Use of Field-Portable X-Ray Fluorescence (FPXRF) Analyzer to Measure Airborne Lead Levels in Korean Workplaces

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Abstract: Use of Field-Portable X-Ray Fluorescence (FPXRF) Analyzer to Measure Airborne Lead Levels in Korean Workplaces: Nam-Soo Kim, et al. Institute of Environmental & Occupational Medicine, College of Medicine, Soonchunhyang University, Korea—We evaluated the possibility of applying field-portable x-ray fluorescence (FPXRF) analysis as a rapid, on-site and near real-time method for evaluating airborne lead contamination in Korean workplaces. A total of 287 airborne lead filter samples were measured in 12 lead-using workplaces during routine industrial hygienic monitoring procedures as required by Korean government regulations. All filter samples were collected using the standard industrial hygiene sampling protocol described in NIOSH Method 7300 using closed-face 37-mm cassettes with preloaded cellulose ester membrane filters with a pore size of 0.8 µm. The samples were first analyzed using the non-destructive, FPXRF analytical method (NIOSH method 7702), and then subsequently analyzed using inductively coupled plasma atomic emission spectrophotometry (ICP) (NIOSH method 7300) as a reference analytical method. Pair-wise comparison of filter samples using the paired t-test revealed no statistically significant differences between the two methods over a wide range of airborne lead levels (0.018–0.201 µg/m³) either over the industries assessed or separately in the 12 lead-using workplaces. Linear regression of the data between the ICP and FPXRF methods produced a slope of 1.03, a y-intercept of 0.13 µg/sample, and a coefficient of determinant ($r^2$) of 0.975 for all the data. For samples in the range from 0 to 100 µg, the corresponding values were 1.07, –1.20 µg/sample, and 0.925, respectively.

Our data suggest that FPXRF data are highly correlated with those from the laboratory-based ICP method in terms of accuracy, precision, and bias. Therefore, FPXRF can be used for the rapid, on-site analysis of lead air-filter samples for values up to 26 µg/sample prior to laboratory confirmation by the ICP method. (J Occup Health 2007; 49: 493–498)

Key words: Lead, FPXRF (Field-portable x-ray fluorescence), ICP (Inductively coupled plasma atomic emission spectrophotometry)

During the last 20 yr, Korean industries using lead have implemented ongoing biological monitoring programs together with the engineering control of workplaces and the introduction of new advanced operating systems. These programs have improved the health of lead workers as quantified by a reduction in blood lead), which is mainly attributable to the respiratory protection program implemented due to strict government regulations and the need to provide workers with clean and comfortable working environments. Korean occupational safety and health laws require mandatory environmental hygiene evaluations to be conducted annually by an independent industrial hygiene team or by a government-certified industrial hygiene institute, with formal evaluation reports provided to the regional labor office.

Reducing lead exposure is difficult when this relies on traditional airborne lead measurement practices, since these have turnarounds of at least a month. This prompted us to consider using a field-portable x-ray fluorescence (XRF) analyzer to facilitate rapid and reliable measurements.

The advantage of the FPXRF method is that it can use the same filter samples collected for classical laboratory analytical methods. Even though field-portable XRF (FPXRF) analyzers are not yet certified for the analysis of airborne lead in the workplace in Korea, they can be used for on-site checks of airborne lead in workplaces in certain circumstances in Korea if immediate data are needed before applying classical laboratory analytical methods, such as atomic absorption fluorescence.
spectrophotometry (AAFS) or inductively coupled plasma atomic emission spectrophotometry (ICP).

This study compared the FPXRF method and the currently used ICP analytical method in order to evaluate the possible application of FPXRF as an alternative fast turnaround method for measuring airborne lead for engineering control in Korean industries using lead.

Methods

We performed 287 field samplings of personal air samplers in 12 lead-using workplaces in the following 3 industries: storage battery industry, primary and secondary smelting industries, and PVC stabilizer manufacturing industry. Field samples were collected during regular industrial hygiene inspections as required (twice yearly) by the Korean Occupational Safety and Health Act, which mandates that lead-using industries make industrial hygiene measurements including that of airborne lead in workplaces with personal air samplers.

