



EVALUATION OF THE LEVEL OF THORIUM IN YARGALMA GOLD ORE BY X-RAY FLUORESCENCE SPECTROMETRY

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ABSTRACT

Energy-dispersive X-ray fluorescence spectrometry following a sample pretreatment was used to evaluate the elemental composition of Yargalma gold ore. The Yargalma gold ore contained Si(31.43%), Pb(8.72%), Fe(2.78%), Au(1.02%), Cu(0.39%), S(0.29%) Ba(0.26%), W(0.14%), Th(0.10%), K(0.07%), Ca(0.06%), Cr(0.06%), Ti(0.01%), Ni(0.02%), Mn(0.02%), and Hg(0.02%) respectively. The analytical study for the first time has provided a baseline data on the level of thorium and other elemental composition in Yargalma gold ore, a baseline information on the anthropogenic impact of environmental pollution in the mining community and the basis for planning management strategy to achieve better environmental quality. The main health concern for environmental exposure to thorium is generally bone cancer, blood disorders and liver tumors.

Key words: Thorium, Goldore, Yargalma, Pellet, X-ray Fluorescence Spectrometry

INTRODUCTION

Thorium is alpha emitting radioactive element that occurs naturally in low concentrations in the earth's crust. Of the 26 known isotopes of thorium only 12 have half-lives greater than one second, and of these only 3 have half-lives sufficiently long to warrant health concern (IAEA, 1995). The members of the decay series poses significantly differing physical and radiological characteristics which greatly influence the potential radiological hazards associated with wastes arising from mining and minerals processing activities. There are numerous mechanisms by which radionuclide's associated with mining and minerals processing waste can enter or give rise to exposure pathways to humans. These may arise during both the operational and post close-out phases (US-EPA, 1989). The main health concern for environmental exposures to thorium is generally bone cancer, blood disorders and liver tumors (US-EPA, 1989).

Environmental exposure to products of unsafe mining and ore processing activities is associated with serious health implications. The poisoning from extraction of gold ore contaminated with lead in Zamfara, Nigeria, contributed to a health epidemic including death and long-term medical conditions (UNEP, 2011). 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 spectrometry (XRFs). The technique is also an effective method for rapid quantification of the economic potential in Nigeria's mineral resources. XRFs is a powerful technique in analytical chemistry. XRFs are a rapid, relatively non-destructive chemical or elemental analysis of rocks, minerals, sediments, fluids and soils

(Fisher *et al.*, 2014). Its purpose is to identify the elemental abundances of the sample. It is used in a wide range of applications, including mining, metallurgy, soil surveys, cement production, ceramic and glass manufacturing, petroleum industry, field analysis in geological and environmental studies, and research in igneous, sedimentary and metamorphic petrology etc (Fetton, 1997 and Jurado-Lopen *et al.*, 2006). XRFs 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. XRFs systems can be divided into two main groups: Energy dispersive system (EDXRFs) and wavelength dispersive system (WDXRFs).

The XRFs method depends on fundamental principles-the geological sample is bombarded by high-energy, short wavelength X-ray. This radiation excites the sample and dislodges the electrons in inner orbital causing ionization of the geological sample. With space in the lower orbitals open, electrons in higher orbitals fall into the lower ones. This releases a secondary radiation, the fluorescence, from the sample.

Energy is released during this process because the binding energy of a low orbital is less than that of a higher orbital. The energy released is roughly equal to the difference in the binding energies of the two orbitals involved. Both the energy and the wavelengths of the secondary radiation are much less than the original X-ray. Characteristic of the secondary radiation such as energy and wavelength are specific to element whose atom they were released from. These can be detected and converted into computer generated data. The XRFs machines output, coupled with a quantitative analysis, will report what percent of each element is within the sample.

However, in XRFs, if the detector allows the determination of the energy of the photon when it is detected, it is known as energy dispersive X-ray fluorescence spectrometry (EDXRFs) but if the detector allows the determination of the wavelength of the photon when it is detected after the photons are separated by diffraction on a single crystal, before being detected, it is known as wavelength dispersive XRFs (WDXRFs). The WDXRFs is occasionally used to scan a wide range of wavelengths (Petrovic *et al.*, 2006).

The elements that can be analyzed and their detection levels depend mainly on the spectrometer system used. The elemental range for EDXRFs goes from sodium to uranium (Na to U). For WDXRFs, the range is even wider, from Berllium to uranium (Be to U). The elemental concentration detection ranges can be as low (sub) ppm to 100% (Funtua, 1996). Elements with high atomic numbers have better detection limits than higher elements. The precision and accuracy of XRFs analysis is very high when good standards are available for instrument calibration (Robertson and Feather, 2004).

