



## DETERMINATION OF POTASSIUM AND SILICON FROM LEFT-OVER OF GOLD ORE USING PROTON INDUCED X-RAY EMISSION

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### ABSTRACT

The purpose of this study is to determine potassium and silicon concentrations (K & Si) in five geological samples using proton induced x-ray emission. PIXE was first introduced by Johansson, at the Lund Institute of Technology in 1970 using MeV proton beams and high resolution Si(Li) detector. It is a highly sensitive, multi-elemental analytical technique which has been well utilized in areas such as thin films, water, air, archaeological, biological and geological samples etc. It was employed in this work to characterize these geological samples collected from maga mining site. Samples were irradiated with proton beam of energy ranged from 2-3 MeV, accelerated by 1.7 MeV Tandem accelerators at Centre for Energy Research and Development, Ile-Ife, Nigeria. The characteristic X-rays emitted from the samples as a result of irradiation were detected with Si(Li) detector. The number of emitted X-rays with characteristic energy peak is a measure of elemental concentration for specific element present in the samples. The spectrum obtained is stored for qualitative and quantitative calculation at a later date using GUPIX software. The potassium and silicon alongside with other elements Fe, S, P, Ti, Ca, Cr, Ba, Sr, Zr, Cu, Rb, Zn, Sr, and Ni were determined. The results obtained indicated that potassium and silicon is of commercial deposit at the regions. The Fe concentrations appear to be deposited in commercial quantities in the area. The health implication of silicon's high concentration causing silicosis of lungs upon inhalation. This problem is common among the miners and the people living around the mining areas. Silicosis is preventable by using nonsilica substitution materials, effective dust control measures, and personal protective equipment.

**Keywords:** Ile-Ife, maga and PIXE

### INTRODUCTION

The planet earth is endowed with both potassium and silicon minerals. They have found usage in many areas of scientific application, notably as in fertilizer, cosmetics; food products etc. The potassium reserve in soil is very high and accounts for nearly 2.1–2.3% of the earth's crust. Therefore, soil K reserves are generally large (Hasanuzzaman *et al*, 2018). It plays an imperative role in the photosynthesis process which eventually increases the crop yield and improves the grain quality (Hasanuzzaman *et al*, 2018). K is sometimes called the “quality element” for its association with better crop production, which is supported by many scientists (Hasanuzzaman *et al*, 2018). As a major constituent within all living cells, potassium is an essential nutrient and is required in large amounts by plants, animals and humans. Humans obtain the majority of their potassium either directly from plants or indirectly through the animal products in their diet. Potassium ranks seventh in order of abundance in the earth's crust (Hasanuzzaman *et al*, 2018). As rocks slowly disintegrate, potassium is released, but the rate of release is frequently too slow to provide the large amounts of this essential nutrient required by crops. Humans and animals

need to obtain an adequate supply of potassium from their food and feed to be healthy and grow normally (Hasanuzzaman *et al*, 2018). The source of this potassium is plants (Johnston *et al*, 2003) and other anthropogenic source such as mining areas. In the human body, most of the potassium is within the cells which contain about 98% of the 120 grams of potassium in the average healthy adult (Johnston *et al*, 2003). In the global cycling of potassium, it is first mined from the naturally occurring deposits and is refined by simple processes. Rather the use of potassium in agriculture is part of a very long global cycle. Today, some 95% of the total potassium output is used as fertilizer (Johnston *et al*, 2003). The soil is made up of silicon compounds that are not biodegradable and this trait keeps life forms to come, live and leave the earth but soil remains forever sustaining all of them. Silicon is an element of earth and carbon is a non mineral element of life. It is available, abundantly on earth's crust. It occurs to the tune of 27.7% in the earth's crust. Silicon rarely appears as an integral component of biological materials. The presence of silicon in plants, animals and humans plays a positive role (Vasanthi *et al*, 2012). Therefore its requirement to animals and humans becomes important for the development of

