

Immediate screening of lead exposure in the workplace using portable X-ray fluorescence

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ABSTRACT

The use of a portable X-ray fluorescence spectrometer (PXRF) equipped with a miniaturised X-ray tube producing a small 8 mm diameter X-ray beam required the validation of two new sampling protocols for the immediate screening of occupational lead exposure.

First, lead in dust and fumes, collected by Institute of Occupational Medicine (IOM) inhalable samplers on 25 mm diameter membrane filters, is quantified using PXRF. To account for irregular dust deposition, the filters are rotated manually by quarter turns. Multiple PXRF readings are collected from the central region and from two locations in the outer region. The inner region is distinguishable from the outer region, but the two outer region locations are indistinguishable.

High correlations ($R^2 > 0.99$) are found between the PXRF results and historical results obtained using a reference method based on a laboratory wavelength-dispersive sequential XRF instrument (WDXRF) for lead loadings between 1–161 μg . The PXRF results from the outer regions of the filters show a bias of –13% with respect to the WDXRF. Once this bias is allowed for, 95% of all PXRF results lie within –28% and +38% of the WDXRF results. Neither instrument accounts for potential dust accumulation on the walls of the IOM sampler. Therefore, methods based on their use can only be considered semi-quantitative.

Second, a protocol combining direct PXRF measurements on workplace surfaces with surface wipes is designed for immediate on-site quantification of removable surface lead residues. The quantification of such residues by this method is compared with subsequent off-site wet chemistry analysis of the surface wipes. The two methods show a good correlation ($R^2 \sim 0.88$). The ratio of the amount of removable residues determined by PXRF and wipe sampling is close to one with range 0.26–3.94.

It is demonstrated that PXRF can be used as an effective tool for the immediate screening of occupational lead exposure. Although this article focused on lead, PXRF can identify simultaneously a number of other metals.

KEYWORDS

Field instrument; in-situ measurements; lead poisoning; metals exposure; XRF spectroscopy; sampling methodology

Introduction

The evaluation of occupational exposure to inorganic lead and its systemic health effects have had renewed attention since its reclassification as a probable human carcinogen by the International Agency for Research on Cancer (IARC) in 2006.^[1] The European Union's Chemical Agents Directive 98/24/EC^[2] specifies the use of Biological Monitoring (BM) and blood sampling for the assessment of workers' lead exposure and takes into account all routes of lead exposure.^[3] Occupational Hygienist professionals routinely use air and surface sampling as it is complementary to BM when evaluating workers risk to lead exposure but has the advantage of being non-invasive

and able to confirm that the workplace is the origin of exposure. Usually, lead exposure is quantified at an off-site laboratory several days after sampling. The development of portable X-Ray Fluorescence (PXRF) instruments has made the immediate screening of exposure to lead, and other metals, in occupational settings^[4–11] (as well as in environmental settings^[12]) a possibility. PXRF could be used to support the Occupational Hygienists interventions in the workplace.

In summary, the lead content in airborne dust collected on membrane filters (method 1) and deposited on work surfaces (method 2) is quantified nondestructively using an energy dispersive Niton XL3t PXRF instrument

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equipped with 50 keV X-ray tube. This instrument uses Fundamental Parameter (FP) analysis combined with a thin film application that directly provide lead results in mass per surface area ($\mu\text{g cm}^{-2}$) and as such does not require empirical calibration using matrix matched standards.

Airborne lead dust

In the UK, the Occupational Exposure Limit (OEL) for lead of $0.15 \text{ mg}\cdot\text{m}^{-3}$ for an 8-hr time weighted average was stipulated in Directive 98/24/EC^[2] and is implemented in the UK via the Control of Lead At Work regulations (CLAW).^[13] CLAW defines “significant exposure” to lead as inhalation that is greater than half of the OEL. The Health and Safety Executive (HSE) publication MDHS 14/4^[14] describes the general method for sampling and gravimetric analysis of aerosols. It presents examples of personal samplers for inhalable dust. The inhalable dust fraction is biologically available for both ingestion and deposition in the respiratory tract. It is that fraction that should be measured when investigating workers exposure to lead. To quantify the amount of inhalable lead, elemental chemical analysis is often used. The filters are first treated with acids to digest the lead particles present, and lead in solution is typically analyzed by inductively coupled plasma—atomic emission spectroscopy (ICP-AES).^[15] Alternatively, rapid elemental analysis can be undertaken nondestructively using X-ray fluorescence (XRF) spectrometry.^[16] Hence, it is conceivable that immediate actions to reduce exposure in the workplace may be taken using on-site PXRF measurements.

