X-ray fluorescence: An accessible and effective technique for evaluation of hazards and economic potential associated with important mineral deposits in Nigeria


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X-ray fluorescence (XRF) was evaluated as a technique that can facilitate identification of potential environmental hazards associated with mining and ore processing as well as provide quantitative evaluation of the economic potential intrinsic to a mineral deposit. Four different geological samples were analyzed using energy dispersive XRF to demonstrate the utility of the technique. The samples were obtained from Dutsen Wai, Birnin Gwari, Dan Sadau, and Talata Mafara, Nigeria. Wolframite, molybdenum, lead and copper ore were analyzed respectively. Wolframite ore contained 61.93% WO3, molybdenum ore contained 16.0% MoO3, lead ore contained 83.1% PbO, and copper ore contained 23.26% CuO.

Key words: Geochemistry, hazards, X-ray fluorescence (XRF), Nigeria, mining, lead.

INTRODUCTION

Environmental exposure to products of unsafe mining and ore processing practices is associated with serious health risks. The poisoning from extraction of lead ore in Zamfara, Nigeria contributed to a health epidemic including death and long-term medical conditions. As a result, environmental remediation of lead contaminated sites was required and safer mining techniques have been adopted. Screening, monitoring, and evaluation of potential risks from exposure to geological materials associated with mining practices can be facilitated by accessible and effective tools and techniques such as X-ray fluorescence (XRF). The technique is also an effective method for rapid quantification of the economic potential in Nigeria’s mineral resources.

XRF is an analytical method to determine the chemical composition of a variety of materials including solids and liquids. XRF can also sometimes be used to determine the thickness and composition of layers and coatings (Thomas, 1982). The method is fast, accurate, non-destructive, and usually requires only a minimum of sample preparation. Applications are very broad and include the materials science and food industries along with ore mining, geochemistry, and environmental analysis of water and waste materials. XRF spectrometer systems can be divided into two main groups: Energy dispersive system (EDXRF) and wavelength dispersive...
system (WDXRF). The elements that can be analyzed and their detection levels depend mainly on the spectrometer system used. The elemental range for EDXRF goes from Sodium to Uranium (Na to U). For WDXRF the range is even wider, from Beryllium to Uranium (Be to U). The elemental concentration detection ranges can be as low as (sub) ppm to 100% (Funtua, 1996). Elements with high atomic numbers have better detection limits than lighter elements. The precision and accuracy of XRF analysis is very high when good standards are available for instrument calibration.

The total measurement time for a single XRF analysis depends on the number of elements to be determined and the required accuracy and varies between 2000 to 5000 s. XRF is a very sensitive technique and but samples must be free of contamination (Okunade, 1999). Even finger prints on a sample can alter the results of an analysis. For accurate results, the spectrometer conditions (e.g., the excitation energy of the X-ray generator) are tuned to the element to be analyzed. Inappropriate settings can lead to poor results. In EDXRF a whole spectrum is measured simultaneously and the area of the peak profile determines the concentration of an element. Measuring the height of the peak profile is an alternative, but information can be lost because the area of a peak profile is less sensitiveto noise than is the height of the same peak.

EDS spectrometers are different from WDS spectrometers in that they are smaller, simpler in design, and have fewer engineered parts. They can also use miniature X-ray tubes or gamma sources. This makes them cheaper and allows miniaturization and portability. This type of instrument is commonly used for portable quality control screening applications, such as testing toys for lead (Pb) content, sorting scrap metals, and measuring the lead content of residential paint. They are very effective for high-speed, multi-elemental analysis. Field portable XRF analyzers currently on the market weigh less than 2 kg, and have limits of detection on the order of 2 parts per million (ppm) of lead (Pb) in pure sand.

The aim of the project is to demonstrate the utility of EDXRF to determine mineral composition by analyzing geological samples from ore mining regions in Nigeria. Results of analyses reported here will provide a basis for developing protocols to aid in detection, evaluation, and remediation of geologic hazards associated with ore body mining in Nigeria and provides a robust tool for economic evaluation of Nigeria's natural resources.

**MATERIALS AND METHODS**

Four geological samples were obtained from four different sites (Dutsenwai, Birningwari, Dansadau and Talatar Mafara) for analysis. In 2010, more than 400 children died in Zamfara, Nigeria from acute lead poisoning caused by unsafe mining and processing lead-containing gold ore. People grinding the ore, often in and around their homes, contaminated at least 180 villages over a wide area. Even large-scale gold mining has significant mercury releases associated with ore processing. It is now known that significant mercury emissions result from cyanide leaching and even from mine tailings where no mercury has been added. Prospect in Birningwari with deposits of Iron and granite led to the suspicion of molybdenum ore. Prospect in Dutsenwai led to the suspicion of wolframite in the area with deposits of iron ore.