bone, fairness of hair and also prevention of certain cardiovascular diseases even though it is a serious health hazard causing silicosis of lungs upon inhalation (Vasanthi *et al*, 2012). Yet silicon products have emerged for use in food, cosmetics and computers which men and women use in day today life (Vasanthi *et al*, 2012). Potassium and silicon are generally natural components of the Earth's crust and therefore are major constituents of soil. It may not be easy to assign a definite cause for an increase in metal content of a soil sample without recourse to the background level of the metal (Wilberforce *et al* 2012). The research aimed at the determination of elemental concentrations of potassium and silicon in the left-over of gold matrix at the mining site of maga area. The Maga was chosen to be the study area of this research due to the availability of the sample of interest at maga local mining station located in Danko-wasagu. The choice of PIXE method in this research was due to its high sensitivity and multi-element capability that analyzes any element from sodium to uranium in a single spectrum (Hasnat, 2007), i.e. very small sample quantities down to 104g for solids and around 1 ml for liquids (Inyang *et al*, 2012), can be detected. Particle Induced X-ray Emission (PIXE) was first introduced by Johansson (Hasnat, 2007) at the Lund Institute of Technology in 1970 using MeV proton beams and high resolution Si(Li) detector (Hasnat, 2007). It is one of the most common and widely used analytical spectrometry techniques at MeV accelerators and the analysis is performed with characteristic X-rays (Zaman *et al* 2016). The accelerator has two stages of acceleration, first pulling and then pushing the charged particles (Hasnat, 2007). When charged particles (proton) with sufficient energy hit on a sample, a vacancy in the inner shells of an atom will be created. The probability of creating a vacancy is higher when the velocity of the incoming ions matches the velocity of the inner shell electrons (Chelarescu *et al*, 2016). For MeV ions this probability for ejecting inner shell electrons is quite high. Such a vacancy can be filled in a number of ways and one of the processes may emit X-rays with the characteristic energy of that particular atomic number. When the X-rays are being detected by a high resolution detector, the well known Z-dependence of the X-ray energies, as well as the intensities of the X-rays lines, allow a

straightforward determination of the target elements (Chelarescu *et al*, 2016). The X-ray spectra were processed using GUPIX software (Akter *et al*, 2014). And more importantly, by measuring the charge, i.e. the number of incoming particles, the concentration of the elements can be accurately quantified (Zaman *et al*, 2016).

### PRINCIPLE OF PIXE ANALYSIS

There are two stages procedure followed in PIXE analysis. Firstly, elements in the target are identified from the energies of the characteristic peaks in the x-ray emission spectrum. Secondly, the quantity of a particular element in the target is determined from the intensity of its characteristic x-ray emission spectrum (Hasnat, 2007). The high-energy protons strike the target atoms and eject electrons from the innermost shell in atoms as shown in Figure I. As a result, a vacancy is created in the innermost shell. It is a common nature of an excited atom that it seeks to regain a stable energy state. Therefore, the created vacancy is filled by an electron coming from an outer shell, at that time an electromagnetic radiation in the form of characteristic x-rays is emitted. The de-excitation may also be possible by the emission of an electron, so-called Auger electron. Figure 2 shows the k-shell ionization, x-ray emission, and emission of Auger electron. The probability of the emission of an x-ray quantum is close to 1 for the heavy elements but only a few percent for the light ones (Hasnat, 2007). The x-ray spectrum is simply determined by the energy levels of the electrons in the atom. The energy level diagram of a medium-heavy element with the x-ray transitions is shown in figure 3. The transitions going to the K shell are indicated as K x-rays. When the vacancy is filled by an electron, comes from the L shell, the transition is denoted as  $K\alpha$ , and when it comes from the M shell,  $K\beta$  (Hasnat, 2007). Similarly, the transitions to the L shell are indicated as L x-rays, and these have some components, especially for heavy elements. Generally, the light and medium-heavy elements are identified by their K x-rays and the heavy elements by L x-rays due to the effective detection of the K x-rays which can be obtained in the range  $20 < Z < 50$  and of the L x-rays for  $Z > 50$ . (Hasnat, 2007)