Dust collected on a membrane filter is likely to fulfill the requirements of a thin film sample, the ideal experimental condition for the quantification of elements by XRF. Unfortunately, a significant amount of dust can potentially accumulate on the internal surfaces of some of the inhalable samplers commonly used such as the Institute of Occupational Medicine (IOM) sampler^[17] that cannot be analysed directly by XRF methods. Harper et al.^[10] reported wall losses of up to 30% for air samples collected at lead-based metal manufacturing and recycling sites. If wall deposits are not taken into consideration, then the XRF results are biased and XRF can only be considered as a screening tool.

The quantification of lead dust sampled on membrane filters by XRF ideally requires the whole deposit to be exposed to the X-ray beam as it may not be uniform. A filter can be rotated under the X-ray beam to average out any non-uniformity, and to a lesser extent, to limit orientation effects on the fluorescence signal. When the X-ray beam diameter is smaller than the active area of

the filter then only a portion of the dust can be interrogated at once. For the XRF readings from that portion of the filter to be representative of the entire dust deposition, the dust must therefore be uniformly distributed over the filter. If it is not the case, then multiple readings from different parts of the active area of the filter need to be combined to obtain a representative result. NIOSH has developed a method (Method 7702^[11]) for the quantification of lead dust collected using closed-faced 37 mm filter cassette. It requires recording XRF measurements at the centre, top and bottom of the filters and combines the readings giving a greater weight to the two off-centre measurements. In the UK, the IOM sampler has been preferred to the closed-faced 37 mm filter cassettes as it has been shown to give the best agreement with the inhalable convention under the widest range of workplace conditions.^[18,19] It is reasonable to expect that the dust deposition on a 37 mm filter collected using the closed-faced cassette will differ from that of an IOM sampler. In IOM samplers, dust deposits unevenly over an active area about 19 mm in diameter and possesses a characteristic pattern mimicking that of the underlying grid filter support.^[20] For that reason, the NIOSH method is unlikely to be applicable and a specific method for the rapid evaluation of the amount of lead dust collected on 25-mm filters mounted in IOM samplers is proposed. The PXRF instrument tested here is equipped with a fixed 8-mm diameter X-ray beam and a fixed sampling stage and thus is unable to sample the entirety of the 19-mm diameter active area of each filter simultaneously. Therefore, a sampling strategy based on multiple readings recorded from different regions of the active area of the filter was developed in order to obtain results representative of the overall dust loading. These results were then compared with results previously recorded using a laboratory-based Philips PW 1480 wavelength-dispersive sequential XRF instrument (WDXRF) that possessed a X-ray beam that illuminated all of the active area of the filters and equipped with the ability to rotate the filters under this beam.

Lead dust on work surfaces

One approach to evaluate the risk from lead ingestion through hand-to-mouth contacts and potential skin absorption in the workplace is through wipe sampling.^[21] In this article, work surfaces rather than workers skin were sampled and the wipes later analysed by ICP-AES. The American Society for Testing and Materials (ASTM) standard ASTM E1792^[22] specifies the type of wipes to be used on surfaces and stipulates that a minimum collection efficiency of at least 75% is required when wiping a smooth test surface (vinyl tile). Such high collection

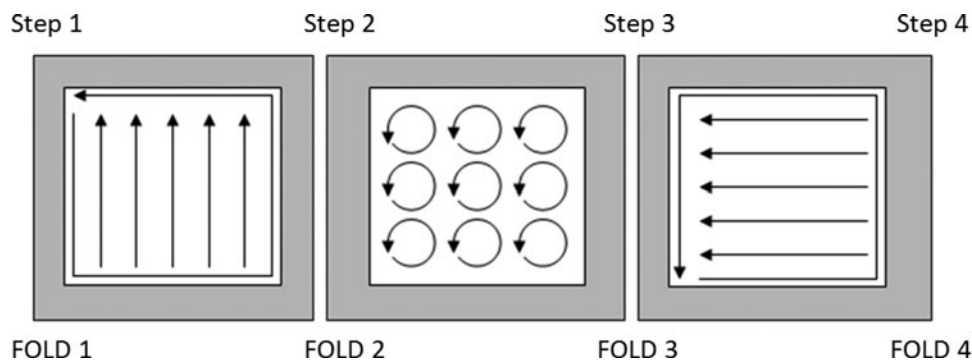


Figure 1. Wiping pattern within a 10 cm by 10 cm template.

efficiency is unlikely to be achieved when wiping rough surfaces such as carpets or concrete (see Chavalitnitikul et al.^[21] and Dost^[7] for examples). The corresponding method ASTM E1728^[23] describes how to wipe work surfaces. It specifies that a moistened wipe material that does not contain the compound of interest at levels exceeding the analytical technique's limit of detection (LOD), should be used to wipe the test surfaces. The test surfaces should be wiped twice following an overlapping "S" pattern followed by a third time concentrating on the edges of the template. An alternative wiping pattern was developed by Wheeler and Stancliffe⁽²⁴⁾ and is reproduced in Figure 1. It is composed of four main steps and makes three passes over the target surface, folding in half the wipe used at each step. The wiping area is defined using a disposable paper template 10 cm by 10 cm in size.

