Portable X-Ray Fluorescence as a Screening Tool for Analysis of Heavy Metals in Soils and Mine Wastes

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ABSTRACT

X-ray fluorescence (XRF) has several advantages over atomic absorption and inductively coupled plasma techniques that make it useful for the screening analyses of environmental samples. These advantages are: rapid turnaround time, multi-element analytical capacity, nondestructive analyses, minimal quantity of sample required and cost-effectiveness. Further, a portable XRF instrument has the capability of providing on-site analyses that can be incorporated immediately into the field investigation program. The realization of the potential of a portable XRF device has led to an increase in its use in remedial investigations at hazardous waste sites. In most cases, however, the accuracy and precision of the analyses, along with the method detection limits, have not been well characterized. In this paper, these parameters are established for a variety of soil/tailings matrices, calibration techniques and field situations.

The authors have used a portable XRF analyzer to determine heavy metals concentrations in soils, sediments and mining wastes at three hazardous waste sites in Colorado and Montana. The elements determined using a Columbia Scientific portable XRF analyzer were lead, arsenic, copper, zinc and iron. These three sites represent several potential applications of XRF analyses, including: (1) on-site selection of sample locations necessary for definition of contaminant boundaries, (2) screening of samples for further analyses through the Contract Laboratory Program (CLP) and (3) statistical and geochemical evaluation of the spatial variation of metals concentrations. The requirements and limitations of XRF analyses for each application are evaluated.

The results obtained substantiate the dependence of method detection limits on sample matrix variability and analyte concentration ranges. The accuracy and precision of the analytical technique also depend on the number and type of calibration standards used. These conclusions are demonstrated by statistical evaluation of the results of the calibration for combinations of 5, 10, 15 and 20 standards. The results of both replicate analyses and XRF versus CLP comparisons are presented and are used to determine potential sources of error and their relative magnitudes for the entire procedure. This knowledge can be directly applied to the design of field programs that more effectively meet the accuracy, precision and detection limit requirements of XRF analyses for remedial investigations at hazardous waste sites.

INTRODUCTION

As part of the remedial investigations at three hazardous waste mining sites, screening for heavy metals contamination was performed with the aid of a portable energy dispersive X-ray fluorescence (XRF) analyzer. At Site A in Colorado, definition of a 1,000 mg/kg Pb isopleth using on-site XRF in conjunction with geostatistics was accomplished. In the identification of hotspots and areas requiring further investigation at Site B in Montana, XRF provided a useful and cost-effective method for screening for As, Pb, Cu and Zn. XRF screening also was utilized to select samples for further analysis through the Contract Laboratory Program (CLP). At Site C in Colorado, analyses for Pb, As, Cu, Zn and Fe in split spoon tailings samples provided additional information on the relationships between degree and depth of contamination. In this way, zones of metal accumulation and leached zones of metal depletion could be identified.

The potential use of XRF spectrometry as a screening technique for trace constituents at hazardous waste sites has been demonstrated by several studies. In these cases, however, analyses were performed by dedicated laboratory instruments employing sophisticated computer software. The additional advantage of immediate results has led to an increased interest in portable XRF systems, which necessarily are less sophisticated. The purpose of this study was to outline the techniques essential to the proper use of portable XRF instruments and to evaluate the results obtained in relation to the designed screening use of the method.

XRF THEORY

The fundamental principle of X-ray fluorescence (XRF) or emission spectrometry is the detection and measurement of the X-rays emitted from excited atoms in a sample. The excited state is achieved when the critical binding energy of an electron in a particular shell is exceeded by the energy of the incoming source particle. When this happens, an orbital electron is removed from the shell (the atom is ionized) and another electron from a higher energy shell takes its place. The excess energy released as an X-ray photon during this process is characteristic of the atom from which it was produced. There are, of course, many complications to this simplified discussion of XRF theory, and a vast amount of literature addresses them in detail.

