A comparison of portable XRF and ICP-OES analysis for lead on air filter samples from a lead ore concentrator mill and a lead-acid battery recycler†

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Personal and area samples for airborne lead were taken at a lead mine concentrator mill, and at a lead-acid battery recycler. Lead is mined as its sulfidic ore, galena, which is often associated with zinc and silver. The ore typically is concentrated, and partially separated, on site by crushing and differential froth flotation of the ore minerals before being sent to a primary smelter. Besides lead, zinc and iron are also present in the airborne dusts, together with insignificant levels of copper and silver, and, in one area, manganese. The disposal of used lead-acid batteries presents environmental issues, and is also a waste of recoverable materials. Recycling operations allow for the recovery of lead, which can then be sold back to battery manufacturers to form a closed loop. At the recycling facility lead is the chief airborne metal, together with minor antimony and tin, but several other metals are generally present in much smaller quantities, including copper, chromium, manganese and cadmium. Samplers used in these studies included the closed-face 37 mm filter cassette (the current US standard method for lead sampling), 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. The filters were analyzed after sampling for their content of the various metals, particularly lead, that could be analyzed by the specific portable X-ray fluorescence (XRF) analyzer under study, and then were extracted with acid and analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES). 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. For lead at the mine concentrate mill, all five samplers gave good correlations ($r^2 > 0.96$) between the two analytical methods over the entire range of found lead mass, which encompassed the permissible exposure limit of 150 mg m^{-3} enforced in the USA by the Mine Safety and Health Administration (MSHA). Linear regression on the results from most samplers gave almost 1 : 1 correlations without additional correction, indicating an absence of matrix effects from the presence of iron and zinc in the samples. An approximately 10% negative bias was found for the slope of the Button sampler regression, in line with other studies, but it did not significantly affect the accuracy as all XRF results from this sampler were within 20% of the corresponding ICP values. As in previous studies, the best results were obtained with the GSP sampler using the average of three readings, with all XRF results within 20% of the corresponding ICP values and a slope close to 1 (0.99). Greater than 95% of XRF results were within 20% of the corresponding ICP values for the closed-face 37 mm cassette using the OSHA algorithm, and the IOM sampler using a sample area of 3.46 cm^2. As in previous studies, considerable material was found on the interior walls of all samplers that possess an internal surface for deposition, at approximately the same proportion for all samplers. At the lead-acid battery recycler all five samplers in their optimal configurations gave good correlations ($r^2 > 0.92$) between the two analytical methods over the entire range of found lead mass, which included the permissible exposure limit enforced in the USA by the Occupational Safety and Health Administration (OSHA). Linear regression on the results from most samplers gave almost 1 : 1 correlations (except for the Button sampler),

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indicating an absence of matrix effects from the presence of the smaller quantities of the other metals in the samples. A negative bias was found for the slope of the button sampler regression, in line with other studies. Even though very high concentrations of lead were encountered (up to almost 6 mg m^{-3}) no saturation of the detector was observed. Most samplers performed well, with >90% of XRF results within ±25% of the corresponding ICP results for the optimum configurations. The OSHA algorithm for the CFC worked best without including the back-up pad with the filter.

Introduction

This study is part of an ongoing investigation into the use of portable X-ray fluorescence (XRF) analyzers for on-site evaluation of airborne lead samples in the workplace. Portable XRF analyzers may have significant advantages over off-site laboratory analysis in terms of faster turn-around of results. The objective of this study is to examine an XRF analyzer for use with the samplers described below in accordance with published methods in specific field situations where lead is the contaminant of interest, in this case a mine concentrate mill and a lead-acid battery recycler. A pilot project in a small lead scrap smelter and wire-drawing operation has already been published,[1] and this paper may be referred to for a full discussion of lead health effects and generally applicable airborne limit values, as well as full description of the samplers used. Also published are the results of the first two investigations of this larger project, at a bronze foundry[2] and solder manufacturer,[3] and these two papers should be consulted for the rationale for methodological differences between the pilot study and this project. The principle difference between these latter two sites was in the presence of other metallic elements. At the bronze foundry, copper, iron and zinc were present at concentrations approximately equal to, or greater than, the lead. At the solder manufacturer only tin approached the airborne lead concentration levels. There was no effect of tin on the measurement of the lead Lβ fluorescence emission, since the emission energy is too low to enable absorption by tin atoms. However, copper, iron and zinc all have excitation energies lower than the lead emission energy so that absorption of the lead emission can occur within the sample, and a low bias was observed between XRF detection and chemical analysis for lead at the bronze foundry. It was difficult to discern which one of the elements present was more likely to be interfering than the others, since the concentration of all elements was strongly correlated.