The total measurement time for a single XRFs analysis depends on the number of elements to be determined and the required accuracy and varies between 2000 to 5000 seconds. XRFs is a very sensitive technique 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 EDXRFs, 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 sensitive to noise than is the height of the same peak.

EDXRF spectrometers are different from WDXRFs spectrometers in that they are smaller, simpler in design, and have fewer engineered parts. They can also use miniature X-ray tubes. 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 in the market weigh less than 2kg, and have limits of detection on the order of 2 parts per million (PPM) of lead (Pb) in pure sand (Jurado *et al.*, 2006).

There is increase and domestication of mining and processing activities which is the mainstay of the local economy, in many villages in Zamfara state, within the last years, with greater involvement of women and children processing lead contaminated gold ore in their home environment, including the use of cooking

utensils for mining activities. Mining activities have potentially impacted negatively on public health, environmental safety and sustainable agriculture in Zamfara State. Indeed, Zamfara state is known for being the site of the worst lead poisoning outbreak in modern history, which is an ongoing crisis (UNEP, 2011). Acute lead toxicity renders the soil unsuitable for plant growth and destroys the biodiversity (Ghosh and Singh, 2005).

A series of lead poisoning in Zamfara state, Northern Nigeria, lead to the deaths of at least 163 people between March and June, 2010, including 111 children, under the age of five years. Since the lead poisoning crisis was reported, it has been estimated that at least 10, 000 people of which 2, 000 children under 5 years of age are in acute danger of death (Reuters, 2010).

The aim of this study is to demonstrate the application of EDXRFs to evaluate the elemental composition of gold ore samples collected from Yargalma mining site of Zamfara state and assess the toxicity of the mining wastes. Results of analysis reported in this study will provide a basis for developing protocols to aid in detection, evaluation, exploitation and remediation of geological hazards associated with metal ore mining and processing in Nigeria and provides a robust tool for economic evaluation and diversification of Nigeria's natural resources.

MATERIALS AND METHODS

Sample Collection and Pre-Treatment

The gold ore samples used for this study were collected from Yargalma local gold ore mining site in Bukkuyum, Zamfara State, North West, Nigeria. Sampling was conducted by collecting six gold ore samples from a gold ore heap, two each from the top, middle and bottom and same were placed into labeled polyethylene homogenization container, and mixed thoroughly to obtain a homogenous sample representative of the entire sampling interval. When compositing was completed, the labeled homogenization polyethylene bags were closed tightly and returned same to the laboratory for pretreatment and analysis (Mason, 1983). The gold ore samples were air dried under laboratory conditions for two weeks.

Sample Analysis

The air dried gold ore samples were ground in agate mortar and pistil and sieved to 75µm particle sizes. Four(4)g of the sieved samples were intimately mixed with 1g of lithium tetraborate binder ($\text{Li}_2\text{B}_4\text{O}_7$) and pressed in a mould under a pressure of 10-15 tons/in² to a pellet. The pellets in triplicate were dried at 110°C for 30 minutes in an oven to get rid of adsorbed moisture and then stored in desiccators for analysis.

