so there is less confidence that the extraction technique has resulted in a negative bias, but it is certainly suggestive. The NAA analyses in Table 4 showed plenty of scatter in comparison to the XRF data, but did not confirm the ICP OES analyses for chromium. NAA in this instance had some value in explaining the anomalies in the ICP/XRF results, but there is no published analytical method for air filters by NAA so that these results can not be considered as reference values. The cause of the ICP OES discrepancy is probably the strength of the acid digestion. Spinel are oxides of metals that are notoriously difficult to digest in acid, and these can be formed in the fume from metal combustion. For example, they are often found in welding fume.<sup>11</sup> A typical formula for a spinel from the environment of the nickel chromium recycler is  $(\text{Mg},\text{Mn})(\text{Cr(III)},\text{Al}_2)\text{O}_4$ , and it can be seen that the analysis of chromium would be severely compromised if this species is only sparingly soluble in 50% nitric acid.

### Results from the copper smelter

In the previous study at a bronze foundry, lead masses by XRF appeared to be lower than by ICP OES. Three other elements (Cu, Fe, Zn) were present at this site besides lead, at similar levels. It was postulated that copper might have affected the lead result according to the following sequence. If copper was being underestimated by the analyzer, then, since copper can absorb the emitted Pb L $\beta$  radiation, an underestimation of copper would lead to an underestimation of its effect on lead and, therefore, an underestimation of the lead. To study this possible effect further, samples were taken from the copper smelter, where concentration values were an order of magnitude or more above the lead. At this facility,

**Table 3** Correlation between two XRF instruments for measurement of Cr, Ni, and Mn on air filters. Sealed source instrument (THERMO NITON) plotted on the *x* axis and tube type (Innov X) instrument on the *y* axis. CFC filter data not shown as the algorithm for the sealed source instrument was not appropriate for the different analyzer geometry of the tube type instrument. GSP data not shown as intercepts for Cr and Mn were outside the normal range of  $-1.5$  to  $+1.5$   $\mu\text{g}$ , also likely a result of different analyzer geometry, combined with the inhomogeneity of the filter deposit

Sampler	Chromium		Nickel		Manganese	
	Slope	<i>r</i> <sup>2</sup>	Slope	<i>r</i> <sup>2</sup>	Slope	<i>r</i> <sup>2</sup>
Button	1.07	0.96	1.08	0.96	1.30	0.96
IOM	1.05	1.00	1.08	0.99	1.28	0.99
25 mm open faced	1.02	0.99	1.07	0.99	1.25	0.99

**Table 4** Comparison of sealed source XRF measurement of Cr, Ni, Fe and Mn on air filters ( $n = 4$ ) with neutron activation analysis of the same filters

	Low bias%	High bias%	Mean bias%
Chromium	27	44	9.5
Nickel	40	6.1	17
Manganese	23	32	13
Iron	28	50	12

copper and iron concentrations (by ICP OES analysis of CFC filters) could be found in excess of  $4000 \mu\text{g m}^{-3}$ , but were more commonly in the range  $100 - 500 \mu\text{g m}^{-3}$ , while lead typically was less than  $100 \mu\text{g m}^{-3}$ . Analysis of variance (ANOVA) and a non parametric test was carried out on the CFC and IOM samples from both the bronze foundry and the copper smelter to test whether there was a significant difference between (a) the copper results by XRF and ICP OES, and (b) the lead results by XRF and ICP OES, and finally to determine if the magnitude of the copper result had any effect on either of these differences. No significant effects were found, even after removal of outliers, and we conclude that there is no significant interference at either site.

The interior surfaces of both CFC and IOM samples were wiped and the wipes analyzed separately. Lead was not present in sufficient quantities to be quantifiable. An average of 25% (maximum 55%,  $n = 17$ ) of the total copper sample was found on the walls of CFC samplers, and 19% (max 38%,  $n = 18$ ) of the total copper sample was found on the walls of IOM samplers.