In the lead–zinc–silver concentrator mill under study, the elemental mix is different again from the other studies. In this mine, the predominant ore-minerals are sulfidic: galena (PbS), sphalerite (ZnS), and pyrite (FeS_2), so that the air filters contain significant quantities of lead, zinc and iron. Silver does not form a discrete mineral, but is present in the galena to a percentage warranting its subsequent extraction. The minerals are present as partings and veinlets in the host quartzite. In the mine, the rock is loosened by blasting and then loaders and haul trucks transport the ore to points where it can be hoisted to the surface. The ore is first crushed in a manganese-steel crusher and milled in a large ball mill at a rate of approximately 416 tons per day (2003). The metallic minerals of interest, galena and sphalerite, are concentrated from the crushed ore by a process known as froth flotation. For froth flotation, the optimum grain size is usually between 400 and 65 Tyler mesh or between 37 and 210 μm physical diameter, which for galena (density = 7.5) equates to an aerodynamic diameter of 100 to 575 μm. The milled ore is fed into a series of cells and mixed with a solution of a chemical (*e.g.* xanthate) which causes mineral grains to adhere to bubbles formed when air is bubbled through the mix. Bubble stabilizers (*e.g.* methyl isobutyl carbinol), pH adjusters and salts which act to promote or depress the flotation of select minerals are also added. By adjusting the solution composition, air flow, and contact time, ore minerals can be effectively separated from each other and from the host rock. Mineral grains adhering to the bubble film are concentrated by skimming off the bubbles into a collector, but may also be flung into the air as the bubbles burst. Ore entering the first flotation circuit can contain as little as one-tenth of one percent mineral. Finally, the concentrates are dewatered and dried on air-supplied rotating fabric filter drums, scraped off and kept in a retaining area before being shipped off-site for smelting. The output from this process is a lead-rich concentrate and a zinc-rich concentrate; silver is concentrated along with the lead, and iron is removed with the gangue mineral. By the time the concentrate emerges from the final cell in flotation circuit, recoveries are approximately 94% silver, 94% lead and 76% zinc. Exposures to lead may occur in the crushing and milling areas, in the flotation area where employees are responsible for maintenance of the flotation cells and obtaining and analyzing samples for concentrate grading, and in the dock where dried concentrate is loaded into trucks for shipment to a smelter. It is known that in lead concentrate mills there is a risk to employees from lead exposure. Although the galena ore is sulfidic, and probably not entirely bioavailable,[4] raised blood lead levels had been noted in this facility in the past, and raised blood lead levels recently have been reported in connection with use of the cosmetic *kohl*, in which powdered galena can be up to half its weight.[5] The US Mine Safety and Health Administration (MSHA) enforces a Permissible Exposure Limit (PEL) for lead in air of 150 μg m^{-3}, adopted from the 1973 American Conference of Governmental Hygienists Threshold Limit Values (ACGIH®-TLV®'s), measured using the CFC sampler and ICP analysis.[6]

At the lead-acid battery recycler the process is fully enclosed and involves first offloading and classifying spent commercial and retail batteries at their raw material processing center (RMPC), where between 30 000 and 35 000 batteries are processed each day. The batteries are then crushed with drainage and recovery of acid followed by a grinding and plastic separation step. The plastic casings are recycled back to the manufacturers and the lead-containing portion of the batteries plus additional recyclable lead material from other sources are gathered in a rather dusty lead containment area, from where it is fed to an initial, coarse smelting step to cast large ingots called pigs. A secondary refining produces smaller billets, which are then melted once more in individual small furnaces where the lead can be further mixed with other metals to achieve a specific composition, for re-sale to battery manufacturers. It is estimated that greater than 95% of lead used in lead-acid batteries in the USA is recycled in this fashion. This facility is regulated by the US Occupational Safety and Health Administration (OSHA), which enforces an airborne Permissible Exposure Limit (PEL) of 50 μg m^{-3}, and which has also promulgated an Action Level of 30 μg m^{-3}, at which level employers are required to institute aspects of a lead control program. All workers at this facility wear personal protective equipment at all times on the shop floor, including powered high-efficiency particulate air filtering respirators. Other elements of the OSHA lead program are complied with, including regular biological monitoring.

Experimental

Mixed cellulose-ester filters were used for all samples. The samplers used in this study are: the 37 mm styrene/acrylonitrile filter cassette with a 4 mm entry inlet (CFC; Omega Specialty Instruments, MA, USA), which is the current US standard method for dust sampling when operated at 2 l min^{-1}; the Institute of Occupational Medicine (IOM; SKC Ltd., UK) sampler, which also operates at 2 l min^{-1}, and which is the only sampler designed specifically to meet the inhalable convention; the German GSP (Gesamtstaubprobenahme, Gesellschaft für Schadstoffmesstechnik GmbH, Germany) or "cone" sampler, which has a 9 mm conical entry inlet opening to a 37 mm filter and is operated at a flow rate of 3.5 l min^{-1}; the Button sampler from the University of Cincinnati (SKC, Inc., PA, USA) which has a porous hemispherical screen and which uses a 25 mm filter and is operated at 4 l min^{-1}; and a 25 mm version of the CFC (Omega Specialty Instruments, MA, USA), operated in the "open-face" mode at 2 l min^{-1}. These samplers have been described in detail previously.[1,2]