Two general types of emission spectrometers can be used: wavelength dispersive (WD) and energy dispersive (ED). Wavelength dispersive systems normally provide very high resolution (sharp narrow peaks) but, because of the additional diffraction step, they suffer from low efficiency (the energies of the characteristic X-rays are attenuated by the diffraction process). Energy dispersive systems, on the other hand, are highly efficient but have less resolving power. Because ED spectrometers do not require high source energies for excitation (i.e., they are more efficient) and elaborate mechanisms for geometric positioning of the detector, they are more adaptable for use in the field. Several compact ED systems are now available, some with sophisticated software capabilities.
The energy dispersive XRF system used in this study was a Columbia Scientific X-MET 840 portable analyzer. The X-MET 840 employs a radioisotope source for sample excitation and a high resolution proportional counter for X-ray detection. For the elements analyzed for in this study (Pb, As, Cu, Zn and Fe), a 100 millicurie source, composed of Cm 244 which emits Pu L X-rays with energy ranging from 12 to 20 KeV, was used. The resolution of the spectrometer, as defined by the full width at half the maximum (fwhm) height of the Mn Kalpha peak at 5.9 KeV, is about 0.83 KeV or 14%. Typical laboratory ED instruments are now capable of resolutions of less than 0.15 KeV or 2.5%.

**SAMPLE MATRIX EFFECTS**

The most important consideration in the measurement of X-ray energy is the influence of sample matrix effects. Matrix effects can either increase or decrease characteristic X-ray intensities and, if not corrected for, can lead to significant accuracy problems. In general, these effects can be divided into either physical or chemical matrix effects.

Physical matrix effects are the result of variations in the physical character of a sample. They may include such parameters as particle size, uniformity, homogeneity and surface condition. For example, consider a sample in which the analyte exists as very fine particles within a matrix composed of much coarser material. If two separate specimens (aliquots) of the sample are ground in such a way that the matrix particles in one are much larger than in the other, then the relative volumes occupied by the analyte-containing particles will be different in each. When measured, a larger amount of the analyte will be exposed to the source X-rays in the specimen containing larger matrix particles, resulting in a higher intensity reading for that specimen.

Chemical matrix effects result from differences in concentrations of interfering elements. These effects appear as either spectral interferences (peak overlaps) or as absorption/enhancement phenomena. Both effects are common in soils contaminated with heavy metals. For example, Fe tends to absorb Cu K X-rays, reducing the intensity measured by the detector. This effect can be corrected for if the relationship between Fe absorption and X-ray intensity can be modeled mathematically. Obviously, establishment of all matrix relationships during the time of instrument calibration is critical.

Sample matrix effects can never be fully eliminated. They can become relatively insignificant, however, through proper sample preparation and calibration techniques. The techniques used in this study are addressed more fully in the following section.

**METHODOLOGY**

**Sample Preparation**

Samples to be analyzed by XRF (including calibration samples) were placed in aluminum pans, air-dried and mixed as well as possible. A representative portion of each sample (40-100 g) was ground to less than 100 mesh, and a 5-10 g aliquot of the resulting powder was then analyzed with the spectrometer. Sample preparation time averaged between 10 and 15 min/sample. Actual analysis time was 4 min/sample.

By saturating the sample preparation step, analytical variations due to physical matrix effects were minimized. In other words, although the physical characteristics of the samples may have been affecting the intensities of X-rays, correction for these effects was not necessary because they were the same for all samples. Of course this assumption was valid only for samples with identical or at least very similar matrices (e.g., for samples collected from the same site). Although the assumption was reasonable from a theoretical standpoint, in practice it was difficult to test. However, one important aspect, homogeneity of the ground powder, was tested. The results of this determination are evaluated later in this paper.

**Calibration**

The calibration of the XRF spectrometer was based on previously collected and analyzed samples from each site. These samples were handled with the same procedures outlined above in "Sample Preparation." After digestion with HNO3/H2O2 according to the procedures specified by the CLP, samples were analyzed by either inductively coupled plasma (ICP) or atomic absorption (AA) techniques by different laboratories with CLP procedures. The samples do not represent "true" calibration standards in the sense that the accuracy of the different CLP laboratories was not beyond repute. Nevertheless, the potential calibration error due to the inaccurately known concentrations in the samples was probably much less than the potential matrix effect errors that would result using "true" standards with unknown matrices.

Calibration was accomplished by first measuring the intensities of the characteristic analyte X-rays, then developing a concentration versus net intensity regression curve. The calibrations employed for each analyte and for each site were essentially mathematical models designed to compensate for sample matrix effects specific to the site. The goal was to optimize the calibration for each analyte by correcting for both spectral overlap and/or element interference, if necessary. Spectral overlap, which occurs when two peaks are not completely resolved, was removed by deconvolution (subtraction of one peak intensity from that of another). Absorption or enhancement of characteristic X-rays due to the presence of interfering elements was handled by multiple linear regression analysis. All of the software necessary for calibration is contained within the instrument.

