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Determination of lead (Pb) concentration from suspected lead-rich gold ores and tailings from Kebbi State, Nigeria

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A B S T R A C T:

Lead poisoning in children has reached epidemic status due to the mining and processing of suspected lead-rich gold ores in residential areas in northwestern Nigeria. Five gold ore samples and five gold ore tailings were collected from mines and mills in Kebbi State, Nigeria, which were subsequently, characterized using proton-induced X-ray emission technology. The results obtained showed that both the gold ores and the tailings are several times higher than average (6.60 ppm) in lead. Thus, this would prepare the area for lead poisoning in children if residential gold mining and processing were allowed to flourish.

Keywords: Lead poisoning, tailings, Kebbi State, Nigeria, Proton induced X-ray emission

1. INTRODUCTION

Lead (Pb) poisoning in children from illegal gold mining in north-west Nigeria is of concern to the Nigerian government and the World Health Organization (WHO). In 2010/2011, many children from the Nigerian state of Zamfara were observed dying from a mysterious disease. At first the doctors could not explain the cause, but investigations and investigations later revealed that it was Pb poison. In fact, illegal gold mining is rampant in the area; Rocks believed to contain gold are excavated underground (15 to 20 m). It is then crushed, the crushed rock is transported to grinding mills in the villages to be pulverized into fine grains. Thereafter, the gold is extracted from the grains by washing or by using mercury. Processing takes place in their homes or at the common water source for the community. However, what the miners don't realize is that the gold ore in the area is lead-rich. After extracting the gold, they leave residues in and around their homes where children play. This eventually led to the epidemic: lead poisoning epidemic in children.

The presence of heavy metals in the residues of ores is a serious hazard to human health, especially at elevated concentrations. Some of them are Pb, Fe, Zn, Ti, V, Ni. etc. If the concentration of any element in the residues exceeds the essential limit, it becomes toxic and harmful to the environment and living beings as well. Therefore, it is important to have detailed information for studies on the trace element profile of gold ore tailings so that appropriate precautions can be taken to improve the environment (Samaila, 2018).

Elemental analysis of gold matrices from Zamfara State was performed by Bello et al. (2012) carried out. Their results obtained show that lead concentrations are exponentially above the average normally found in gold matrices. The average lead concentration in gold matrices around the world is 6.60 ppm (parts per million). On November 11, 2011, WHO reported in Global Report and Alert that lead poisoning from mining activities in Zamfara State, Nigeria, detected in March 2010, continues to affect villagers in three Local Government Areas (LGAs): Anka, Bukkuyum and Maru. While the full extent of the problem is still not fully understood, a survey conducted by the US Centers for Disease Control and Prevention (US CDC) on behalf of Nigeria's Federal Department of Health has found at least 43 villages in Zamfara state with confirmed cases of lead poisoning (blood lead concentration >10 g/dL) (Environmental Health News, 2013). On August 30, 2012, Reporter365.com reported that processing gold ore in residential areas in Zamfara State was banned. It further noted that although the awareness campaign on the dangers of gold processing was underway, artisanal miners continued their activities. As a result, new cases of lead poisoning were discovered in the state capital.

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This research collected gold ore samples from mine sites in Kebbi State and performed multi-element analysis using the proton induced X-ray emission (PIXE) technique. The choice of technique was influenced by her mastery of the work being done. Although neutron activation analysis is available at the Nigerian Research Reactor (NIRR-1), one element of interest (lead) was not analyzed because of its high affinity for neutrons.

2.0 Material and Method

2.1 Sample collection and preparation

Ten samples collected: five gold ore samples and five tailings from five mines and five processing sites respectively. To avoid contamination, each was packed separately. They were then taken to the Energy and Development Center where they were pulverized to the level required for the investigative technique. After pulverization, ten pellets were produced (one pellet from each gold ore sample and one from each tailing). The PIXE technique was then subjected to quality control to test its performance. The standard used in the proficiency test was NIST 278 (Obsidian Rock). The standard was irradiated in the accelerator for ten minutes, after which it was analyzed. The projectile used to activate the standard was a proton. The proton was used instead of other projectiles (electron, alpha) because after activation it generates less background radiation (bremsstrahlung) in the sample. Five pellets each are made from tailings and gold ores and then attached to the sample holder (special ladder, similar to a slide projector, which allows the analysis of many hundreds in a row). The aluminum foil paper is placed behind the pellets before it is attached to the special ladder to avoid the masking tape sticking to the pellets. It is then carefully lowered into the sample chamber. Once the sample is securely placed in the sample chamber, the chamber is evacuated by a special vacuum pump attached to the chamber. The sample is now ready for irradiation (Samaila, 2019)