### Accuracy

The accuracy estimates in Table 5 were obtained using data from the three studies where lead was the dominant metal present in the analysis (lead ore processing mill, solder manufacturer and lead acid battery recycler). The three studies where lead was not the dominant metal (bronze foundry, nickel chromium recycler, copper smelter) were not included in the analysis. Two methods for determining the overall accuracy of the XRF analysis of filters were used. Accuracy was determined after correction for bias, and any method based on these results should include this bias correction to assure accuracy within the ranges given. The CFC correction however is insignificant and could be ignored. A full discussion of the statistical methods used to obtain these results has been published.<sup>11</sup>

**Table 5** Accuracy after bias correction of XRF Pb method for  $n$  data points between  $10 \mu\text{g}$  and  $300 \mu\text{g}$  in comparison to ICP OES method with assumed  $\text{RSD}_{\text{ref}} = 5\%$ . The ISO GUM approach to estimated uncertainty, reduced by observed outliers, is presented together with comparable bootstrap estimates. For complete explanation see ref. 10

Sampler	$N$	Bias	Outliers	ISO GUM		Bootstrap	
				$\hat{A}$	$A_{95\%}$	$\hat{A}$	$A_{95\%}$
GSP (ave.)	83	0.077	0	23.1%	27.4%	20.5%	25.1%
CFC (OSHA)	70	0.006	0	24.6%	29.8%	29.8%	31.8%
25 mm	57	0.062	1	26.0%	33.5%	33.1%	37.6%
Button	68	0.089	2	21.0%	30.1%	24.0%	26.5%
IOM	58	0.00	1	34.2%	44.0%	39.7%	43.3%

### Limit of detection and quantitation

The lowest sample ICP OES value detected by the sealed source XRF analyzer on a CFC filter was  $3.8 \mu\text{g}$ . This ICP OES value was given for two filters, and they were recorded by the THERMO NITON XRF analyzer as  $2.5 \mu\text{g}$  and  $3.3 \mu\text{g}$ . Values from  $1$  to  $3 \mu\text{g}$  were not detected. On 25 mm filters (IOM or 25 mm open face cassette), values of  $2 \mu\text{g}$  by ICP OES were detected about half of the time. Thus, a conservative limit of detection (LOD) is probably  $4 \mu\text{g}$ , and thus blank filters were generally recorded as “non detect” by the analyzer. Twenty eight data points falling between  $5$  and  $15 \mu\text{g}$  per CFC filter by ICP OES were used to develop a limit of quantitation (LOQ), in accordance with Appendix 1 in the ESI.† At the 90% confidence level, the LOQ is  $4.6 \mu\text{g}$  per filter. At the 95% confidence level the LOQ is  $12.3 \mu\text{g}$  per filter, which is less than one half the OSHA action level. However, even with triplicate filter measurements, the tube type instrument could not achieve these limits as it provided negative values for lead at low loadings. An LOD and LOQ were not calculated for the tube type instrument.

### Comparison of samplers with each other

One extremely surprising result of this study was the comparison of lead concentration results (by ICP OES analysis of the filters) between pairs of different samplers taken from the same location or person at the same time (some studies involved area sampling only, some personal sampling only, and some a mixture of both). A comparison of mean sampler ratios for all pairings is shown in Table 6. All 95% confidence intervals include a ratio of unity, so it is not possible to detect a difference between these samplers with the numbers of pairs listed. However, it is possible to consider the 95% confidence limits as upper limits on the possible differences between samplers, especially when the standard deviation is small (note the Button sampler is the source of the largest standard deviations). For example, the result expected from the published studies of sampler performance with coarse particles in the laboratory, or from most previously published field studies where coarse particles are observed, is an IOM/CFC ratio of 1.5 or higher. Clearly, this is not the case with these results. In particular, the similarity between the filter concentrations derived from the 51 pairs of IOM and CFC samplers is striking, and we believe it important to reproduce the figure published elsewhere<sup>12</sup> again here, as Fig. 1. It is tempting to suggest that it is the result of sampling aerosols with a size distribution with most mass contribution from particles smaller than about  $30 \mu\text{m}$ , where most samplers are expected to have similar results. However, the range of environments sampled within these six industries was large, and included processes such as crushing lead ore and waste batteries, and the handling of the crushed materials, where the presence of large particles is very likely. The observation of similar filter concentrations prompted us to examine the possibility of other deposits within the sampler, revealing that for some samplers, half of the aspiration could be on the filter and the other half on the interior sampler walls. This was recognized as being important during the development of the IOM sampler<sup>13</sup> and, therefore, protocols for the use of the IOM mandate inclusion