Field samples were collected using the standard Korean method\(^5\), which is equivalent to the standard industrial hygiene sampling protocol described in NIOSH “Guidelines for air sampling and analytical method development and evaluation”\(^5\). Gillian personal air samplers (Gillian-3 Sampler, Gillian U.S.A.) were used to collect field air samples using closed-faced 37-mm cassettes with preloaded cellulose ester membrane filters with a pore size of 0.8 μm. All pumps were pre-calibrated at an airflow of 2.0 ± 0.1 (mean ± SD) l/min using a Gillian calibrator before field sampling. To comply with the sampling time of the standard Korean method of field sampling of airborne lead, at least 360 minutes sampling time was applied to all field samplings ranging from 360 to 497 min.

**Field Portable X-ray Fluorescence (FPXRF) method of filter analysis**

A FPXRF analyzer (XL-309, NITON, Bedford, Massachusetts) was used to implement the NIOSH 7702 method\(^5\). Filter samples were transferred from their cassettes to a cardboard and acetate sleeve specially designed for XRF air-filter analysis. The sealed sample was placed on a filter test platform that was designed to hold the 37-mm filters securely under the test window of the instrument. The platform has precut edges on which the sleeve is placed so as to position the filter for the instrument. The platform has precut edges on which the filter is placed. The filter was placed on a filter test platform that was designed to hold the 37-mm filters securely under the test window of the instrument. The platform has precut edges on which the filter is placed.

**ICP Laboratory method of filter analysis**

For laboratory analysis of field samples, the ICP method was implemented based on NIOSH Method 7300\(^5\), which is the standard laboratory analysis method for airborne lead used at the Institute of Industrial Medicine, Soochunhyang University.

Following the non-destructive analysis of the filter using the XRF method, the filter and acetate film were moved to a glass tube using tweezers. Then 10 ml of 10% nitric acid was added to the glass tube and the tubes were soaked in a water bath at 50–60°C for 4–5 h. To avoid possible bias from the acetate film, the acetate film and the filter were pretreated in the same way. The analysis was performed with an ICP-7500 device (Shimadzu, Japan).

Data analysis

1) Calculation of LOD and LOQ

The instrumental limit of detection (LOD) and limit of quantitation (LOQ) were determined based on NIOSH Standard Operating Procedure (SOP) 018\(^9\). NIOSH SOP 018 defines LOD as the mass of analyte that gives a mean signal that is three standard deviations (SDs) higher than the mean blank signal, and LOQ as the mass corresponding to the mean blank signal plus ten SDs.

2) Calculation of bias, precision, and accuracy

The XRF method point bias was estimated by subtracting the ICP analytical value (μg/sample) from the XRF analytical value (μg/sample), and dividing by the ICP analytical value (μg/sample) at each data point.\(^5\) The total bias of the data set was determined by taking the mean of the point bias estimate. The 95% confidence interval was determined by multiplying the appropriate t-value by the SD and then dividing by the square root of the sample size.

The precision of the XRF method was estimated by making three repeated readings of the filter samples whose lead loading range of the method was represented at the target loading range of the method. These three readings were averaged for each sample, and the precision was defined as the SD divided by the mean at each sample point.

The accuracy of the XRF method was estimated based on the bias and precision of the XRF method with the Nomogram Relating Accuracy to Precision and Bias. The 2.5%, 50%, and 97.5% confidence statistics for bias and precision obtained with the Bonferroni procedure were used to determine the 5%, 50%, and 95% confidence statistics, respectively.

3) Statistical analysis

The primary goals of the analysis were to (1) compare the data of FPXRF with those of ICP, (2) calculate the LOD and LOQ, and (3) evaluate the analytic performance of the FPXRF method in terms of its accuracy, precision, and bias.

Descriptive data analysis was first applied to compare the mean and median values for the two methods, and linear regression modeling was used to evaluate associations of airborne lead in filters between the two...
methods. Actual geometric means of the airborne lead concentration at each workplace were calculated whilst considering the sampling durations.