2.2 Theory of Method (PIXE)

The PIXE technique is a multi-element analytical method that allows absolute determination of concentrations, but in the laboratory the comparative method is usually preferred because of the significant uncertainties in literature values for nuclear parameters. . In this approach, a standard containing a known amount of the element to be determined is irradiated along with the samples. Proton flux, cross-sections, irradiation times, and all other variables associated with counting are assumed to be constant for both the standard and the sample.
Equation of the absolute method is given as:

$$Y(Z) = \frac{N_{av}\omega_{K,Z}b_{K,Z}t_{K,Z}\varepsilon_Z^i\Omega/4}{A_z} N_p C_Z \int_{E_0}^{E_f} \frac{\sigma_Z(E)T_Z(E)}{S_M(E)} dE \ldots\ldots\ldots (1)$$

where Y(Z) is the elemental concentration, $E_0$and E_f are the entry and exit proton energies, **Ω**/4 is the fractional solid angle subtended by the detector, ε_Z^i the detector's intrinsic efficiency, and $t_{K,Z}$the transmission through any absorbers interposed between specimen and detector. Whereas the equation of comparative method is:

$$\frac{C_Z(SP)}{C_Z(ST)} = \frac{Y_Z(SP)}{Y_Z(ST)} \frac{I_Z(ST)}{I_Z(SP)} \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

When specimens are thick enough to stop the beam, then we have $E_f = 0$ in Eq. 1. For this work the samples are thick enough to stop the beam of protons. It is clear that all the matrix (M) effect (i.e., those due to proton slowing and X-ray attenuation) are contained in the integral, which we denoted by $I_Z(M)$ where M denotes the specimen (SP) or the standard (ST).The standards are usually single elements or very simple compounds containing the elements of interest or their near neighbours in the chart of nuclides. The major merit of this ratio method is its cancellation of instrumental factors such as solid angle, efficiency, and calibration factors for charge integration. This is especially important given the practical difficulties in obtaining accurate knowledge of the detector's line shape and intrinsic efficiency at the low X-ray energies characteristic of the light elements that are so often the major elements in environmental specimens. It also alleviates the problems of the deteriorating accuracy with which K-shell ionization cross sections and fluorescence yields are known as the atomic number falls from Z = 20 to 10.
Proton-induced X-ray emission as an analytical technique is a relatively recent innovation, first reported in 1970 by collaborators at the Lund Institute of Technology. PIXE, like other X-ray spectroscopic techniques used for elemental analysis, uses the X-rays emitted by the atoms in a sample when that sample is exposed to an excitation source. Using a proton beam as an excitation source offers several advantages over other X-ray techniques (Samaila, 2019). Among them are; a higher data accumulation rate across the entire periodic table and better overall sensitivities, especially for the lower atomic number elements. Of course, the main disadvantage of PIXE is that it requires the use of a particle accelerator. The concentrations of the essential elements (P, Cl, K, Ca, Mn, Fe, Cu and Zn) of some native and imported rice species commonly consumed in Nigeria were examined. This is done in order to select the rice with high nutrient content to combat malnutrition, especially among children (Samaila, 2019.

3.0 Results and Discussion

After activation and analysis of standard, the result obtained was tabulated below:

Table 1: Certify concentration values and analyzed concentration values of standard (Obsidian rock)

Symbol	Concentration (ppm)	Cert. Values (ppm)
Si	341397±6281	341436
Cl	584 ±88	
K	34511 ±106	34530
Ca	7020 ±90	7026
Ti	1439 ±22	1469
V	30 ±15	
Mn	401 ±10	403
Fe	14275 ±51	14268
Cu	6.8 ±3	5.9
Zn	55 ±6	55*
Rb	127 ±18	127.5
Sr	64 ±13	63.5
Zr	375 ±39	
Ba	1222 ±165	1140*
Ce	67 ±42	62.2*