For EDXRF analysis, the samples were ground manually in an agate mortar and pestle to grain size of less than 125 um. Pellets of 19 mm diameter were prepared from 0.3 to 0.5 g of powder mixed with three drops of organic liquid binder (PVC in Toluene) in a hydraulic press. EDXRF measurements were performed using an annular 25mcCi 109Cd as the excitation source that emits Ag-K X-rays (22.1 keV) in which case all elements with lower characteristic excitation energies were accessible for detection in the samples. The system consists further more of a Si (Li) detector with resolution of 170 ev for the 5.90 kev line coupled to a computer controlled analog to digital converter (ADC) card (Iwanczyk et al., 1996).

The Mo target serves as a source of monochromatic X-rays which are excited through the sample by primary radiation and then penetrate the sample on the way to the detector. In this way, the absorption factor is experimentally determined which the program uses in the quantification of concentration of the elements. In addition, the contribution to the Mo-K peak intensity by the Zr-K is subtracted for each sample (Boer, 1999).

**RESULTS AND DISCUSSION**

The following are the geological samples analyzed using energy dispersive XRF. From the suspected wolframite sample, 61.93% wolframite ore was obtained with trace impurities as shown in Table 1. 16% of molybdenum ore was obtained from the suspected molybdenum sample with 52.2% silica and trace ore impurities as shown in Table 2. 83.1% lead ore was obtained from the lead ore.

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**Table 1. Wolframite soil analysis.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Al2O3</th>
<th>P2O5</th>
<th>SO3</th>
<th>CaO</th>
<th>TiO2</th>
<th>Cr2O3</th>
<th>MnO</th>
<th>Fe2O3</th>
<th>CuO</th>
<th>SrO</th>
<th>MoO3</th>
<th>WO3</th>
<th>BaO</th>
<th>Rh2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (%)</td>
<td>0.79</td>
<td>7.5</td>
<td>0.67</td>
<td>0.4</td>
<td>19.55</td>
<td>0.02</td>
<td>0.22</td>
<td>0.21</td>
<td>4.76</td>
<td>0.12</td>
<td>3.2</td>
<td>61.93</td>
<td>0.1</td>
<td>0.46</td>
</tr>
</tbody>
</table>

**Table 2. Molybdenum ore soil analysis.**

<table>
<thead>
<tr>
<th>Compound</th>
<th>SiO2</th>
<th>P2O5</th>
<th>SO3</th>
<th>CaO</th>
<th>TiO2</th>
<th>V2O5</th>
<th>MnO</th>
<th>Fe2O3</th>
<th>ZnO</th>
<th>CuO</th>
<th>Cl</th>
<th>MoO3</th>
<th>As2O3</th>
<th>K2O</th>
<th>PbO</th>
<th>Re2O7</th>
<th>Rh2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (%)</td>
<td>52.2</td>
<td>5.1</td>
<td>8.3</td>
<td>3.03</td>
<td>1.25</td>
<td>0.02</td>
<td>5.86</td>
<td>3.32</td>
<td>0.2</td>
<td>0.1</td>
<td>0.5</td>
<td>16</td>
<td>3.2</td>
<td>2.9</td>
<td>1.0</td>
<td>0.23</td>
<td>0.23</td>
</tr>
</tbody>
</table>
suspected sample as shown in Table 3. 23.26% copper ore was obtained from the suspected copper ore sample with 53.8% silica and traces of impurities as shown in Table 4.

Wolframite is a highly valued ore as the main source of the metal tungsten, a strong and quite dense material with a high melting temperature used for electric filaments and armor-piercing ammunition, as well as hard tungsten carbide machine tools. Molybdenum ore sample contains molybdenum which is a valuable alloying agent, as it contributes to the hardenability and toughness of quenched and tempered steels. It also improves the strength of steel at high temperatures. Molybdenum is used in alloys, electrodes and catalysts. The lead ore sample contains lead which is a major constituent of the lead-acid battery used extensively in car batteries. It is used as a coloring element in ceramic glazes, as projectiles, in some candles to thicken the wick. It is the traditional base metal for organ pipes, and it is used as electrodes in the process of electrolysis. One if its major application is in the glass of computer and television screens, where it shields the viewer from radiation. Other applications are in sheeting, cables, solders, lead crystal glassware, ammunitions, and bearings and as weight in sport equipment. Copper ore sample contains copper which is used for electrical equipment (60%); construction, such as roofing and plumbing (20%); industrial machinery, such as heat exchangers (15%) and alloys (5%). The main long established copper alloys are bronze, brass (a copper-zinc alloy) and copper-tin-zinc.