At the mine concentrate mill, air samples were collected from the crushing and milling area, the froth flotation area, and in the concentrate loading area. A few samples were taken as personal samples, but, due to the low numbers of employees, most were area samples. Personal samples were collected from workers engaged in both crushing the ore and loading the finished product, as well as from workers tending the froth flotation process. Area samples were taken from samplers mounted on tripods at a height of approximately 3–6 feet (1–2 m) or from convenient locations on equipment. In order to obtain results over as wide a range of sample loadings as possible, area samples were frequently collected from locations deliberately selected to incur large loadings. The range of concentrations indicated in the full set of results is, therefore, not representative of actual employee exposures. Samples were taken for approximately 4–6 hours. The numbers of samples from each sampler type collected were as follows: 26 GSP; 28 CFC; 22 IOM; 26 Button; 25 25 mm open-face cassettes.

Table 1 Locations of area and personal samples by sampler type in the lead-acid battery recycler (RMPC = raw material processing center)

Area sampled	37 mm	GSP	IOM	Button	25 mm
Casting	21	14	7	6	11
Refinery	27	2	16	15	10
Refinery/casting	5	3	2	6	2
Furnace	26	12	12	10	11
Crusher	6	1	2	3	1
Material transfer room	2	3	2	1	1
Containment	8	11	3	8	4
RMPC	4	1	3	0	5
Non-specific	0	0	1	2	1
Totals	99	47	48	51	46

At the lead-acid battery recycler, about half the samples were personal and half area. Personal samples were collected from 33 workers engaged in all parts of the process on one full shift and the first half of the following shift. Area samples were obtained from 13 specific locations throughout the process, and were selected based on proximity to worker exposures, expected filter loading, representative points along the process, and safety with respect to workers and the equipment. All samples, personal and area, were taken for approximately 4–6 hours, to control the loading on the filters, and the personnel and area locations were selected in order to obtain a variety of loading characteristics in terms of both element content and total filter mass loading. Personal sample results, therefore, were again not intended to be indicative of the range of full-shift exposures. The total number of samples collected was 291. The work areas from which these personal and area samples were collected are given in Table 1, showing that the area coverage was similar between sampler types (but doubled for the CFC for reasons noted below). The numbers of samples from each sampler type actually used in the analysis were as follows: 46 GSP; 99 CFC (49 analyzed with support pad, 50 analyzed without pad); 48 IOM; 50 button; 43 25 mm open-face cassettes.

The XRF analyzer used (^{109}Cd excitation source, Model XL701, NITON Corporation, Billerica, MA, USA) is the same as that used in the first parts of the current program of work,[2,3] and is considered by the manufacturer to be an improvement (see ref. 3 for details) over the otherwise essentially similar model previously evaluated for the method published as NIOSH NMAM number 7702,[7] and used in the pilot project for this study.[1] Note that method 7702 does not specify a particular make or model of analyzer should be used, but only one instrument was evaluated in the development of the method. Other instruments are under evaluation.

The analytical window for the XRF analyzer model under test is 2 cm × 1 cm. The method as written using the CFC and 37 mm filters requires taking three readings across the filter with the XRF detector, in order to account for non-uniform sample distribution, and then the three readings are combined according to a formula given in the method. The formula is based on field calibrations in different industries, and for the NIOSH method is:

$$2 \times \text{middle (center) reading} + 3.8 \times \text{top reading} + 3.8 \times \text{bottom reading}$$

A similar US Occupational Safety and Health Administration (OSHA) method[8] incorporates both the filter and the support pad in the XRF analysis and has a different algorithm, also developed from the analysis of field samples, which is:

$$1.75 \times \text{middle (center) reading} + 3.25 \times \text{top reading} + 3.25 \times \text{bottom reading}$$

(note: these numbers were rounded up when reported previously, the above values are those actually in the OSHA method and in use in these studies).

The XRF analyzer was set to report readings in μg cm^{-2}. For the CFC filters, the three readings across the filter were entered into a spreadsheet and the algorithms for the NIOSH and OSHA methods were used to determine the total mass of lead present on the filters. For the filters from the GSP samplers, three readings were taken according to the procedures for CFC filters, but the results were calculated using the unweighted average of all three readings, or the central reading only, adjusted for the ratio of the XRF reading in μg cm^{-2} to the nominal area of the filter covered by the sample deposit (7.5 cm^2). For samplers using 25 mm filters (Button and IOM), homogenous deposition was assumed and the results from analyzing the central portion only again were corrected by the ratio of the XRF reading in μg cm^{-2} to the nominal area of the filter covered by the dust deposit (3.46 cm^2 for the Button sampler, 3.46 or 2.84 cm^2 for the IOM, and 3.80 cm^2 for the 25 mm cassette). In previous studies,[1–3] there was more than one interpretation of the exact edge of the IOM filter deposit, so two values were used in this study and compared.