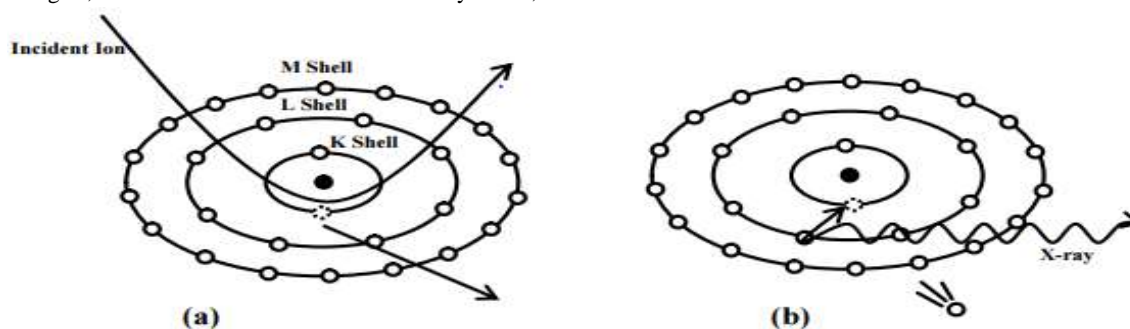


Fig. 1: Basic principle of PIXE. (a) Indicates ion interaction with inner shell electron. (b) Indicates emission of electron, fall of upper shell electron and radiation of x