Table 1 summarizes the results of the calibration obtained for each element at each site. The table provides the number of calibration standards (n), the range of concentrations in the standards, the instrument detection limit (discussed in next section) and the resulting correlation coefficient. In all cases, the calibration was excellent with correlation coefficients typically greater than 0.95.

<table>
<thead>
<tr>
<th>Site</th>
<th>Element</th>
<th>n</th>
<th>Analytical Range (ug/kg)</th>
<th>Correlation Coefficient (r)</th>
<th>IDL (ug/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Pb</td>
<td>1</td>
<td>0-1,000</td>
<td>0.999</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>1</td>
<td>0-1,200</td>
<td>0.949</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>1</td>
<td>0-0.3200</td>
<td>0.963</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>1</td>
<td>0-0.2-500</td>
<td>0.943</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>1</td>
<td>0-0.4-800</td>
<td>0.955</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>1</td>
<td>0-0-250</td>
<td>0.983</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>1</td>
<td>0-0.3-500</td>
<td>0.993</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>1</td>
<td>0-0.3-500</td>
<td>0.997</td>
<td>60</td>
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<tr>
<td></td>
<td>Fe</td>
<td>1</td>
<td>0-180,000</td>
<td>0.997</td>
<td>140</td>
</tr>
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</table>

1 Overall standard deviation (root mean square of the residuals) for the regression
2 Model #5 (10 calibration samples)
3 Instrument detection limit

**ANALYTICAL PRECISION**

Replicate analyses were performed to determine the analytical precision of the X-MET 840. For each site, a check sample was analyzed at regular intervals throughout the analytical run. The results, shown in Table 2, include both instrumental error and error due to spectrometer drift. The data indicate that replicate
precision (as indicated by CV, coefficient of variance or standard deviation divided by the mean) is generally less than ± 20% for concentrations approaching the method detection limit. At higher concentrations, however, precision is generally less than ± 5%.

Table 2

<table>
<thead>
<tr>
<th>Site</th>
<th>Element</th>
<th>Mean (mg/kg)</th>
<th>SD (mg/kg)</th>
<th>CV (%)</th>
<th>MDL (mg/kg)</th>
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<tbody>
<tr>
<td>Site A</td>
<td>Pb</td>
<td>93</td>
<td>409</td>
<td>42</td>
<td>12.7</td>
</tr>
<tr>
<td>Site B</td>
<td>Pb</td>
<td>16</td>
<td>143</td>
<td>32</td>
<td>22.4</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>16</td>
<td>515</td>
<td>33</td>
<td>15.3</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>16</td>
<td>846</td>
<td>21</td>
<td>2.5</td>
</tr>
<tr>
<td>Site C</td>
<td>Pb</td>
<td>35</td>
<td>715</td>
<td>14</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>As</td>
<td>35</td>
<td>31</td>
<td>7</td>
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<tr>
<td></td>
<td>Cu</td>
<td>35</td>
<td>597</td>
<td>27</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>Mn</td>
<td>35</td>
<td>729</td>
<td>20</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>Fe</td>
<td>25</td>
<td>13,800</td>
<td>870</td>
<td>6.3</td>
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</table>

1 Method detection limit
2 Model 1 (20 calibration samples)

XRF DETECTION LIMITS

The limiting factor for XRF precision is the error associated with the X-ray counting process. This error results from the random nature in which X-rays are emitted from the radioisotope source, excited in the sample and counted by the detector. Thus, the lower limit of detection can be estimated from the standard deviation of the counting statistic. For this study, the instrument detection limit (IDL) of the spectrometer was calculated as three times the standard deviation of the counting statistic. It is important to note that the magnitude of the counting error, and thus the lower limit of detection, is directly related to both the total number of X-rays counted and the number of X-rays due to interference and background. Thus, the IDL varies as a function of both measurement time and sample matrix. For example, as shown in Table 1, the IDL for Pb at each site is 120 mg/kg (Site A), 75 mg/kg (Site B) and 45 mg/kg (Site C).

In a similar manner, the method detection limit (MDL) can be estimated from the replicate precision data (Table 2). As noted above, replicate measurements also include the error due to instrumental drift. A comparison of Table 2 with Table 1 indicates that, in general, MDLs are only slightly higher than IDLs, suggesting that instrumental drift was not a significant source of error for the XRF analyses.