Filter support pads were not included in the analysis of CFC samplers from the mine concentrate mill, but were included in the analysis of half the CFC samplers from the battery recycler. The OSHA method ascribed the difference between their algorithm and that used by NIOSH to the fact that the OSHA protocol calls for the support pad to be included under the filter in the analysis. Although no proof is offered in the method, 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. Therefore, two sets of CFC samples were taken; one set was analyzed with the support pad and one set without. At the mine concentrate mill, after removing the filters, the interior of some of the GSP, IOM, CFC and 25 mm open-face sample cassettes were wiped with a new Ghost Wipe (Environmental Express, SC, USA), opened and folded a few times to make a very small square. The wipe was then folded again so as to make sure the exposed side was protected, placed in a plastic bag and sent for analysis. Field blank filter cassettes were also wiped in this manner. This procedure is rather tedious, and so was carried out on a little less than half the samples collected, and on none of the samples taken at the battery recycler.

The XRF analyzer's calibration was checked with thin film standards from Micromatter Company (Deer Harbor, WA), and results were within specified tolerances. All XRF measurements involved counts accumulated for 240 nominal seconds. This time-period is considered the best trade-off between accuracy and speed of analysis. The sample 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. The cardboard holders were placed on a test stage provided by NITON, so that the filter holder could be placed under the analyzer's X-ray beam. The samples were then extracted and analyzed by NIOSH Method 7300 (metals by ICP)[9] modified to 50% nitric acid extraction because of the Mylar film covering the filters. Certified reference filters were incorporated as quality checks. 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.[1] Some log-normality is associated with the data, but no transformation was used in the development of linear correlations. For some of the graphs presented in the figures, a few data points at high loadings were removed from the regression where it was considered that their presence might cause an undue influence to the trendline. This is appropriate since linear regression is used only to determine whether a systematic bias might exist between the XRF and the reference method, and it is not used as a measure of accuracy (uncertainty). The robust measure of accuracy which includes all data points, described in the pilot project paper[1] was used. This method essentially compares each XRF value directly with its corresponding ICP reference value as to whether it meets or exceeds a pre-determined measure of closeness to that value (*e.g.* ±20%, 25% or 30%). This estimate is conservative in that the uncertainty in the reference method is not addressed. Through this method, 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. As stated, no experimental data points are removed for the accuracy calculation.

Results from lead mine concentrate mill

Most of the filter results for lead based on the ICP analysis were above the limit of detection found in the pilot study for XRF analysis. In prior studies[1–3] good results were obtained after culling samples with ICP values for lead below 5 μg per filter for 25 mm filters, 7 μg per filter for the GSP sampler filters and 10 μg per filter for the CFC sampler filters. These values are under study as the limits of quantitation for the XRF technique and were also used to cull four results in this study. The results obtained in this study were rather evenly spread over the range from low to high, and so linear regression was performed on the data without transformation as shown in Fig. 1–5 of the supplementary data.† The percentage numbers of samples, whose XRF values fell within ±20%, 25% or 30% of the corresponding ICP values, also were recorded. Summary statistics are provided in Table 2.

Lead was the metal present in the largest quantities on the filters, followed by iron, and then zinc. For the CFC samples, this represents lead concentration ranges of 9.1 to 1150 μg m^{-3} (mean: 196 μg m^{-3}, geometric mean: 110 μg m^{-3}), iron concentration ranges of 7.7 to 734 μg m^{-3} (mean: 79 μg

Table 2 Summary statistics for sampler evaluation from the mine concentrate mill (filter catch only). For the linear regression 2 GSP high loading samples and one high loading 25 mm open-faced filter sample were removed from the regression, but these points were not removed from the accuracy calculation

Sampler	Algorithm	r^2	Slope	Accuracy 20%	Accuracy 25%	Accuracy 30%
GSP	Average	0.986	0.949	100	100	100
	Center	0.969	1.125	62.5	75.0	79.2
CFC	NIOSH	0.983	1.156	79.2	87.5	87.5
	OSHA	0.984	1.001	95.8	95.8	100
IOM	3.46	0.985	1.074	95.5	95.5	95.5
	2.84	0.985	0.881	86.4	86.4	90.9
Button		0.996	0.888	100	100	100
25 mm		0.993	0.983	92.0	96.0	96.0

m^{-3}, geometric mean: 46 μg m^{-3}), and zinc concentration ranges of 6.8 to 117 μg m^{-3} (mean: 42 μg m^{-3}, geometric mean: 33 μg m^{-3}). Manganese, copper and silver were found in much smaller quantities, being below detection limits for the ICP on many CFC filters. Maximum concentrations observed were 46 μg m^{-3} manganese, 15 μg m^{-3} copper and 8 μg m^{-3} silver. Other elements (*e.g.* Al, Mg) were also detectable, but were of no interest in this study. Field blanks of both 37 mm and 25 mm filters generally gave 50% non-detectable ICP results for lead, with the highest value being less than 3 μg filter^{-1}, in line with our other studies. Field blank filter cassettes wipes gave ICP results slightly higher than in our previous study (<7 μg wipe^{-1} compared to <2 μg wipe^{-1}) which may be attributable to the wipe procedure being employed in the field rather than back at the laboratory, or to not changing gloves between wipes (which practice was abandoned in the field as being too time-consuming). Filter samples below the limits of quantitation for lead included 1 GSP and 2 CFC, but none of the IOM, Button or 25 mm open-face cassette samples, resulting in usable sample numbers of 25 GSP, 26 CFC, 22 IOM, 26 Button and 25 25 mm open-face cassettes. As noted above, in order to obtain the most representative graphical correlations between the XRF values and the corresponding ICP analyses, a few results (2 GSP and one 25 mm open-faced cassette) whose very high values would still have skewed the trendlines have been removed from the graphs. However, both of these values were included in the calculation of accuracy. A summary of all statistics for bias and accuracy is given in Table 1. All trendlines were forced through the origin. The slopes showed little bias from unity compared to the negative bias seen with many of the corresponding graphs from the bronze foundry,[2] in line with the results from solder smelter study.[3] The one slope with a slight negative bias was the Button sampler, again in line with previous results, indicating the depth of deposit may be adding a matrix interference.