Dost^[7] proposed a method for the direct evaluation of removable lead residues from smooth and hard surfaces combining wipe sampling and PXRF. He used a radioisotope based PXRF spectrometer (Spectrace 9000 instrument) having an X-ray beam diameter of about 22 mm. Single PXRF readings were recorded before and after wiping a work surface by repositioning the instrument on the exact same spot using a template. This provided nondestructive, in-situ, and immediate direct readings of total (before wiping) and removable (difference between before and after wiping) lead residues present on that surface. This method was not thought to be compatible with the use of a PXRF instrument having only an 8-mm X-ray beam diameter.

Here, a new sampling protocol combining direct PXRF surface measurements with surface wipes was developed to take into consideration the small beam size of the instrument and to limit the influence of nonuniform dust depositions, background lead levels, and surface roughness on the direct PXRF readings. The roughness of each targeted surface was measured before sampling. This was to identify surfaces for which wipe sampling might be expected to be inefficient. Multiple direct PXRF readings on each targeted surfaces are required before and after

wiping to limit the dependence of the results on dust uniformity. To validate the PXRF sampling protocol, the wipes collected on-site were subsequently analysed using a laboratory-based reference ICP-AES method. Once validated, the protocol does not require the analysis of the surface wipes other than to confirm the PXRF results. The new protocol was tested over a wide range of surface substrates at six workplaces that generated lead dust from a wide range of processes. The details of the sampling protocol are presented together with the level of agreement between the removable lead residues obtained by direct PXRF surface readings and laboratory analysis following wipe sampling.

Instrumentation and method

The energy dispersive Niton XL3t PXRF instrument has an 8-mm diameter X-ray beam generated by bombarding electrons onto a gold anode target. The instrument sensitivity to the lead L_{β} fluorescent line located between 12.4 and 12.8 keV was maximised using a maximum tube setting of 40 kV and a copper-rich beam filter.

Lead in dust deposited on surfaces is quantified by FP analysis using a "Standard Thin Film" software application loaded on the PXRF instrument.^[25] There is no need for empirical calibration where a set of known calibration standards are produced covering the full range of concentrations expected for the elements of interest and having the same matrix composition as the samples to analyze. It requires only the use of generic standards to validate the instrument factory calibration.

A thin dust deposit on an impermeable membrane filter invisible to X-rays is an ideal thin film sample whereas a thin dust deposit on a workplace surface is not. It becomes a multi-layered sample having an infinitely thick substrate that might contribute to the overall fluorescent signal and hence affect the quantification of lead. This situation can be further complicated by the dust deposit characteristics: excessive dust loadings (no more

Table 1. PXRF calibration checks and analytical performance for lead quantification on membrane filters (n = 35, except for repeatability where n = 12).

Micromatter Standard ID	Certified loading ($\mu\text{g cm}^{-2}$)	Mean Measured Loading ($\mu\text{g cm}^{-2}$)	Bias (%)	Precision (%)	Analytical Uncertainty (%)	Repeatability (%)
31080	16.40 \pm 0.8	16.7	1.7	3.3	3.7	3.9
31081	50.10 \pm 2.5	56	11.7	1.7	11.8	1.9
31082	251 \pm 12.6	274.5	9.6	1.4	9.7	0.8

than 500 μg of lead dust should be collected on a 25-mm diameter filter^[14]), inhomogeneous depositions, or large differences in particle sizes. There is no practical way to directly evaluate or correct for all those effects. However, one can compare the XRF results with the results of an accepted standard technique free of such limitations.

PXRF lead dust quantification performance

All PXRF measurements were recorded using a 40 sec exposure time. The PXRF's limit of detection (LOD) for lead is 0.43 μg and the limit of quantification (LOQ) is 1.42 μg when using an active filter area of 2.84 cm^2 . The OEL for lead is calculated at 72 μg per filter assuming a nominal flow rate of 2 L min^{-1} and a 4-hr sampling period (half a typical 8-hr work shift). The LOD and LOQ values are dependent on X-ray exposure time, dust and substrate compositions. Therefore, the above only provides an estimation of the actual LOD and LOQ for direct readings on surfaces.

Calibration checks were performed using three lead MicromatterTM (Vancouver, Canada) standards (see Table 1) prepared by condensation of vaporised metal under vacuum on a NucleoporeTM polycarbonate aerosol membrane. This produces highly uniform thin film deposits for which lead loadings are certified by gravimetry to $\pm 5\%$.