**Table 6** Comparison of concentration values between samplers located side by side (ICP OES analysis of lead in filters only). SD standard deviation of the mean sampler ratio, CI confidence interval

Sampler pairing	<i>n</i>	Mean sampler ratio	SD	Lower 95% CI	Upper 95% CI
Button/GSP	35	1.26	0.792	0.996	1.52
37 mm/Button	43	1.11	1.06	0.793	1.43
37 mm/25 mm	53	1.11	0.713	0.916	1.30
IOM/GSP	41	0.987	0.471	0.843	1.13
37 mm/GSP	45	1.09	0.608	0.915	1.27
IOM/Button	41	0.991	0.418	0.864	1.12
Button/25 mm	29	1.24	1.02	0.863	1.61
25 mm /GSP	37	1.04	0.435	0.896	1.18
IOM/25 mm	34	0.875	0.388	0.745	1.01
37 mm/IOM	51	0.984	0.378	0.880	1.09

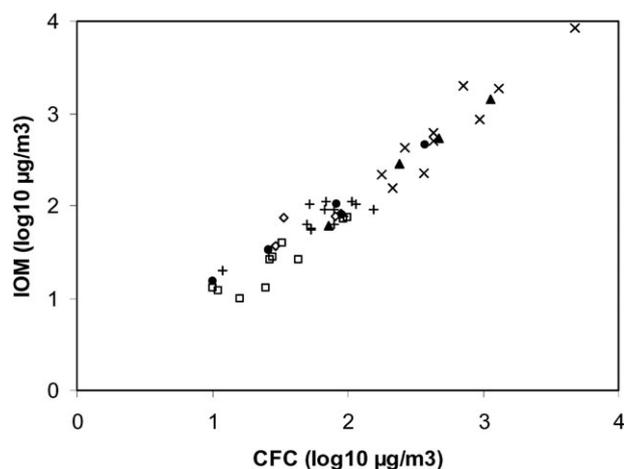
of the wall deposits as part of the sample. For the CFC, this observation had also been made previously by the US OSHA,<sup>14</sup> whose methods include the contribution of wall deposits in both gravimetric analyses, through the use of an internal capsule in the CFC, and analyses for metals by including a wipe of the CFC interior.<sup>12</sup> Unfortunately, this was not considered in almost all of the studies that were carried out comparing the CFC and IOM samplers, except for those carried out in France.<sup>15</sup> As a part of the program summarized here, the CFC and IOM sampler wall deposits were compared at the lead ore processing plant (for lead) and at the copper smelter (for copper). A different relative distribution between filter and wall deposits was observed when compared to results from the French studies, but this is not surprising as the two sites in our study probably represent a different size distribution of the aerosol (although it may also be due to a slight difference in the geometry of the IOM capsule).<sup>12</sup> The conclusion of these studies is that the aspiration efficiency of the two samplers (CFC and IOM) is not as different as previously supposed. However, the problem for the analysis of air samples by on filter XRF is that wall deposits cannot be accounted for, and so the result can only be a minimum estimate of the concentration, perhaps as little as 50% of the total sampler aspiration. Given that the

percentage of wall deposit varies considerably between samplers from even the same environment, it is impossible to account for the wall deposits by a correction factor.