GSP

ICP values for lead generally ranged from below the limit of quantitation up to 410 μg filter^{-1} and all except the two highest values (700 and 950 μg filter^{-1}) are plotted in Fig. 1 of the ESI† against both the average of the three (top, bottom, and center) XRF readings and the central XRF reading only. For the average of all three readings the slope of the regression line was 0.95 with a correlation co-efficient of 0.99. All (100%) of the XRF results were within 20% of the corresponding ICP results. For the center reading only the slope of the regression line was 1.12 with a correlation coefficient of 0.97. However, the percentage of XRF results falling within ±20, 25 or 30% of the corresponding ICP results was less than ideal (*i.e.* 90 or 95%). As in the bronze foundry study, the center reading is biased higher than the average, indicating a slightly greater deposition towards the center of the filter. Wipe samples taken from the GSP samplers indicated a substantial deposition, up to 40% of the total aspiration into the sampler (mean 24%).

CFC

ICP values for lead ranged up to 450 μg filter^{-1} and are plotted in Fig. 2 of the ESI† against the results from the three (top, bottom and center) XRF readings processed through both the OSHA and NIOSH algorithms. For the OSHA algorithm the slope of the regression line was 1.00 with a correlation coefficient of 0.98. 100% of the XRF results were within ±30%, and 95.8% of XRF results were within ±25% and ±20% of the corresponding ICP results. For the NIOSH algorithm the slope of the regression line was 1.16 with a correlation coefficient of 0.98. The percentage of XRF results falling within ±20, 25 or 30% of the corresponding ICP results was less than ideal. Wipe samples taken from the CFC samplers indicated a substantial deposition, up to 35% of the total aspiration into the sampler (mean 19%).

IOM

ICP values for lead ranged up to 680 μg filter^{-1} and are plotted in Fig. 3 of the ESI.† The data are presented for both filter areas which have been proposed for this sampler. For the 3.46 cm^2 filter area that best fit the data from the bronze foundry and solder smelter studies[2,3] the slope of the regression line was 1.07 with a correlation co-efficient of 0.99. 95.5% of XRF results were within ±20% of the corresponding ICP results. For the 2.84 mm^2 filter area that was measured on samples from the bullet casting study,[1] and which best fit the data in that study, the slope of the regression line was 0.88 with a correlation co-efficient of 0.99. However, the percentage of XRF results falling within ±20, 25 or 30% of the corresponding ICP results was less than ideal. Wipe samples taken from the IOM samplers indicated a substantial deposition, up to 30% of the total aspiration into the sampler (mean 17%).

Button

ICP values for lead ranged up to 830 μg filter^{-1}, and the results are plotted in Fig. 4 of the ESI.† The slope of the regression line was 0.89 with a correlation coefficient of 1.00. Despite the negative bias in the slope 100% (all) of the XRF results were within ±20% of the corresponding ICP results. Wipe samples were not taken from the Button samplers.

25 mm open-face cassette

ICP values for lead generally ranged up to 350 μg filter^{-1} and are plotted in Fig. 5 of the ESI,† minus one very high value

(784 μg filter^{-1}). The slope of the regression line was 0.98 with a correlation co-efficient of 0.99. 96.0% of the XRF results were within ±25% and 92.0% of XRF results were within ±20% of the corresponding ICP results. Wipe samples taken from the 25 mm open-face samplers indicated a substantial deposition, up to 37% of the total aspiration into the sampler (mean 19%).

Results from the lead-acid battery recycler

None of the CFC samples was below the OSHA action limit concentration of 30 μg m^{-3}, and the highest concentration recorded was almost 6 mg m^{-3}, or almost 120 times the permissible exposure limit, so it is no surprise that all of the filter results for lead based on the ICP analysis were well above any values likely to be considered as the limit of detection for the XRF analysis technique. The results obtained in this study were again rather evenly spread over the range from low to high, and so linear regression was performed on the data without transformation as shown in Fig. 6–11 of the supplementary data.† The percentage numbers of samples, whose XRF values fell within ±20%, 25% or 30% of the corresponding ICP values, also were recorded. Summary statistics are provided in Table 2. Note that the results refer to the catch on the filters of the samplers only; no evaluation was made of deposition on internal surfaces of the samplers at this facility, even for the IOM sampler where this is traditionally defined as part of the sample.