The standards were directly positioned on a test stand immediately above the PXRF sampling window. The bias, precision, and overall analytical uncertainty were calculated using 35 separate measurements conducted over different days. The repeatability was also determined by recording 12 consecutive measurements on each standard on the same day.

Methodology for the quantification of lead on filters

Worker exposure to airborne lead dust was investigated at seven different sites between 2002 and 2009 using IOM personal samplers. The workplaces included crystal glass manufacturers, foundry and metal manufacturers, car and car part manufacturers, and a lead acid battery recycling site. Membrane filters of mixed cellulose

esters were collected during crystal glass mix preparation, crystal melting in a furnace, crystal blowing, crystal carving, cutting and polishing, lead soldering, lead ingot melting, lead casting, lead sheet cutting and rolling, and lead acid battery break-up. The characteristics of the dusts collected cover a wide range of loadings, particle size distributions, and elemental compositions that provided a good test of the capability of the PXRF instrument.

A steel template with an aluminium screw-fit sample cup was placed on a test stand to ensure consistent positioning of the sample filters above the instrument X-ray beam. Each filter was kept flat sandwiched between two 150- μm thick molybdenum masks, themselves screwed inside the aluminium sample cup with the dust layer on the top, and the back of the filter facing the X-ray beam. The filter in the screw-fit cup sat approximately 1 mm above the test stand surface. This 1 mm upward shift caused an estimated 15.4% ($\pm 2\%$) attenuation of the lead fluorescent signal that was corrected for in all results reported including Table 1.

The dust deposition on each filter formed a pattern with a 4-fold symmetry mimicking the areas shielded by the IOM grid filter support (Figure 2). Filter patterns diverging from the one presented here (either because of the misuse of the IOM sampling head or direct emission towards the filter) were discarded. Two sample positions were selected.

In position 1, only the central part of the filter is analysed (Figure 2a). The black circle represents the filter area exposed to the 8-mm diameter X-ray beam. Four readings are collected from the same central part of a filter by successively rotating the filter cup by 90° increments relative to the instrument source/detector alignment. These readings are labelled C₁, C₂, C₃, and C₄. The individual readings are not reported in this publication.

In position 2, the outer region of the filter is predominantly analysed (Figures 2b and c). Four independent locations are sampled by successively rotating the filter cup by 90° increments. Figure 2b and c present two alternative sampling options. Figure 2b illustrates sampling taking place over the central horizontal and vertical main IOM grid support line patterns (labelled L₁, L₂, L₃, and L₄), while Figure 2c avoids them (labelled Q₁, Q₂, Q₃, and Q₄).

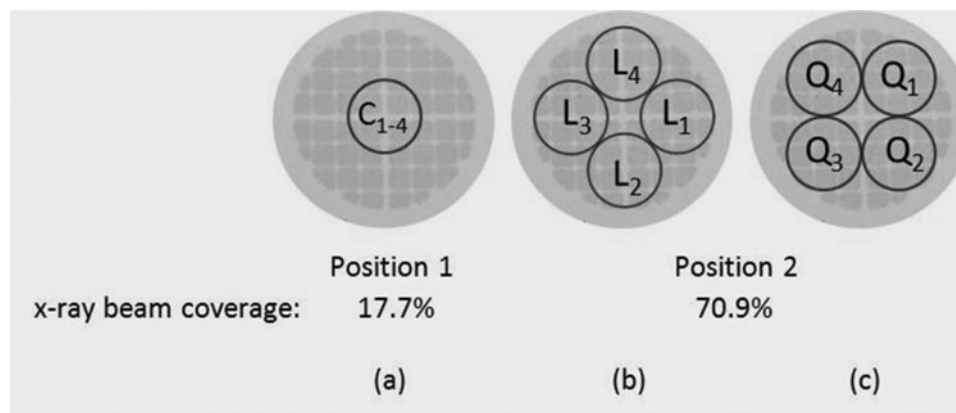


Figure 2. Photograph of a 25 mm diameter dust filter collected using the IOM sampler with schematic representation of a 8 mm PXRF X-ray beam (black circle).

It is the averages of the four PXRF readings collected in regions Cs, Qs, and Ls that are presented and discussed further in this article.

The historical results reported previously using the WDXRF spectrometer were obtained following procedures described in MDHS 91.^[16] Those results were given to the nearest microgram. The overall uncertainty of this method for both sampling and analysis were in accordance with the standard BS EN 482.^[26]

Quantification of lead on workplace surfaces

Lead on surfaces was evaluated by combining PXRF and wipe sampling at six workplaces processing lead-based materials and anonymised as sites 1–6 (see Table 2).