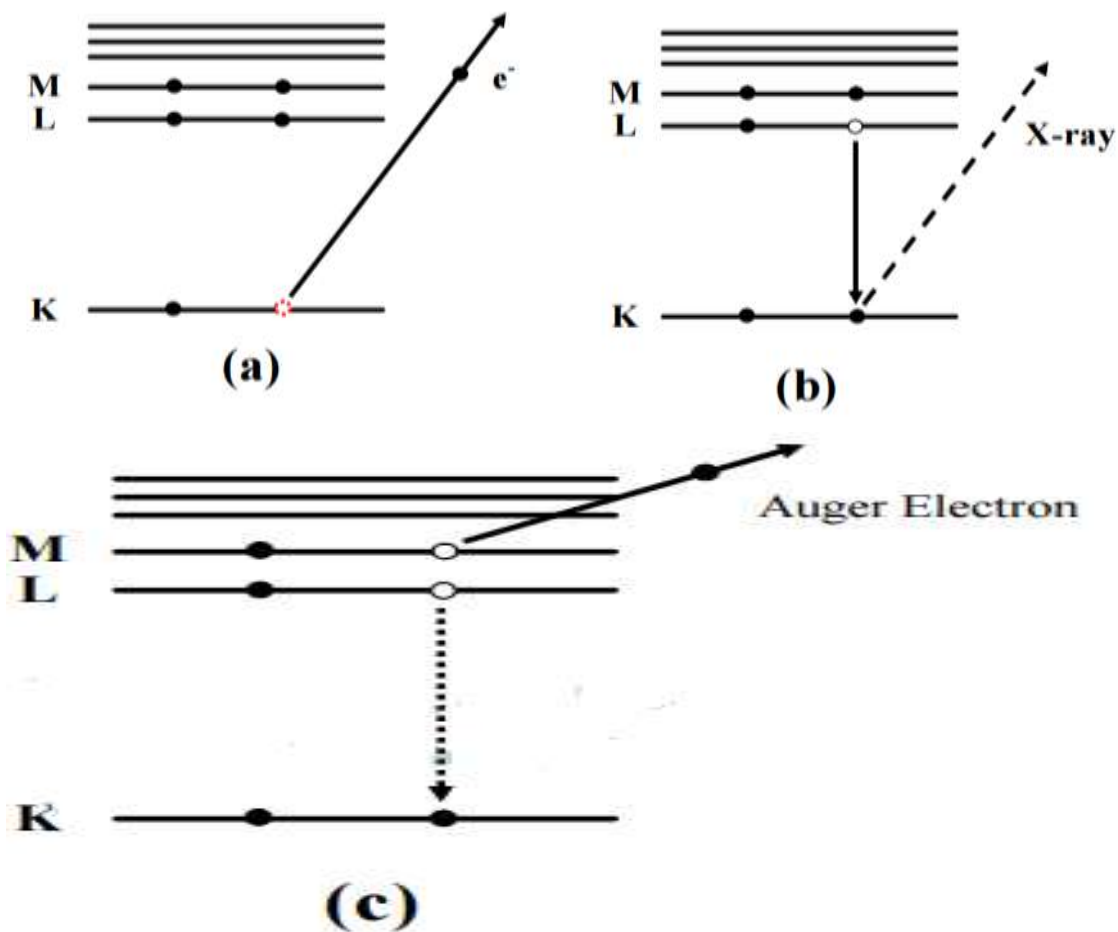


Fig. 2: k-shell ionization, x-ray emission, and emission of Auger electron. (Hasnat Md. Kabir, 2007)

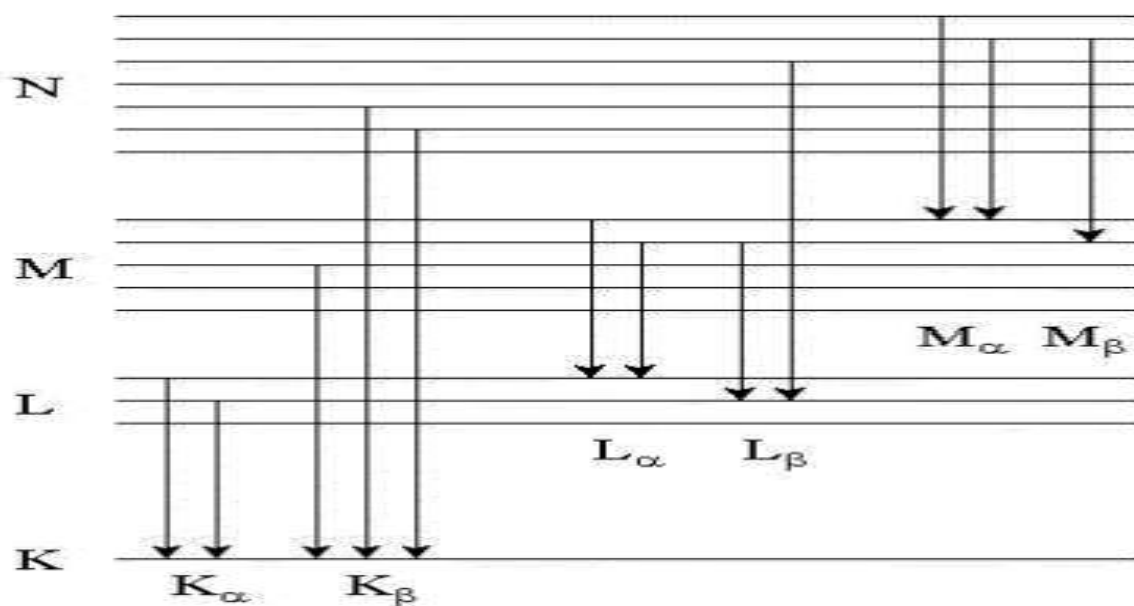


Fig. 3: Some common x-ray transition (Hasnat, 2007)

The energy of characteristic x-ray is equal to the difference between two shell electron binding energies those take part in the transitions express as

$$E_{x\text{-ray}} = E_1 - E_2 \dots\dots\dots (1)$$

Where  $E_{x\text{-ray}}$  is the characteristic x-ray energy,  $E_1$  is the vacant shell electron binding energy and  $E_2$  is the donor shell electron binding energy. Using x-ray spectrum, energy level diagram and knowing x-ray energies, it can be possible to determine the elements those are in the specimen.