Lead was by far the metal present in the largest quantities on the filters, followed by antimony (approximately 5% of the lead values), tin (approximately 2.5% of the lead values) and zinc (approximately 1% of the lead values). For the CFC samples, this represents concentration ranges of 109 to 5950 μg m^{-3} lead (mean: 1073 μg m^{-3}, geometric mean: 771 μg m^{-3}), concentration ranges of 5.7 to 301 μg m^{-3} antimony (mean: 47 μg m^{-3}, geometric mean: 34 μg m^{-3}), concentration ranges of non-detected to 180 μg m^{-3} tin (mean: 25 μg m^{-3}, geometric mean: 20 μg m^{-3}) and concentration ranges of 3.8 to 91 μg m^{-3} zinc (mean: 14 μg m^{-3}, geometric mean: 9.9 μg m^{-3}). Copper, magnesium, chromium, manganese, and cadmium were also present at low levels, being below detection limits for the ICP analysis on some CFC filters. Maximum concentrations on CFC samples were 121 μg m^{-3} copper, 101 μg m^{-3} magnesium, 15 μg m^{-3} chromium, 35 μg m^{-3} manganese and 6 μg m^{-3} cadmium. Iron could be present in large quantities (up to almost 800 μg m^{-3}), but was not detectable in many samples. Iron pyrite (FeS_2) in powdered form was sometimes shoveled into the smaller furnaces, and is probably the source of the iron. There was no difference between field blanks for 37 mm and 25 mm filters, and when combined (n = 33) gave a mean ICP result for lead of 3.6 μg filter^{-1}, with the highest value being 6.4 μg filter^{-1}. These values are higher than in previous studies, but, given the very high lead concentrations encountered in this facility it is not surprising to see a small increase in general background. As noted above, in order to obtain the most representative graphical correlations between the XRF values and the corresponding ICP analyses, a few results (2 GSP, 3 CFC (without pad), 1 CFC (with pad), 2 Button and 2 25 mm open-faced cassette), whose very high values would have skewed the trendlines, have been removed from the graphs. However, all of these values were included in the calculation of accuracy. A summary of all statistics for bias and accuracy is given in Table 3. All trendlines were forced through the origin. The slopes showed little bias from unity compared to the negative bias seen with many of the corresponding graphs from the bronze foundry,[2] in line with the results from solder smelter study.[3] The one slope with a slight negative bias was the button sampler, again in line with previous results, indicating the depth of deposit may be adding a matrix interference.

Table 3 Summary statistics for sampler evaluation from the lead-acid battery recycler. Two high samples removed from GSP, and 1 from 25 mm open-faced cassette, for regression analysis only

				Accuracy		
Sampler	Algorithm	r^2	Slope	20%	25%	30%
CFC without pad	NIOSH	0.953	1.178	60.0	72.0	82.0
	OSHA	0.953	1.022	88.0	88.0	94.0
CFC with pad	NIOSH	0.977	1.269	28.6	55.1	65.3
	OSHA	0.976	1.102	83.7	89.8	98.0
GSP	Average	0.926	0.904	80.0	93.3	97.8
	Middle	0.869	0.923	68.9	80.0	93.3
IOM	3.46	0.977	0.968	89.6	91.7	93.8
	2.84	0.977	0.795	25.0	62.5	83.3
Button		0.983	0.853	84.0	96.0	96.0
25 mm		0.985	0.929	93.0	95.3	95.3

GSP

ICP values for lead generally ranged from 180 μg filter^{-1} up to 980 μg filter^{-1} and all except two very high values (1800 and 2400 μg filter^{-1}) are plotted in Fig. 6 of the ESI† against both the average of the three (top, bottom, and center) XRF readings and the central XRF reading only. For the average of all three readings the slope of the regression line was 0.90 with a correlation co-efficient of 0.93. 97.8% of the XRF results were within ±30%, 93.3% were within ±25% and 80.0% were within ±20% of the corresponding ICP results. For the center reading only the slope of the regression line was 0.92 with a correlation coefficient of 0.87. 90% of the XRF results did not fall within either ±20 or 25% of the corresponding ICP results. However, 93.5% were within ±30%. As in the bronze foundry study,[2] the center reading is biased higher than the average, indicating a slightly greater deposition towards the center of the filter.

CFC without support pad

ICP values for lead ranged from 64 μg filter^{-1} up to 490 μg filter^{-1} and are plotted in Fig. 7 of the ESI† against the results from the three (top, bottom and center) XRF readings processed through both the OSHA and NIOSH algorithms. Three highly loaded samples (860, 1200 and 1300 μg filter^{-1}) are not included in the graph. For the OSHA algorithm the slope of the regression line was 1.14 with a correlation coefficient of 0.96. 93.9% of the XRF results were within ±30%, and 90.9% of XRF results were within ±25% and ±20% of the corresponding ICP results. For the NIOSH algorithm the slope of the regression line was 1.19 with a correlation coefficient of

Table 4 Comparison of bias estimates between samples with and without the support pad

Correction	No support Pad mean (95% CI) ($N = 33$)	Support pad Mean (95% CI) ($N = 42$)	P value[a]
NIOSH	0.143(0.085, 0.202)	0.258(0.221, 0.294)	0.0013
OSHA	−0.090(−0.060, 0.042)	0.091(0.059, 0.123)	0.0013

[a] P value from t statistic for two independent samples.