**Conclusion**

This report demonstrates the utility of the X-ray fluorescence method to obtain fast and accurate elemental analysis of geologic samples the extraction of which could be detrimental to the environment and present serious health hazards to the population of Nigeria. The work has analyzed four different geological samples which represent a variety of economically important ore mining interests in Nigeria. The samples were obtained from four different sites ("Dutsenwai", "Birningwari", "Dansadau" and "Talatar Mafara") for analysis of wolframite, molybdenum, lead and copper ore respectively. Wolframite ore contained 61.93% WO3, molybdenum ore contained 16.0% MoO3, lead ore contained 83.1% PbO, and copper ore contained 23.26% CuO (Figures 1, 2, 3 and 4). The mining sector is responsible for some of the largest releases of heavy metals into the environment of any industry. It also releases other air pollutants including sulfur dioxide and nitrogen oxides in addition to leaving behind tons of waste tailings, slag, and acid drainage. Occupational and environmental exposure to heavy metals, silica, and asbestos can occur during mining and milling operations. The smelting process (extracting the metal from the ore) is associated with the highest exposures and environmental releases. The hazards to human health caused by exposure to heavy metals including lead, cadmium and mercury and other metal like copper, molybdenum and wolfram have been thoroughly documented. These metals are associated with a range of neurological deficits in both children and adults in addition to a range of other systemic effects. Exposure to airborne silica and asbestos can cause lung cancer, pneumoconiosis and numerous other health effects while pollution controls can minimize exposures to workers and surrounding communities, these safeguards are often absent in mining and smelting operations in developing countries. Even relatively efficient mining operations result in enormous waste, emissions to air and water, and a legacy of environmental contamination in nearby communities. Around the world, unsafe mining and smelting practices have been responsible for a continuing series of environmental and human health disasters, which cause great human tragedy and undermine social stability, economic development and sustainability goals.

Partnerships between scientists, the mining industry, and health officials will be required to create effective environmental protection policies that include both detection and monitoring of hazards as well as remediation of known toxins that present immediate risk to the public. A technique that can facilitate these activities

<table>
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<th>Compound</th>
<th>Al2O3</th>
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<th>TiO2</th>
<th>K2O</th>
<th>MnO</th>
<th>Fe2O3</th>
<th>ZnO</th>
<th>CuO</th>
<th>NiO</th>
<th>Re2O7</th>
<th>OsO4</th>
<th>PbO</th>
<th>BaO</th>
<th>Cr2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (%)</td>
<td>1.2</td>
<td>9.66</td>
<td>3.5</td>
<td>0.21</td>
<td>0.094</td>
<td>0.32</td>
<td>0.025</td>
<td>0.399</td>
<td>0.2</td>
<td>0.369</td>
<td>0.033</td>
<td>0.15</td>
<td>0.15</td>
<td>83.1</td>
<td>0.57</td>
<td>0.061</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
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<th>V2O5</th>
<th>MnO</th>
<th>Fe2O3</th>
<th>CuO</th>
<th>NiO</th>
<th>MoO3</th>
<th>BaO</th>
<th>Bi2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (%)</td>
<td>7.0</td>
<td>53.8</td>
<td>0.5</td>
<td>5.02</td>
<td>0.2</td>
<td>0.046</td>
<td>0.208</td>
<td>7.814</td>
<td>23.26</td>
<td>0.048</td>
<td>0.3</td>
<td>0.12</td>
<td>1.2</td>
</tr>
</tbody>
</table>
Figure 1. Wolframite soil analysis.

Figure 2. Molybdenum soil analysis.

Figure 3. Lead ore soil analysis.
and that is both affordable and readily accessible is EDXRF. This technique can also provide a rapid evaluation of the economic potential of a geologic deposit thereby proving its value both to the mining industry and to the health of the community impacted by the ore extraction process.

RECOMMENDATION

Researchers should be encouraged and fully supported by the government of the Federal Republic of Nigeria. These goals can be met by ensuring that more research centers are created and encouraged by robust funding sources and that industry is incentivized to partner with researchers to preserve the environment for the future.

REFERENCES