$*\ Info\ values$

From Table 1 it can be safely assumed that the PIXE technique had a good reputation in the analysis of geological samples. Satisfied with the result of the analyzed standard, the technique was then applied to the gold ores and tailings. All parameters used during activation and analysis of the standard (irradiation time, beam flux, and detector angle) were retained. The results obtained are tabulated in Tables 2 and 3

Table 2: Result depicting elemental concentration (ppm) in Tailings

Analyte	Sam F	Sam G	Sam H	Sam I	Sam J
Pb	3826±99	791±53	864±49	_	1030±44
Si	287099 ± 6086	352624±6241	475067±6745	326131±6261	550376±6549
P	1178 ±702		2120±555	663±732	1090±537
S	1355 ± 176	621.±149	5102±172		7413±183
K	20231±84	20144±84	3120±39	41904±117	3842±44
Ca	1574±54	147±49	123±20	1663±89	155±23
Ti	13570 ±51	723±17	97±11	1954±24	153±14
V	346±45				
Cr	747±15	1141±15	1281±15	1281±15	1339 ±17
Mn	399±15			102.±10.9	
Fe	50798±96	24904±64	22837±61	124072±47	333870±77
Ni	14±5			12.6±3	
Cu	408±10	61.7±5.9	46±4.6	7.4±2.7	465±11
Zn	291±12	34±8	28±5.9	52±5	
Rb	122±21	87±19	48.4±12.7	88±16	
Sr	502±32	104±18.8	33.4±11.8	207±23	39±16
Zr	206±43	167±29		480±42	
Ba		549±110	329±58	1331±196	538±68

Given that the average lead concentration in gold ore is 6.60 ppm, Table 2 shows that all samples have a concentration well above the average. Samples F and J were notable for being richer in lead compared to the other samples. The lead concentration in Sample I is below detection

Table 3: Elemental concentration (ppm) in gold ores.

Analyte	Sam A	Sam B	Sam C	Sam D	Sam E
Pb	942±50	444±35	3279±93	2119±74	529±49
Si	401634± 6707	444312±6575	373672±6389	437781±6610	443747±6567
S	5512±195	1134±146	4332±198	6319±192	451±131
K	20605±84	7808±55	21195±86	10365±62	9133±59
Ca	248±49	522±29	376±51	1439±38	267±31
Ti	703±16	332±13	2148±24	1517±19	644±16
Cr	751±12	550±11	736±13	614±12	604±12
Fe	18568±57	19161±57	33595±77	18804±56	15148±51
Cu	2451±21	97.5±4.9	272±8	402±9	34±5
Zn	32±10	25.4±4.5	30±9	35.9±6.8	-
Rb	52±13	50±12	82±20	33±11	-
Sr	57±14	63±13	127±23	80±15	-
Zr	138±26	76±23	175±34	240±32	148±31
Ba	607±107	382±76	625±211	-	409±102
P	-	879±557	-	-	-
V	-	36.3±9.7	-	47±13	-
Mn	-	96.1±9.8	-	146±10	66.±10
Cl	-	-	116±77	92±65	-
Ce	-	-	-	99±36	-
Ni	-	-	-		7.6±4.7

Comparing the results of Tables 2 and 3, a higher lead concentration is observed in Table 3, indicating that some lead was lost during processing or diffused through weathering. It is worth noting here that the tailings appeared to be less lead rich compared to gold ores. In addition to lead, other elements prominently represented in both tables include the following: Cr, Cu, Fe, Ti, Ba, Ca, and S. Further study is needed for one or two of these elements to conclude whether their deposits are of commercial quantity.

4.0 Conclusion

Since the samples were taken from areas that have a desert character: three months of precipitation per year; the average temperature on a standard day is 40±2°C; windy and dusty. It is safe to conclude that the mix of these determinants prepares the area for lead poisoning. The unique dress code that is also noticed in the area; Adults wore a headgear (turban) that covered the entire head, leaving a tiny opening for vision. This is to protect the head from the scorching sun and minimize inhalation of dust that is airborne most of the time. With the children, it's the other way around: they're naked, but the boxer shorts usually won for that. They play in and around the gold processing plants and occasionally help out. The children are therefore not protected

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