The surfaces sampled at each site included, when available, desktops, worktops, tabletops, chair seats, and floors in the administrative offices, canteens, changing rooms, and process areas. Only results from smooth and hard surfaces are reported here. Rough surfaces (that include textiles, soft furnishing, carpets, concrete, and wood) were excluded because of low dust recovery by wipe sampling.

The surface sampling method is as follows. While wearing nitrile disposable gloves, the operator places a 10 cm by 10 cm disposable paper template flat over the surface to be investigated. Three PXRF measurements are recorded in succession within this template by simply positioning the instrument at three arbitrary locations over this demarcated area. Then the demarcated area is wiped using at least four half GhostTM wipes, following a consistent pattern as presented in Figure 1. Finally, a

new sequence of three PXRF measurements is recorded within the same template but at three new arbitrary locations. Hence, PXRF readings are collected from six different locations within the template. There is no need for accurate repositioning of the instrument on an identical location before and after wiping as prescribed by Dost.^[7] The difference between the average of the first and second sequence of readings, named Δ PXRF, corresponds to the removable lead residues from that surface.

Four successive half wipes are used on each target surface to ensure a high removable dust recovery. The first two half wipes are placed in a labelled tube together. The third and fourth half wipes are placed in a second tube together. Pairing successive half wipes minimise the number of results below LOD and reduces the overall cost of wipe sampling. The bottled, paired half-wipes and the lead dust are digested in nitric acid at 95°C for 1 hr followed by analysis for lead by ICP-AES.^[15] Hydrofluoric acid was added to leaded glass samples. The extraction efficiency was evaluated by spiking blank Ghost wipes with known amount of lead pipetted from a standard solution.

As the surface roughness increases, the wipe efficiency is reduced and the correlation between PXRF and wipe sampling is expected to deteriorate. Rough surfaces were identified using a Taylor Hobson Surtronic Duo roughness meter to measure R_z , a simple peak-to-valley average value characteristic of the surface tested. R_z cannot fully characterise the complexity of a surface's topography. However, a critical threshold R_z value over which surfaces can be judged too rough for effective wipe sampling could

Table 2. Details on workplaces visited.

Site ID	Activity/Sector	Main Processes	Products	Matrix	Lead Content
1–3	recycling	dismantling, breaking	cathode ray tube televisions (CRT)	glass	>20 wt%
4	design, repairs	grinding, cutting	crystal glass objects	glass	>10 wt%
5–6	manufacturing	casting, pasting	batteries	metal, "paste"	up to 100 wt%

Table 3. Summary of the regression models.

Filter Regions and Locations	R ²	Slope	Lower 95%	Upper 95%
Center, Cs	0.9915	0.7419	0.7206	0.7633
Outer, Qs	0.9971	0.8767	0.8621	0.8914
Outer, Ls	0.9969	0.8228	0.8085	0.8371

be identified using both professional judgement and evidence from the degradation of this correlation.

An independent one tailed Student's t-test was performed on the means of the PXRF readings recorded before and after wiping a surface to determine the appropriateness of comparing Δ PXRF with the wipe results. The significance level for the test, p , was set at $p = 0.1$.

Dust emitted from a nearby source (crystal glass grinding or cutting) or that transferred by contact with other contaminated surfaces (shoes, hands) generates highly heterogeneous depositions on surfaces. In such a situation, more than three PXRF readings may be required to pass the Student's t-test. However, it was not practicable to undertake a t-test while sampling and a rule of thumb approach was applied: three readings were deemed sufficient when subsequent readings differed by less than a factor of two. If not, an additional three readings were recorded and the average was based on the mean of these six readings.

Results and discussion

Lead dust on membrane filters

The PXRF results recorded over the regions Cs, Qs, and Ls of the filters were compared against the historical results obtained from the same filters using the WDXRF instrument. According to the WDXRF instrument, lead on the 42 individual filters examined ranged from 1–161 μg . Only one filter was loaded with less than the PXRF LOQ of 1.42 μg . The relationship between the two instruments was investigated using fitted linear regression models. Table 3 summarizes the regression results for regions Cs, Qs, and Ls of the 42 filters analyzed.

These results would suggest that lead dust collected on the filters is not uniformly distributed. There is less dust measured in the central region of the filters compared to the outer regions reflecting that the grid support lines are more prominent in this central region of the filters (see Figure 2).