**Results**

The samples were first analyzed with the (non-destructive) XRF method and then with the ICP method. The data obtained are summarized in Table 1. The mean and median values did not differ significantly between the two methods. The airborne lead concentration at the 12 lead-using workplaces varied widely, from 0.018 to 0.201 µg/m³ (Table 2). The mean airborne lead content at the 12 lead-using workplaces varied from 25.5 to 262 µg/sample, and did not differ significantly between the two methods.

The overall scatter plot of airborne lead concentrations as obtained using the XRF and ICP methods were strongly correlated (coefficient of determinant: $r^2=0.975$), and gave a regression equation with a slope of 1.03 and a y-intercept of 0.13 µg/sample (Fig. 1). Pair-wise comparisons between the two methods using the paired $t$-test revealed no statistically significant differences ($p>0.05$).

How well the FPXRF performed around the Korean Permissible Exposure Level (PEL) of 50 µg/m³ for an 8-h time-weighted average was assessed by considering only lead concentrations up to 100 µg/sample obtained using the ICP method (no figure presented). In this range the regression coefficient was 0.925, the slope was 1.07, and the y-intercept was –1.20 µg/sample. A pair-wise $t$-test revealed no significant differences between the two methods ($p>0.05$).

We plotted airborne lead concentrations of the ICP and XRF method by the three types of lead-using industry (storage battery, primary smelting industry and secondary smelting, and litharge making workplaces) and calculated their coefficients of determinants (no figures presented). The coefficients of determinants of the three types of lead-using industry were between 0.964–0.982. Pair-wise $t$-tests performed for the three types of lead-using industry revealed no significant differences between the two methods ($p>0.05$).

**Table 1.** Mean and geometric mean values of airborne lead (µg of lead/sample) obtained using field-portable x-ray fluorescence (FPXRF) analyzer and inductively coupled plasma atomic emission spectrophotometry (ICP)

<table>
<thead>
<tr>
<th>Method</th>
<th>N</th>
<th>Mean ± SD</th>
<th>GM</th>
<th>GSD</th>
<th>Range (min-max)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FPXRF</td>
<td>287</td>
<td>96.34 ± 157.48</td>
<td>49.45</td>
<td>3.28</td>
<td>0.8–1290.0</td>
</tr>
<tr>
<td>ICP</td>
<td>287</td>
<td>93.55 ± 150.99</td>
<td>45.47</td>
<td>3.54</td>
<td>0.1–1095.0</td>
</tr>
</tbody>
</table>

SD: standard deviation, GM: geometric mean, GSD: geometric standard deviation.

**Table 2.** Analytical summary of sample-filter data of 12 lead-using workplaces obtained using FPXRF and ICP

<table>
<thead>
<tr>
<th>Workplace number</th>
<th>Type</th>
<th>N</th>
<th>FPXRF (mg/sample) Mean ± SD</th>
<th>ICP (mg/sample) Mean ± SD</th>
<th>PbA (mg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>GM</td>
<td>GSD</td>
<td>Range (min–max)</td>
</tr>
<tr>
<td>1</td>
<td>A</td>
<td>26</td>
<td>27.8 ± 29.8</td>
<td>18.4</td>
<td>3.8</td>
</tr>
<tr>
<td>2</td>
<td>A</td>
<td>17</td>
<td>23.4 ± 19.9</td>
<td>19.5</td>
<td>2.6</td>
</tr>
<tr>
<td>3</td>
<td>A</td>
<td>13</td>
<td>63.1 ± 71.5</td>
<td>42.9</td>
<td>2.3</td>
</tr>
<tr>
<td>4</td>
<td>A</td>
<td>30</td>
<td>34.9 ± 21.6</td>
<td>27.0</td>
<td>2.4</td>
</tr>
<tr>
<td>5</td>
<td>A</td>
<td>23</td>
<td>56.5 ± 75.7</td>
<td>35.9</td>
<td>2.6</td>
</tr>
<tr>
<td>6</td>
<td>A</td>
<td>76</td>
<td>67.1 ± 65.1</td>
<td>44.9</td>
<td>2.6</td>
</tr>
<tr>
<td>7</td>
<td>A</td>
<td>5</td>
<td>78.4 ± 51.4</td>
<td>67.0</td>
<td>1.9</td>
</tr>
<tr>
<td>8</td>
<td>B</td>
<td>55</td>
<td>189.5 ± 262.8</td>
<td>102.1</td>
<td>3.3</td>
</tr>
<tr>
<td>9</td>
<td>C</td>
<td>16</td>
<td>74.7 ± 41.2</td>
<td>61.6</td>
<td>2.0</td>
</tr>
<tr>
<td>10</td>
<td>C</td>
<td>7</td>
<td>240.3 ± 169.4</td>
<td>115.5</td>
<td>4.5</td>
</tr>
<tr>
<td>11</td>
<td>C</td>
<td>7</td>
<td>253.7 ± 304.9</td>
<td>169.7</td>
<td>2.8</td>
</tr>
<tr>
<td>12</td>
<td>D</td>
<td>12</td>
<td>232.7 ± 229.8</td>
<td>146.7</td>
<td>2.8</td>
</tr>
</tbody>
</table>