XRF VERSUS TRADITIONAL METHODS: STATISTICAL TESTS ON PAIRED DATA

Following XRF analyses at each site, a selected number of ground specimens were sent to the U.S. EPA's CLP for confirmatory analyses. These samples were analyzed by either ICP or AA methods. The results obtained were then compared to the XRF results in order to evaluate the adequacy of the XRF method.

Figs. 1 through 5 are examples of the scatter diagrams obtained for XRF versus CLP analyses. To better evaluate the degree of fit of the data, statistical parameters were calculated. The results of these analyses are given in Table 3 and include the average relative deviation (d), relative standard deviation (Sd), t and Wilcoxon test statistic and the corresponding two-tailed t-test and Wilcoxon test critical values at the 95% confidence level. Readings below the MDL and significant outliers were not included in the statistical analysis.
mem (solid diagonal line) for Zn concentrations above approximately 1,000 mg/kg. Such deviations are probably the result of uncorrected matrix effects due to an inadequate number of calibration samples at higher concentrations. Below 1,000 mg/kg, the average relative deviation is 0% (see Table 3 and Fig. 2).

![Figure 4](image1)

**Figure 4**

XRF vs. CLP for As in Site B Soil Samples

![Figure 5](image2)

**Figure 5**

XRF vs. CLP for Fe in Site C Tailings Samples

The agreement between the XRF and CLP results was evaluated using Student's t-test and Wilcoxon's signed-rank test. The t-test determines whether the means of two normally distributed populations are the same, while the Wilcoxon test determines whether two populations are symmetric (same or similar shapes) and, if symmetric, whether they differ in location. Since normal distributions also are symmetric, the Wilcoxon test is probably the preferred test. The Wilcoxon test typically is termed a non-parametric or distribution-free test while the t-test is appropriate only for normally distributed data.

Through statistical analyses, it was determined that, for all elements, neither the CLP nor the XRF data were distributed normally. Rather, the populations more closely resembled log-normal symmetric distributions. Further, most element distributions were bimodal. Therefore, the t-test was applied to the log-transformed data, and the Wilcoxon test was applied to the non-transformed data. The results given in Table 3 were evaluated as follows:

- Agreement between the XRF and CLP populations was indicated for values of t between ± 1.95. Values of t outside of ± 1.95 indicated that the two population means were significantly different at the 95% confidence level.
- Agreement between the XRF and CLP populations was indicated for values of W.95 that fell outside of the critical range of W+ and W− (or both W+ and W− must be greater than W.95). For example, from Table 3, a value of W.95 = 171 is given for Site B Pb. Since this value lies outside of the W− = 203 and W+ = 358 range, the means of the two populations do not differ significantly at the 95% confidence level.

As indicated in Table 3 by the asterisk, both statistical tests indicate significant differences in the two methods only for Pb at Site C and Cu and Zn at Site B.

**SIGNIFICANCE OF THE NUMBER OF CALIBRATION SAMPLES**

To correct for absorption or enhancement interferences, an adequate number of calibration samples must be included in the regression model. The exact requirements will depend on the number of potentially interfering elements, their concentration range(s) and the requirements of the particular investigation. The greater the knowledge about how a sample matrix varies at a particular site, the more sophisticated the calibration model can be and, therefore, the more accurate the results.

To address the significance of the number of calibration samples, five different models were developed for Site C. Each model (1 through 5) covered similar analytical ranges but had pro-

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<table>
<thead>
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<th>Table 3</th>
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<tr>
<td>X-MET and CLP Comparison</td>
</tr>
<tr>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>Site</td>
</tr>
<tr>
<td>--------</td>
</tr>
<tr>
<td>Site A</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Site B</td>
</tr>
<tr>
<td>Site C</td>
</tr>
</tbody>
</table>

1 Model 5 (20 Calibration Samples)
* = significant difference

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<table>
<thead>
<tr>
<th>Table 4</th>
</tr>
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<tbody>
<tr>
<td>Site C Zinc versus Number of Calibration</td>
</tr>
<tr>
<td>------------------------------------------------</td>
</tr>
<tr>
<td>Number of Calibration Samples</td>
</tr>
<tr>
<td>---------------------------------</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>3</td>
</tr>
<tr>
<td>4</td>
</tr>
<tr>
<td>5</td>
</tr>
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gressively larger numbers of calibration samples. The results ob-
tained for each model then were compared to the corresponding
CLP results. As shown in Table 4, a significant improvement in
the comparison for Zn occurred between model 1 (5 calibration
samples) and model 2 (10 calibration samples), but the relative
improvement became increasingly less above 10 calibration samples.
This same trend was observed for the other Site C elements and
indicated that at least 10 calibration samples were necessary to
adequately analyze the samples (i.e., to correct for the variation
in matrix element concentrations), but more than 10 probably
were not necessary.