High R² regression coefficients in excess of 0.99 are obtained from each filter region with a small difference between central and outer regions of the filters. The PXRF consistently under-estimates the lead loadings relative to the WDXRF by about 26% when the central region of the

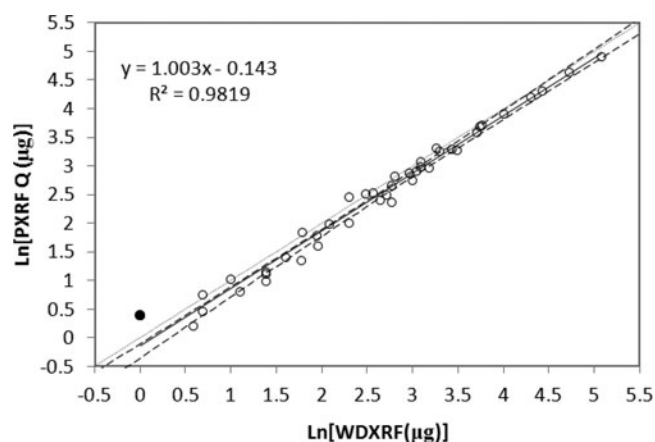


Figure 3. PXRF results for the outer region (Q) of the filter against WDXRF results – open circles: data points above PXRF LOQ; solid circle: data point below PXRF LOQ; dotted line: 1:1 correlation line; continuous thick line: fitted linear regression model; dashed curves: 95% confidence interval on the regression line.

filters is analyzed and 15% when the outer region is analysed (average of Cs and Qs). The 95% confidence intervals of the slope of the regressions would suggest that the locations Cs, Qs, and Ls could be distinguished. However, a 2-way ANOVA statistical analysis was performed (not shown), which confirmed that the inner region (Cs) could be distinguished from the two outer regions but that they (Ls and Qs) were indistinguishable.

In the following, the analysis focuses on the PXRF results collected from the outer region of the filters at locations Qs as these were found to underestimate the WDXRF by only 15% and are statistically indistinguishable from locations Ls.

Figure 3 presents the PXRF readings after natural logarithm transformation to take into account the wide range of loadings encountered and to limit its effect on the regression model. As the mass of lead on the filters increases, the scatter on the data decreases. For lead loadings below the PXRF LOQ (i.e., below 1.42 μg , solid circle in Figure 3), the instrument precision is reduced and the correlation with the laboratory based instrument diverges.

The equation of the best linear fit including the intercept to the natural logarithmic transformed data (shown in Figure 3) indicates a slope close to one with a small negative offset. The 95% confidence interval of the regression line shown by the dashed curves does not fully include the 1:1 correlation line represented by a dotted line. This confirms that PXRF consistently underestimates the lead loadings determined by WDXRF.

The level of agreement between the WDXRF and PXRF results obtained from the outer region at location Qs is evaluated using the Bland and Altman method.^[27] Figure 4 presents the difference between observations

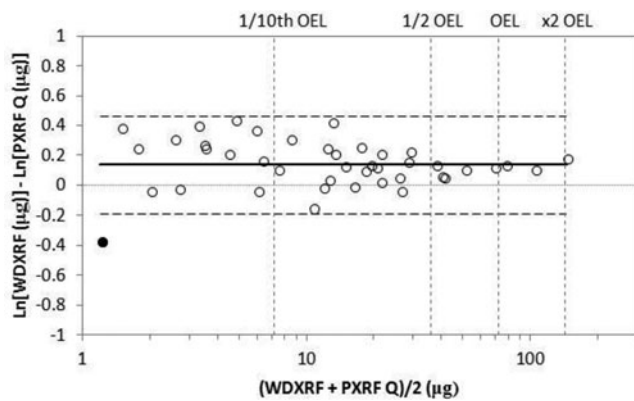


Figure 4. Level of agreement between the two XRF instruments results – open circles: data; solid circle: data point below PXRF LOQ; dotted line: no difference between instruments; continuous thick line: fitted linear regression model; thick dashed lines: 95% limits of agreement between instruments.

after natural logarithmic transformation against the mean of the observations on a \log_{10} -scale. The dotted horizontal line represents the “null difference” between the logarithms of the results, or alternatively a WDXRF to PXRF ratio of one.

The data points are scattered around 0.135, the mean value of the natural log-differences represented by a horizontal thick line. On a linear scale, this value corresponds to a WDXRF/PXRF ratio of 1.15. The PXRF results from the outer region of the filters are on average 13% less than the WDXRF results. Because this is a systematic bias of PXRF against the chosen reference method, the PXRF results can be corrected for it. As the mass of lead on the filters increases, the scatter on the data decreases and converges towards this mean WDXRF/PXRF ratio. For indication only, different fractions of OEL for lead (1/10,

1/2, 1, and x2) are represented by vertical dashed lines in Figure 4 (these are calculated assuming a nominal flow rate of 2 L min^{-1} and a 4-hr sampling period).