## Study conclusions

Air samples have been collected in six workplaces where lead is encountered, selected to represent a range of different environments. In each case, the sample filters were analyzed using a non destructive, portable XRF analyzer, and then by acid digestion and ICP OES. Results from two sites are provided here, while results from the other four have been published previously. XRF results from the three facilities where lead was the major element present in the airborne dust have been combined and tested for accuracy against the corresponding ICP OES results. The CFC, GSP, Button and 25 mm open face samplers all gave results within 35% of the corresponding ICP OES values once corrected for bias in the XRF analysis. At the three facilities where lead was not the major element present, results were not quite as good, but this might be a result of increased variance in the reference method. For the sealed source XRF instrument and the CFC sampler, the limit of detection is 4 µg per filter and the LOQ (95% confidence limit) is 12.3 µg per filter. Insufficient low lead samples were available to calculate these figures of merit for the other samplers, but they are expected to be similar. All samplers had some bias, but in the case of the CFC it is included in the algorithm for calculating the lead mass, so that no further correction is necessary.

Samples had been collected side by side, and when the filter analyses were compared, there were no significant differences between them. This was a surprising result in view of published accounts of differences, particularly between the IOM and CFC samplers. However, protocols call for analysis of wall deposits for the IOM capsule, but not always for the CFC. When wall deposits were compared from samples at the lead mine and the copper smelter, they were found to be not significantly different, and of a magnitude that would account for at least some of the differences found in other studies. This confirms previously published observations. The presence of wall deposits in many samplers begs the question as to their inclusion as part of the sample. Further studies are taking place to determine the particle size of these deposits as an aid to understanding their significance. Obviously, if wall deposits must be included, XRF analysis, which can only be performed



**Fig. 1** Comparison of filter only analyses for lead (Pb) from side by side IOM and CFC samplers (*n* = 51;  $y = 1.02x$ ,  $r^2 = 0.93$ ). × ← lead acid battery recycler, ◇ bronze foundry, ▲ lead ore processing mill, + copper ore smelter, □ nickel chromium recycler, ● solder manufacturer. Also published in ref. 12.

on the filter, can only give a minimum estimate of the total lead in the sample.

The conclusions regarding portable XRF analysis may be summarized by sampler:

CFC—without support pad and using three readings combined according to the OSHA algorithm, results of the filter analysis meet accuracy requirements, and the limit of quantitation is below one-half of the OSHA action level. However, wall deposits are significant and are not included in the XRF analysis.

IOM—sample deposit is not sufficiently homogenous for this kind of on-filter analysis. Wall deposits, while less than with the CFC for similar environments of sampling, are still often significant and are not included in the XRF analysis.

GSP—results of the filter analysis using the average of three readings across the filter meet accuracy requirements after a small bias correction. Wall deposits have not traditionally been included with analysis of this sampler, although they were found to exist in the one study where they were examined. The fact that the GSP filter-only analyses were not significantly different from the filter-only analyses of the other samplers suggests that it might be necessary to account for wall deposits in this sampler too.

Button—results of the filter analysis with a single XRF reading met accuracy requirements once corrected for a large negative bias, which is probably a result of heavy filter loading. The filter loading causes a practical problem in that sampling times must be kept short (around 90 minutes maximum) in dusty areas to avoid pump shut-off. This sampler has no walls for sample to collect on. The fact that the filter-only analysis is not significantly different from other samplers with which it was paired suggests that the aspiration efficiency of this sampler is lower than the others. Under-sampling of very large particles compared to other samplers has been noted in some other studies, but this cannot be confirmed in this program.<sup>16</sup>

25 mm open-face cassette—results of the filter analysis with a single XRF reading met accuracy requirements after a small bias correction. However, wall deposits are very significant and, as noted, cannot easily be included in the XRF analysis.

The main conclusion of the study bears repeating. While most samplers (except the IOM) provided filter deposits that could be analyzed for lead acceptably by a portable XRF analyzer when lead was the dominant metal present, all samplers had a good probability of having wall deposits that cannot be analyzed by either portable or bench-top XRF analyzers. These wall deposits are often a significant part of the sample and there is no likelihood of correcting for their absence in the analysis. If these sampler wall deposits are considered part of the sample then direct on-filter analysis is not possible. The one sampler that is unlikely to have wall deposits, the Button sampler, had comparable filter deposits to the others, suggesting that it might be undersampling the atmosphere. The GSP sampler has been considered to meet the inhalable sampling convention without considering wall deposits. However, the results of this study suggest that this might not be the case.