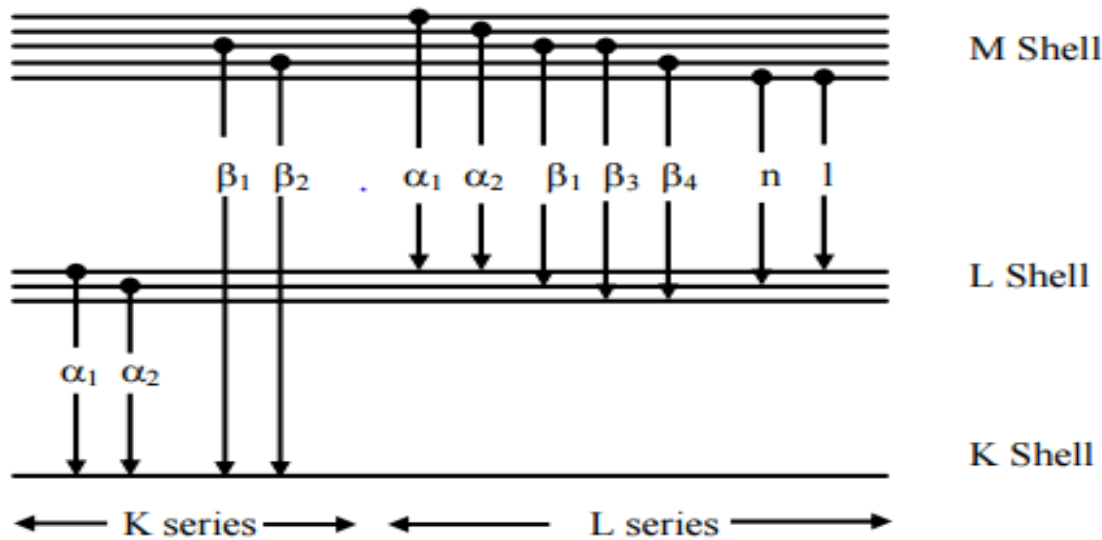


Fig. 4: Energy levels and X-ray transitions in medium-heavy element (Hasnat, 2007).

**METHODOLOGY**

*Study area*

Maga village is located in Danko/wasagu Local Government Area of Kebbi state, North-western Nigeria. The town lies on latitude 6°E and longitude 11°N (Hassan, 2013) and falls within

the Sokoto basin. The deposit from where a sample for this research work was obtained is about few km away from Wasagu town (BINTA HASSAN, 2013). The map below show the location of study area:



Fig. 5: Map of Kebbi state, indicating location of study area. (Hassan, 2013).

### Sample collection and Preparation

The geological samples (leftovers) were collected from five different locations of maga mining area. PIXE requires little or minimal sample preparations, therefore care must be taken in handling the material to be analyzed (Ezeh *et al*, 2017). Each sample collected was crushed to small pieces using mechanical crusher. The crushed samples were dried at 105°C to constant weight (Abdullahi, 2012). The dried samples were ground to form fine powder. Then the powdered samples were sieved using a standard set of sieves to a diameter range of less than 125µm. Every powdered sample was shaken using an electric shaker to be sure that the sample was homogenized. The samples (leftover) were mixed with binding agent such as chemflex TM. Five pellets are made of 13 mm diameter and about 1 mm thickness (Rahman *et al*, 2016) and thereafter fastened to the specimen holder (Abdullahi 2012). The aluminum foil paper is placed behind the pellets before it is fastened to the special ladder to avoid the masking tape sticking to the pellets. It is then meticulously lowered into the specimen chamber. Once the specimen is securely placed in the specimen chamber, the chamber is made vacuous by a special vacuum pump affixed to the chamber (Abdullahi, 2012).