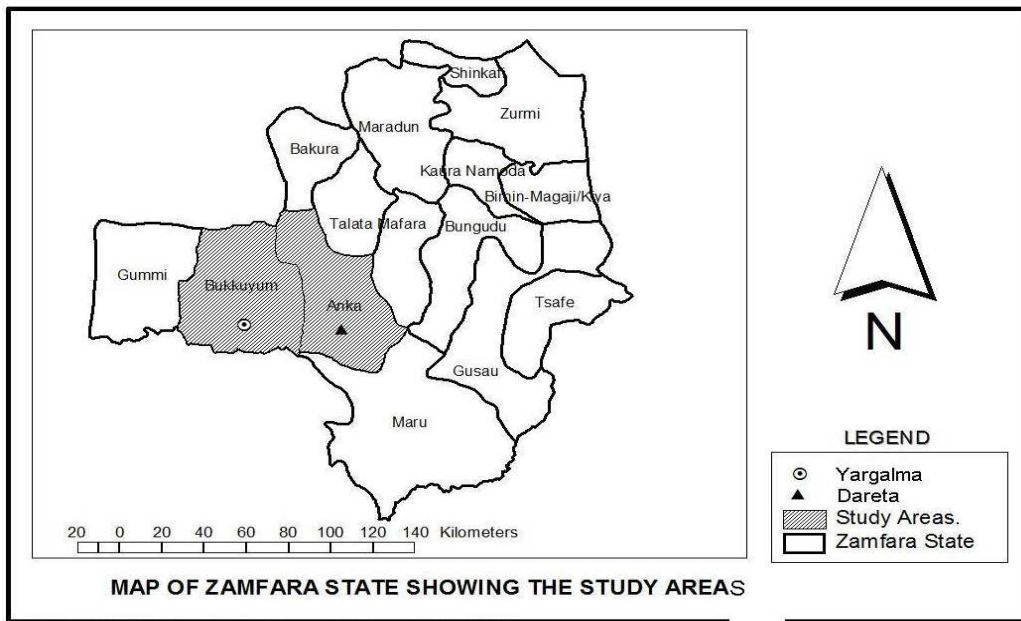


Fig. 1: Map of Zamfara State Showing the Study Areas

The analysis was carried out using EDXRF spectrometer model Lelyweg1, 760ZEA, Almelo, Netherland. EDXRF measurements were performed using an annular 25mci 109Cd as the excitation source that emits Ag-K X-rays (22.1Kev) 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 170ev for the 5.90keV 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 used 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 (De Boer, 1999).

RESULTS AND DISCUSSION

The studied area is shown in figure 1. Figure 2, shows the average elemental composition of the Yargalma gold ore as analyzed. The following are the average percentage elemental composition of the Yargalma gold ore, as analyzed and include: Si(31.43%), Pb(8.72%), Fe(2.78%), Au(1.02%), Cu(0.39%), S(0.29%), Ba(0.26%), W(0.14%), Th(0.10%), K(0.07%), Ca(0.06%), Cr(0.06%), Ti(0.05%), Ni(0.02%), Mn(0.02) and Hg (0.01%) respectively.

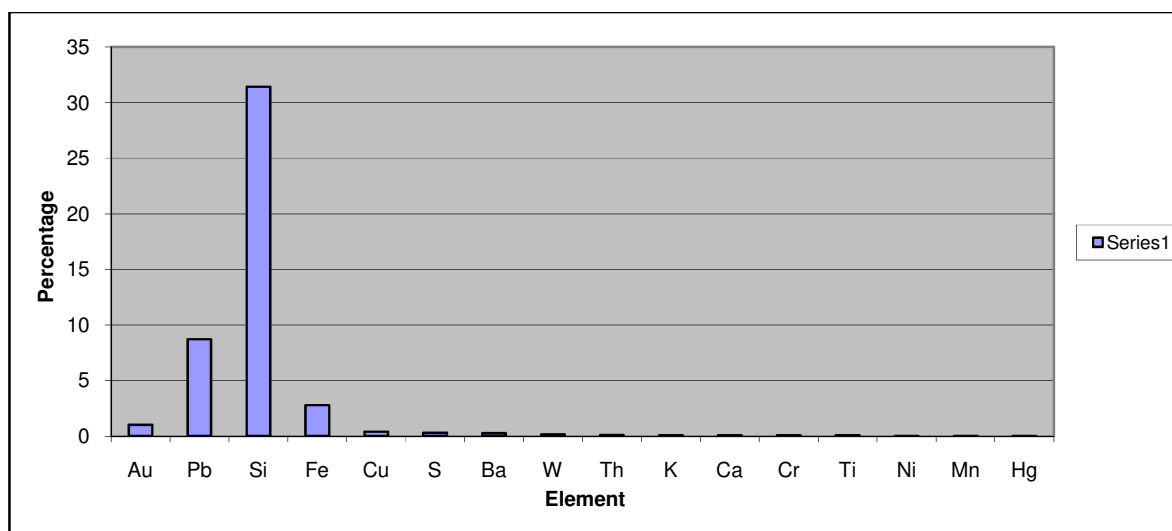


Fig. 2: Elemental Composition of Yargalma Gold Bearing Rock

The analytical result provides the elemental constituents of the Yargalma gold ore, baseline information on the anthropogenic impact of environmental pollution in the mining community and basis for planning management strategy to achieve better environmental quality. It could be recalled that there is increase and domestication of mining activities in many villages in Zamfara state, especially Yargalma village, within the last years with greater involvement of women and children, processing lead contaminated gold ore in their home environments. Thorium (Th) which is alpha emitting radioactive element, mercury and lead are toxic even in low concentrations, Galas-Gorcher(1999) are constituent parts of the Yargalma gold ore. Unless adequate measures are put in place to strictly regulate mining activities in Yargalma village by government agencies, the incidence of mortality and morbidity arising from mining and processing activities will continue to be on the increase.