## Disclaimer

The findings and conclusions in this report are those of the author(s) and do not necessarily represent the views of the National Institute for Occupational Safety and Health. The mention of any company names or products does not imply an endorsement by NIOSH or the Centers for Disease Control, and nor does it imply that alternative products are unavailable, or unable to be substituted after appropriate evaluation.

## Acknowledgements

Thanks to Yinghua Sun (NIOSH/HELD/BEB) for assistance with parts of the statistical analysis.

## References

- 1 Health and Safety Executive, *Methods for the Determination of Hazardous Substances, Lead and Inorganic Compounds of Lead in Air*, MDHS 7, HSE, London, 1987.
- 2 Method 7702: Lead by field portable XRF, National Institute for Occupational Safety and Health, in *NIOSH Manual of Analytical Methods*, ed. P. Eller, National Institute of Occupational Safety and Health, Cincinnati, OH, USA, publication 94-113, 4th edn, 1994 (supplement issued Jan. 15, 1998).
- 3 C. J. Elskamp, Method OSA1: Lead (Pb) in Workplace Air by NITON 700 Series Field Portable X-ray Fluorescence (XRF) Analyzer, *OSHA Manual of Analytical Methods*, Occupational Safety and Health Administration, OSHA Salt Lake Technical Center, Salt Lake City, UT, USA, April, 2003, <http://www.osha.gov/dts/sltc/methods/onsite/osa1/osa1.html>, accessed Feb. 29, 2004, but since withdrawn.
- 4 M. Harper, B. Pacolay, P. Hintz and M. E. Andrew, *J. Environ. Monit.*, 2006, **8**, 384-392.
- 5 M. Harper and B. Pacolay, *J. Environ. Monit.*, 2006, **8**, 140-146.
- 6 M. Harper, B. Pacolay and M. E. Andrew, *J. Environ. Monit.*, 2005, **7**, 592-597.
- 7 P. L. Drake, N. J. Lawryk, K. Ashley, A. L. Sussell, K. J. Hazlewood and R. Song, *J. Hazard. Mater.*, 2003, **102**, 29-38.
- 8 Method 7300 (Issue 2): Elements by ICP, in *NIOSH Manual of Analytical Methods*, ed. P. Eller, National Institute of Occupational Safety and Health, Cincinnati, OH, USA, publication 94-113, 4th edn, 1994.
- 9 M. Harper, T. S. Hallmark, M. E. Andrew and A. J. Bird, *J. Environ. Monit.*, 2004, **6**, 819-826.
- 10 D. L. Bartley, J. E. Slaven, M. C. Rose, M. E. Andrew and M. Harper, Uncertainty determination for non-destructive chemical analytical methods using field data and application to XRF analysis for lead, *J. Occup. Environ. Hyg.*, 2007, in press.
- 11 P. J. Hewitt and M. G. Madden, *Ann. Occup. Hyg.*, 1986, **30**, 427-434.
- 12 M. Harper and M. Demange, Concerning sampler wall deposits in the chemical analysis of airborne metals, *J. Occup. Environ. Hyg.*, 2007, **4**, D81-D86.
- 13 D. Mark, *Ann. Occup. Hyg.*, 1990, **34**, 281-291.
- 14 F. Stones, S. Edwards, D. Crane and G. Schultz, *The Deposition of Sample Analyte on Cassette Walls. Poster Presentation*, American Industrial Hygiene Conference & Exposition, Atlanta, GA, USA, 2004.
- 15 M. Demange, P. Görner, J.-M. Elcabache and R. Wrobel, *Appl. Occup. Environ. Hyg.*, 2002, **17**, 200-208.
- 16 M. Harper, M. Z. Akbar and M. E. Andrew, *J. Environ. Monit.*, 2004, **6**, 18-22.