0.96. However, the XRF results did not meet the criteria of being within ±20, 25 or 30% of the corresponding ICP results 90% or more of the time. Table 4 provides a comparison of biased estimates between samples with and without the support pad for both OSHA and NIOSH algorithms. There is a significant difference in the XRF/ICP bias between samples analyzed with the support and those analyzed without, and the only situation where the bias estimate includes zero is the OSHA algorithm without the support pad.

CFC with support pad

ICP values for lead ranged from 43 µg filter^{-1} up to 810 µg filter^{-1} and are plotted in Fig. 8 of the ESI† against the results from the three (top, bottom and center) XRF readings processed through both the OSHA and NIOSH algorithms, with the exception of one high value of 1200 µg filter^{-1}. For the OSHA algorithm the slope of the regression line was 1.1 with a correlation coefficient of 0.98. 97.6% of the XRF results were within ±30%, and 90.5% of XRF results were within ± 5% and 85.7% were within ±20% of the corresponding ICP results. For the NIOSH algorithm the slope of the correlation was 1.26 with a correlation coefficient of 0.98. However, the XRF results did not meet the criteria of being within ±20, 25 or 30% of the corresponding ICP results 90% or more of the time. As noted above, the XRF/ICP bias estimate for these samples did not include zero, even using the OSHA algorithm.

IOM

ICP values for lead ranged from 35 µg filter^{-1} up to 1500 µg filter^{-1} and are plotted in Fig. 9 of the ESI.† All results are included. The data are presented for both filter areas which have been proposed for this sampler. For the 3.46 cm^2 filter area that best fit the data from the bronze foundry and solder smelter studies[2,3] the slope of the regression line was 0.97 with a correlation co-efficient of 0.98. 93.8% of XRF results were within ±30% of the corresponding ICP results, 91.7% of XRF results were within ±25% and 89.6 were within ±20% of the corresponding ICP results. For the 2.84 mm^2 filter area which best fit the samples from the bullet manufacturer pilot study,[1] and the solder study,[3] the slope of the regression line was 0.80 with a correlation co-efficient of 0.99. However, the XRF results did not meet the criteria of being within ±20, 25 or 30% of the corresponding ICP results 90% or more of the time.

Button

ICP values for lead generally ranged from 220 µg filter^{-1} up to 2400 µg filter^{-1}, and the results are plotted in Fig. 10 of the ESI,† minus one very heavily loaded sample (3600 µg filter^{-1}) and one likely outlier (2200 µg filter^{-1}). The slope of the regression line was 0.85 with a correlation coefficient of 0.98. Despite the negative bias in the slope 96% of the XRF results were within ±30 and 25%, and 86% within ±20%, of the corresponding ICP results.

25 mm open-face cassette

ICP values for lead generally ranged from 95 µg filter^{-1} up to 1700 µg filter^{-1} and are plotted in Fig. 11 of the ESI,† minus two very high values (2800 and 3100 µg filter^{-1}). The slope of the correlation was 0.93 with a correlation co-efficient of 0.99. Despite the slight negative bias in the slope 95.3% of the XRF results were within ±30 and 25%, and 93% within ±20%, of the corresponding ICP results.

Discussion

Sampler filter results with the XRF analyzer complement those of the previous two studies in this project. Correlations between XRF and ICP values close to 1:1 were obtained for most samplers and, in particular for the GSP and CFC (OSHA algorithm). XRF results obtained using the Button sampler in both the mine concentrate mill and the lead recycler were close to the corresponding ICP results despite the bias evident in the slopes of the correlation lines. Unfortunately, there were many occasions in which loading of the Button sampler caused pumps to fault as has been noted in previous studies.[2,3] Button samples could be taken only for about 90 minutes without serious risk of pump faults in the dusty atmospheres of the environments studied here. One possible solution is to use a larger nominal filter pore-diameter (*e.g.* 2.0 or 5.0 µm), or to use the pump at a lower flow-rate. It is possible that both options might not have a dramatic effect on the performance of the sampler. It is apparent that the effective filter loading area of the IOM sampler causes problems with on-filter analysis using this XRF analyzer. 3.46 cm^2 was the best estimate in the bronze foundry study, and for both these sites, while 2.80 cm^2 was the best estimate in the in the pilot study and at the solder smelter. This might be due to particle size differences, since the concentrate mill is likely to be characterized by larger particle sizes than the smelter environments, and the bronze foundry may be dominated by dust from the "shake-out" operation where contaminated sand molds are removed and the lead-acid battery recycler may be dominated by dust from the crushing process and the handling of crushed material. A further investigation will be made to characterize the particles in these workplaces. Larger XRF units, with windows that could include the whole filter would be preferable, but may not be portable.