REFERENCES

- DeBoer, D.K.G (1999). Calculation of X-Ray Fluorescence Intensities from Bulk and Multi Layer Samples. *X-Ray Spectrometry* 19, 145-154.
- Fisher, L. Gazley, M.F., Baensch, A., Barnes, S. J., Cleverly, J. and Duclaux, G. (2004). Resolution of Geochemical and Lithostratigraphic Complexity: a Workflow for Application of Portable X-ray Fluorescence to mineral Exploration. *Geochem. Explor. Environ Anal*; 14, (2), 149-159.
- Fitton, G. (1997). X-Ray Fluorescence Spectrometry; in Gill, R.(ed), *Modern Analytical, Geochemistry: An Introduction to Quantitative Chemical analysis for Earth, Environmental and Material Science*: Addison Wesley Longman, UK.
- Funtua, I. (1996). Application of the Transmission Emission Method in EDXRF for the Determination of Trace Element in Geological and Biological Materials. *J. Trace Microprobe Tech.* (3) 17:293-297.
- Galas-Gorcher, H. (1991). Dietary Intake of Pesticide Residues: Cadmium, Mercury and Lead. *Food Adds.* 8:793-80.
- Ghosh, M. and Singh, S.P. (2005). A Review Phytoremediation of Heavy Metals and Utilization of its by Products. *Applied Ecol. Environ. Rex.* 73:1-18.
- International Atomic Energy Agency (IAEA). (1995). *Classification of Radioactive Waste*, IAEA-safety series No. 111-G-1-1, Vienna.
- Iwanczyk, J.S. Patt, B.E., Wang, V.J., Khusacioz, A.K.H. (1996). Comparison of Hg¹², Cd, Te and Si (P-i-n) X-Ray Detector. *NIM A.* PP 186-192.
- Jurado-Lopez, A., Luque, M. D., and Perez, M.R. (2006). Application of Energy Dispersive X-Ray Fluorescence to Jewellery Samples Determining Gold and Silver. *Gold Bulletin*, 39 (1), 16-21.
- Mason, B.J. (1983). Preparation of Sampling Protocol: Technique and strategies. EPA 60014:83-20.
- Okeanade, I.O.(1999). Sampling Method and X-Ray Fluorescence Analysis Procedure in Air Pollution Studies. *Nuclear Methods in National Development Proceedings of the First National Conference on nuclear Methods (NCNM) Held at Congo Conference Hotel, Zaria, Nigeria*
- Petrovic, N., Budelan, D., Cokic, S., and Nestic, B. (2001). The Determination of the Content of Gold and Silver in Geological Samples. *Journal of the Serbian Chemical Society.* 66 (1) 45-52.
- Reuters, T. (2010). Lead Poisoning from Mining kills 163 in Nigeria. <http://ukreuters.com/article.com/article/idUKTPRE6535920100604>. Retrieved 4th June, 2016.
- Robertson, M.E.A, and Feather, C.E. (2004). Determination of Gold, Platinum and Uranium in South African Ores by High-Energy XRF Spectrometry; *X-ray spectrometry*, 33, 164-173.
- Thomas, G.D. S. (1982). X-Ray Fluorescence Analysis of Elemental Samples. Barnes and Nobles links.
- United Nation Environmental Protection (UNEP). (2011). Lead Poisoning, Northern Nigeria, Outbreak, UNEP, Zamfara.
- United States Environmental Protection Agency (USEPA) (1989). Health and Environmental Protection Standards for Uranium and Thorium Mill Tailings, 40CFR Part 192, 7-1-89 Edu. EPA, Washington, DC.

CONCLUSION

This study demonstrates the application of the EDXRFs technique to obtain fast and accurate elemental composition of geological material and also exposes the anthropogenic impact of the waste tailings on environmental degradation and human health. The mining industry is responsible for the largest releases of heavy and toxic metals into the environment more than 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. The hazards of human health caused by exposure to heavy metals including thorium, lead, cadmium and mercury are associated with a range of neurological deficits in both children and adults. The EDXRF technique can also provide a rapid evaluation of the economic potential of a geological deposits thereby proving its value both to the mining industry and to the health of the community impacted by the ore extraction process.