A: Battery, B: Primary smelting, C: Secondary smelting, D: PVC-stabilizer manufacture. SD: standard deviation, GM: geometric mean, GSD: geometric standard deviation. * Actual geometric mean (GM) and geometric SD (GSD) values for the airborne lead concentration of each workplace calculated while considering the sampling duration using the standard Korean sampling method.
The mean and SD values of the blank signal obtained from 30 blank samples using the XRF method with a three-readings analysis according to NIOSH SOP 018 were 1.28 and 2.75, respectively, and hence the LOD was \(3 \times (2.75)+1.28=6.79\) µg/sample and the LOQ was \(10 \times (2.75)+1.28=26.22\) µg/sample.

The point bias estimates of each paired data point ranged from \(-49.3\) to \(3.99\). Twenty-two values of less than \(6.79\) µg/sample (as determined by ICP) were eliminated from the data set. The total bias for the remaining data set (266 samples) was \(0.041 \pm 0.29\) (95% confidence interval: \(0.012–0.072\)). The 95% confidence interval for bias conforms to the NIOSH bias criterion of less than \(\pm 0.10\), indicating that the XRF method meets the NIOSH bias criterion for an approved analytical method.

The precision of the XRF method was estimated by performing three readings analysis of 114 filter samples ranging from 7.8 to 674.2 µg/sample. The mean and SD were calculated for the three-readings analysis for each sample. The mean and 95% confidence interval were \(0.055\) and \(0.007\), respectively. The point precision estimates around 30, 50, 100, 200 and 400 µg/sample were \(0.0398\) at 31 µg, \(0.0339\) at 51.6 µg, \(0.0473\) at 100 µg, \(0.0191\) at 199 µg, and \(0.0241\) at 401 µg.

The accuracy of the XRF method was estimated using the Nomogram Relating Accuracy to Precision and Bias. The single value estimate of accuracy was 13.5%. The 5% and 95% confidence statistics for accuracy were 9.6% and 18.2%, respectively. The former was obtained using the 2.5% confidence statistic for the bias (0.012) and the 2.5% confidence statistic for the precision (0.047), whereas the latter was obtained using the 97.5% confidence statistic for the bias (0.072) and the 97.5% confidence statistic for the precision (0.062). The 90% confidence interval for accuracy (9.6% to 18.2%) is better than the 25% accuracy criterion of NIOSH.

**Discussion**

Those involved in assessing environmental quality have accepted FPXRF methodology as a viable cost- and time-effective analytical approach for analyzing a variety of hazardous materials. FPXRF analysis offers many advantages and few disadvantages compared to the conventional laboratory methods that have historically been employed for the analysis of environmental samples.

In Korea, two preceding studies using FPXRF have been published. The first one evaluated the possibility of FPXRF for an occupational setting with 20 quality control filter samples and 72 field samples from one lead storage battery. The second paper compared FPXRF with 51 field samples from a high volume air sampler. Both papers suggested the possible usage of FPXRF as supplementary evaluation of airborne lead in Korean lead-using industry.