Wall deposits were found in all samplers at the mine concentrate mill, with the relationship between filter concentration and wipe concentration being roughly the same for all samplers ($p = 0.57$). This is shown in Fig. 1 where the wall wipe results are graphed against the combined wall and filter results. The CFC and IOM wall losses are similar, and previous studies in similar industries have shown that adding CFC wall losses to the filter catch in side-by-side measurements with IOM samplers brings the CFC results close to the

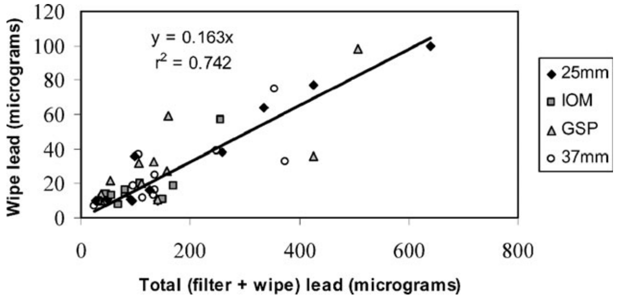

Fig. 1 Plot of ICP wipe results *vs.* ICP total (filter + wipe) results for those samplers from the mine concentrate mill where wall deposits were evaluated.

values from the corresponding IOM samplers (filter plus cassette walls).[10,11] However, it should be noted that in the previous study of the solder smelter,[3] a difference was observed between the CFC and 25 mm open-face cassette wall losses, while no difference is seen in this study. This might be attributable to difference in aerosol particle size distribution between sites, and this remains to be investigated. It is also possible that there may be a trend of increasing percentage wall loss with decreasing total catch, but it is not possible to distinguish this from an increase in overall variation with lower loading. The decision to include wall deposits as part of the CFC samples is arguable. Current NIOSH individual methods do not mention the possibility of wall deposits, or whether to include them, although the principle is discussed in the preamble chapter O (part 7) to the full Manual of Analytical Methods.[12] By using an internal capsule in the CFC, OSHA includes wall deposits in gravimetric analyses. Some, but not all, OSHA metals procedures call for an internal wipe that is digested with the filter (*e.g.* OSHA ID 125G for metals does, but ID 206 for beryllium does not).

The original evaluation of the IOM sampler for the inhalable convention included the wall deposits. However, there has been some recent evidence that the high wind-speed conditions required for testing samplers for conformance to the current version of the inhalable convention may not be applicable to the majority of workplaces,[13] and work has been published to show that the IOM sampler collects significantly more than the inhalable convention for low wind speeds,[14] so that a better match to the convention may be the filter-only result from the IOM sampler.[15] If wall deposits for the IOM and CFC are similar in magnitude when the samplers are used in these types of workplaces, and the total catches are similar according to the work of Demange *et al.*[10,11] then it stands to reason the filter catches are also likely to be of similar magnitude. This brings up the interesting possibility that the filter deposit of the CFC may itself be a reasonable estimate of inhalable particulate under calm air conditions, assuming the inhalable convention itself does not change for low wind speeds. Recent work suggests that an inhalable convention for calm air might indeed be different, but the difference may depend on the proportion of mouth to nose breathing.[16]

The essentially unbiased correlations in both of the studies reported here indicate the absence of interfering elements, providing further evidence that copper, rather than iron or zinc, was responsible for the biases observed in the bronze foundry study. A bias is observed with the Button sampler in both studies, and this has been noted previously and attributed to the larger dust loadings on this sampler. The lead-acid battery recycler had generally high concentrations and it is possible to see a bias, although smaller than that with the Button sampler, with both the GSP sampler (slope = 0.92) and the 25 mm open-face cassette (slope = 0.93) samples from this site. The GSP sampler and 25 mm open-face cassette have similar dust deposit thicknesses (GSP is approximately twice the flow-rate, while having approximately twice the filter area). However, correction for a possible similar bias in the IOM data would not account for the discrepancy in the best area estimate noted above.

Conclusions

In these two studies lead concentrations ranged from close to the detection limit of the XRF instrument to very high concentrations (up to almost 6 mg m^{-3}), and no saturation of the detector was observed. The overall accuracy for portable XRF analysis for some of the samplers over the range of workplace environments studied may be of the order required for regulatory compliance decisions, and when further results from other studies have been obtained a specific calculation of overall accuracy (uncertainty) will be made. The standard US sampling method (CFC) with the OSHA algorithm worked best without including the back-up pad with the filter, although the best results of all were obtained with the GSP sampler using an average of all three readings. The IOM sampler does not appear to have a sufficiently consistent sample deposit area for use with this method, and the combination of filter size and porosity and required flow-rate make the Button sampler impracticable for use in these dusty environments without some sort of change to the method protocol. All of these samplers are currently being used in a similar study at a specialty (Ni, Cr, Cd) recycling facility.

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.

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