The 95% limits of agreement represented by two horizontal thick dashed lines stands between -0.187 and 0.458 , equivalent to 0.83 and 1.58 on a linear scale. Once the systematic bias is allowed for, the 95% limits of agreement lie within ± 0.323 , equivalent to 0.72 and 1.38 on a linear scale. In most cases (i.e., 95% of cases), the WDXRF to PXRF ratios lie within these two extreme values of 0.72 and 1.38 . Most PXRF results from the outer region of the filters are within -28% and $+38\%$ of the WDXRF results. This was evaluated including one lead loading of $1 \mu\text{g}$ as measured by WDXRF, significantly below the LOQ of the PXRF instrument, but that represents a plausible situation when sampling in the workplace.

Lead dust on membrane filters - further discussion

The WDXRF and PXRF methods did not account (or intend to correct) for dust accumulation of the walls of the IOM samplers. An alternative method to account for that would be to wipe the internal surfaces of such sampler and analyse the residues on that wipe by XRF, in addition to the filter. That would provide an integral evaluation of inhalation exposure to lead dust. Unfortunately, wiping the internal surfaces of each sampler and preparing the wipe for PXRF analysis in the workplace would be time consuming. Acid-soluble disposable internal capsules or caps able to collect wall deposits are currently developed for use with the closed-face filter cassettes and analysis by ICP-AES.^[28] It may be possible to develop disposable

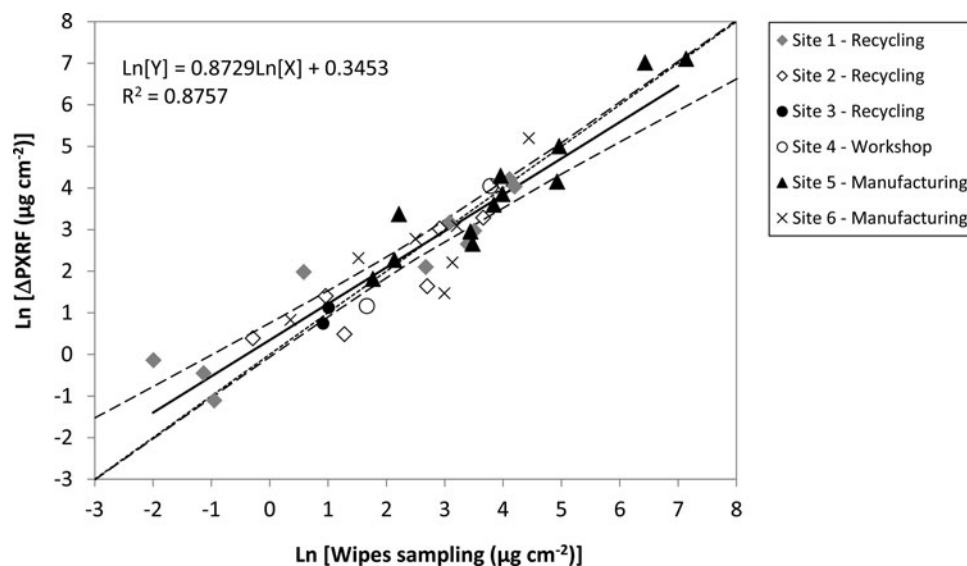


Figure 5. Degree of correlation between the two sampling methods - dotted line: 1:1 correlation line; continuous thick line: fitted linear regression model; dashed curves: 95% confidence interval on the regression line.

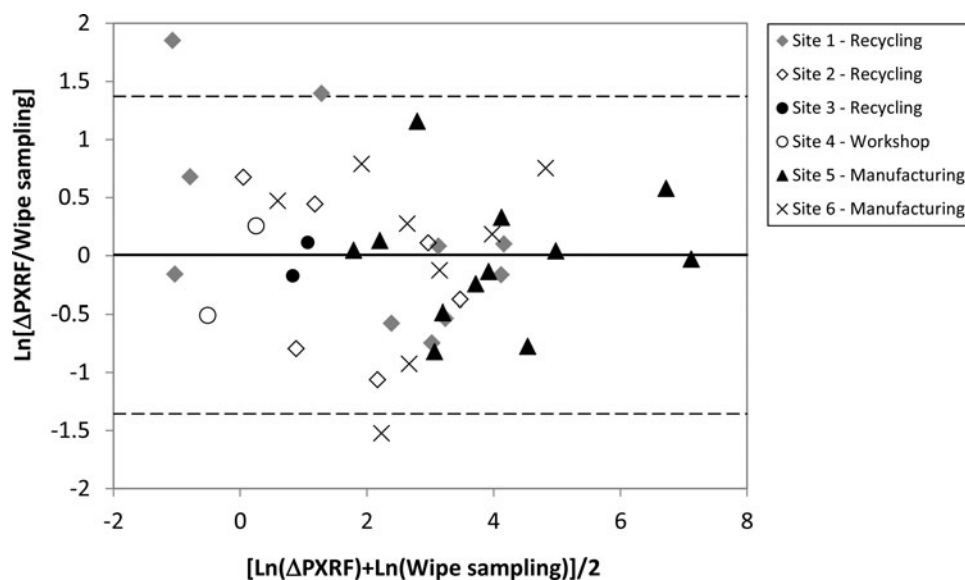


Figure 6. Level of agreement between the two sampling methods – continuous thick line: fitted linear regression model; dashed lines: 95% limits of agreement between methods.

internal capsules that could be used with the IOM sampler and analysed, once collapsed flat, by XRF.