ANALYSIS OF VARIANCE

The purpose of this section is to address the various sources of
error associated with the XRF analytical technique. The
magnitude of these errors, as measured by their variances (S²),
then can be evaluated for the statistical significance relative to the
overall variance of each element (contaminant) within the sample
environment. In this way, it is possible to determine whether or
not the XRF technique can distinguish between different concentra-
tions of an element within a contaminated area and, therefore,
whether the technique is valid for screening analysis.

For this determination, total variance was broken down into
three components, as shown by:

\[ S_{\text{Tot}} = S_{\text{Sample}} + S_{\text{Calib}} + S_{\text{Anal}} \]  

where each variance component was evaluated as follows:

- Sample variance (S² Sample) was determined from the concen-
tration distribution of the entire population.
- Calibration variance (S² Calib) was determined from the stan-
dard deviation (SD) of the calibration curve (Table 1). This
variance included both the error due to uncorrected matrix ef-
fects and the error due to the uncertainty in calibration sample
concentrations.
- Analytical variance (S² Anal) was determined from the stan-
dard deviations of both replicate precision (Table 2) and sample
preparation. This variance included instrumental (counting)
error, drift error and error due to the nonhomogeneity of the
ground specimen.

Homogeneity was determined by analyzing separate aliquots of
the ground specimen. The standard deviation obtained from the
analytical variance was of the same order as that obtained for the replicate
precision analyses. Therefore, the error due to powder
nonhomogeneity was negligible for these samples.

The percentage of the total variance of each component is
shown in Table 5; the variance due to the samples (S² Sample) is
by far the primary component in all cases. Calibration variance
(S² Calib) and analytical variance (S² Anal) are relatively minor.
This result indicates that the XRF technique is adequate for
distinguishing between different concentrations of the con-
taminants at the three sites. In other words, the error due to the
X-MET calibration and analysis is insignificant relative to the
total variance of each element.

CONCLUSIONS

The data presented in this study indicate that the portable
X-ray fluorescence technique is suitable for screening As, Pb, Cu,
Zn and Fe in soils contaminated with mine wastes. The XRF ver-
sus CLP comparisons show no statistically significant differences
between the two analytical results for these elements over most
concentration ranges. As determined by the components of
variance analysis, the errors resulting from the XRF method are
minor compared to the sample variance at each of the three sites.
This result illustrates the ability of the XRF method to
discriminate between different contaminant levels under the
highly variable concentration conditions likely to be encountered
at mining waste sites.

<table>
<thead>
<tr>
<th>Site</th>
<th>Element</th>
<th>S² Sample</th>
<th>S² Calib</th>
<th>S² Anal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site A</td>
<td>Pb</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Site B</td>
<td>Pb</td>
<td>90</td>
<td>9</td>
<td>1</td>
</tr>
<tr>
<td>Cu</td>
<td>95</td>
<td>4</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>86</td>
<td>14</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Site C</td>
<td>Pb</td>
<td>76</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>As</td>
<td>64</td>
<td>19</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>87</td>
<td>12</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>98</td>
<td>2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>99</td>
<td>1</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

1 Model 5 (20 Calibration Samples)

The results confirm the importance of obtaining an adequate
number of calibration samples in order to model the matrix varia-
tions present within the samples. For Site C, at least 10 calibration
samples were necessary to correct for sample matrix effects.
Although more than 10 samples did further improve the calibra-
tion, the degree of improvement was not significant, especially in
light of the intended screening use of the XRF technique.

For the three sites discussed in this paper, a total of about 1,000
soil/tailings samples have been analyzed with the X-MET 840
X-ray fluorescence analyzer. These analyses have helped establish
heavy metal relationships, including both the spatial extent and
relative degree of contamination. The ease of sample preparation
and analysis in the field (i.e., rapid turnaround times) has been in-
valuable for on-site coordination of field sampling activities.
Also, selection of more representative sample sets for further
CLP characterization has been achieved. These advantages have
made XRF screening for heavy metals a very cost-effective means
of maximizing the amount of information obtained from a field
sampling campaign.

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