In many occupational settings, such as in the storage battery industry, standard occupational laboratory-based hygiene evaluations of airborne in workplaces using

![Fig. 1.](image-url) Relationship between airborne lead levels as measured by field portable x-ray fluorescence analyzer (FPXRF) and inductively coupled plasma atomic emission spectrophotometry (ICP). Regression equation: \(Y = 0.13 + 1.03 X (r^2 = 0.975)\).
AAGFM or ICP are sufficient when a rapid turnaround time is not required due to the presence of stable operating conditions.

While the blood lead levels in those working in most lead-using industry have decreased during the past decade, those working in Korean lead-using industry have realized the limitation of the respiratory protection program for further reductions in blood lead in many workers, and hence have initiated fundamental engineering control of their workplaces to reduce airborne lead to meet the PEL. Moreover, the necessity for a rapid turnaround schedule and on-going monitoring of airborne lead in workplaces has increased interest in the possible application of FPXRF in Korea. The present study shows that the data obtained from FPXRF are in good agreement with those obtained from the standard ICP method in real field evaluations.

The overall coefficient of determinant ($r^2$) for FPXRF and ICP over a wide range of airborne lead levels (0.001–1.244 µg/m$^3$) in 12 lead-using workplaces was 0.975, and paired t-tests revealed no significant differences between the two methods. The $r^2$ values for the two methods were 0.972, 0.964, and 0.982 in the three types of lead-using industry, also with no significant differences being present. Our results are similar to those obtained in previous FPXRF studies.

Morley et al. reported that the regression coefficient for data near PEL was less than 1 (i.e., 0.826), with a positive method bias due to the high detection limit of FPXRF, and considered that applying FPXRF methods rather than the standard laboratory method would help to protect workers. However, in our study with a similar range of airborne lead levels (0–100 µg/sample), the regression coefficient of FPXRF and ICP was 1.07, and did not show any differences from slopes in the overall range analysis.

The estimated LOD and LOQ using the NIOSH SOP 018 method with 30 blank filters were 6.79 and 26.22 µg/sample, respectively, and hence values of less than 6.79 µg/sample should be reported as non-detectable, and those between 6.80 and 26.22 µg/sample should be regarded as imprecise results. In our study we had 20 non-detectable and 61 imprecise data results, representing 28% of the 287 samples.

Our LOD was similar, but our LOQ was higher than those reported by Morley et al. The LOQ of 26.22 µg/sample is sufficiently sensitive to evaluate the lead exposure below the PEL (0.05 mg/m$^3$) and is still acceptable for quantifying the lead exposure around the Occupational Safety and Health Administration action level (0.03 mg/m$^3$).

Even though the XRF method is known to be less accurate than laboratory methods, our study has revealed that its performance—in terms of its accuracy, precision, and bias—is still acceptable. The 95% confidence interval of the XRF method for bias (0.012–0.072) conforms to the NIOSH bias criteria, its precision was 0.055 ± 0.007, and the 90% confidence interval for accuracy was 9.6% to 18.2%, which is better than the 25% accuracy criterion of NIOSH.

XRF data conform to US EPA QA1 and QA2 according to OSWER Directive 9360.4-01. QA is a screening objective and QA2 is a verification objective that requires confirmation of a minimum of 10% of the XRF samples by a US EPA-approved laboratory (AA or ICP). The regression coefficient ($r^2$) of the ICP and XRF data sets must be at least 0.7 to meet QA2 objectives. Our very high value of $r^2$ easily exceeds the criteria of QA2.

One of the disadvantages of FPXRF is the use of radioisotope sources for sample excitation; these sources have finite useful lifetimes (defined by their half-life) and hence must be replaced at regular intervals. Furthermore, the use of radioisotope source-based equipment is subject to strict regulations of the government radioisotope agency, and such sources can only be handled by certified personnel.

Despite these disadvantages, FPXRF represents a rapid, non-destructive and on-site technique for pre-screening of airborne lead filters and maximizing analytical coverage with minimal cost. The ability to analyze data on airborne lead in the workplace in near real time will help industrial hygienists and related personnel to evaluate the magnitude of problems of working conditions and provide anticipated industrial hygiene action to improve working conditions in advance of final laboratory analysis of field samples. In Korea, the introduction of FPXRF will greatly contribute to reducing the burden of airborne lead on workers in lead-using industries, particularly during renovations and the installation of new operation systems.

References

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