Lead on workplace surfaces

Paired wipes and PXRF readings from 119 target workplace surfaces contaminated with lead dust were collected at 6 sites processing lead-based products. Where the difference between PXRF readings recorded before and after wipe sampling (Δ PXRF) was not statistically significant, it was excluded from the comparison with wipe sampling. Paired data from surfaces for which R_z was greater than a critical threshold value of $45 \mu\text{m}$, were also excluded. This threshold value is somewhat arbitrary but was evaluated post-hoc based on the loss of correlation observed in the paired data collected. The remaining 40 paired wipes and Δ PXRF results are analysed thereafter.

The removable lead residues, as estimated by wipe sampling, extend from 0.14 – $1257 \mu\text{g cm}^{-2}$. Over that range, the Δ PXRF to wipe results ratios were found to be scattered around 1 and the paired results were all within one order of magnitude with most results within a factor of 3. In Figure 5, the lead loadings estimated by PXRF are plotted against the loadings obtained by wipe sampling after natural logarithmic transformation. All data points are closely scattered about the 1:1 correlation line represented by a dotted thin line. The relationship between the natural logarithmic transformed results was investigated using a fitted linear regression model with intercept. The best linear fit, represented as a thin continuous line through the data symbols, provides a squared regression coefficient between the outcomes and the data of about 0.88. This indicates a good correlation between

the PXRF and wipe results. The 1:1 correlation line is included within the 95% confidence interval of the regression line represented by the dashed curves. There is no evidence to suggest that wipe sampling underestimates removable lead residues when compared to direct PXRF surface readings.^[7]

The Bland and Altman^[27] level of agreement between the removable lead residues estimated by PXRF and wipe sampling is evaluated in Figure 6 where the ratio of the arithmetic difference between observations and the wipe sample is plotted against the mean of the observations, both after natural logarithmic transformation. Figure 6 presents the mean Δ PXRF to wipe results ratio as a continuous line at 0.007 with the 95% limits of agreement represented by two dashed lines at -1.357 and 1.371 . Back transformed on a linear scale, the mean value for the ratio of the removable lead residues estimated by PXRF and wipe sampling is close to 1 (i.e., 1.01) and 95% of all paired measurements are between ratios of 0.26 and 3.94.

Conclusions

First, a practical workplace sampling method is presented here for the immediate and nondestructive quantification of lead in dust and fumes collected by IOM samplers on 25-mm diameter membrane filters. This method is designed for use with an 8 mm diameter X-ray beam PXRF instrument taking less than 3 min to analyze the outer regions of a filter as four subsamples immediately after its collection. The PXRF method is evaluated against a laboratory-based WDXRF reference method.

Such methods, however, do not account for dust accumulation of the walls of the IOM sampler and thus need to be regarded as semi-quantitative.

The means of series of four PXRF readings recorded from the outer region of the filters systematically underestimated the lead loadings as determined by WDXRF by about 13%. However, after bias correction and using the Bland and Altman^[27] method, we demonstrated that 95% of the means of these PXRF readings are within -28% and $+38\%$ of the results obtained using the laboratory-based WDXRF instrument.

Second, a protocol combining direct PXRF surface readings with wipe sampling was presented for the quantification of removable lead residues from smooth and hard surfaces. Suitable surfaces were defined as having a peak-to-valley average roughness value R_z smaller than $45\ \mu\text{m}$. A good correlation was found between PXRF and wipe sampling (R^2 close to 0.88) with no evidence for wipe sampling underestimating the amount of removable lead residues evaluated directly by PXRF. Most PXRF to wipe sampling result ratios lay between 0.26 and 3.94.

The sampling methods developed and presented here demonstrate that once evaluated against a laboratory-based reference method, the PXRF is a practical workplace screening tool that could help Occupational Hygienists identify poorly controlled processes and individuals at greater risk of exposure to lead in the workplace. It provides rapid on-site analysis and hence immediate tangible evidence in support of decisions and actions taken to reduce exposure in the workplace. Because the PXRF method is nondestructive, samples collected in the workplace can also be verified by analysis at a later stage using an alternative method or by another independent laboratory. Although this article focused on the evaluation of lead-containing dust on surfaces, PXRF is able to identify simultaneously a number of other metals that might be of concern in the workplace and that could be screened in the same manner.

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