### Irradiation of samples

The samples were irradiated using 1.7MeV tandem accelerator at the Centre for Energy Research and Development (CERD), Obafemi Awolowo University (OAU) Ile-Ife, Osun state Nigeria. The target was placed at an angle of 45° with respect to the proton beam from the accelerator (Arif *et al*, 2016). The samples were irradiated by 2-3 MeV collimated proton beam having the diameter of 3mm and 15 nA current. During the whole process, the detector dead time was adjusted to 5%. The samples were irradiated for 1-10 minutes to obtain reasonable counts for each element (Arif *et al*, 2016). For each left-over sample irradiation, 10 µC charges were collected through the Faraday Cup connected with the sample wheeler by copper spring (Zaman *et al* 2016). The X-ray photons emitted from the samples were detected and converted into voltage pulses by the Si(Li) detector with other associated circuitry. The number of emitted X-rays with characteristic energy peak is a measure of elemental concentration for specific element (Wilberforce 2016). The detector was positioned at a distance of about 15 cm from the target, at right angle to the incident proton beam (Zaman *et al* 2016). Mylar absorber was used to protect the detector from damage probability by high energetic X-rays (Zaman *et al* 2016). Signals from the detector were processed by the usual PIXE electronics and displayed by a multichannel analyzer as channels (energy) versus peak height (counts) spectrum (Arif *et al*, 2016). After a PIXE spectrum has been measured, there are essentially two steps in the spectral analysis. The first step is to analyze the spectrum to determine areas of characteristics of elemental peaks. The second step is to estimate the yield of X-rays so that elemental concentrations can be estimated from the peak areas and the expected yields. The first

step is performed by the computer program (Begum *et al*, 2006). The data acquisition for this research work was done using the well-established software. The collected spectrum data files were analyzed by the software GUPIX and the concentration of the elements found in the samples have been projected in this paper (Zaman *et al* 2016). The precision and trueness of the method were checked by analyzing the single Standard Reference Materials (SMRs) under the same condition as the sample. PIXE technique gives the accurate concentration of the elements present in the samples with high precision (Kamal *et al*, 2007).

### Data analysis

X-ray spectra have been analyzed using X-ray unfolding software GUPIX. GUPIX is developed in the Guelph University, Canada. It is capable to analyze PIXE spectra from thin, thick and layered targets (Kamal *et al*, 2007). The choice of GUPIX was based on the fact that it uses all updated best available databases i.e. (cross-sections, fluorescence and Coster-Kronig probabilities, stopping powers (Kamal *et al*, 2007) and attenuation coefficient. GUPIX has some useful options like matrix iteration, layer thickness iteration, adding invisible element to the fit and analyzing spectra in batch (Kamalet *al*, 2007). Data were analyzed using GUPIX software that can simply, automatically and quickly fit the PIXE spectra to obtain the elemental concentrations. Elemental concentration calculation of each element  $C_z$  is based on the following equation

$$C_z = \frac{Y}{Y_i Q \epsilon T H} \quad (\text{Hossen } et al, 2016) \dots \dots \dots (2)$$

Where  $Y_i$  is the X-ray theoretical intensity (i.e. the yield per micro-Coulomb of charge per unit concentration),  $Y$  is the x-ray experimental intensity or yield,  $Q$  is the measured proton beam charge,  $\epsilon$  is the efficiency of the detector and  $T$  is the transmission through any filter or absorbers between the target and the detector (Hossen *et al*, 2016),  $H$  is an instrumental constant equivalent to the product of the geometrical solid angle of the x-ray detector and any systematic normalization factor present in the charge integration system (Hossen *et al*, 2016).

### RESULTS AND DISCUSSION

Twelve (12) elements were detected in the analysis of the leftover samples collected from five location of maga mining site. The research was carried out at the Centre for Energy Research and Development (CERD), Obafemi Awolowo University (OAU) Ile-Ife, Osun state Nigeria (Inyang *et al*, 2012). Using a model of 5SDH 1.7 MeV Tandem accelerator built by the National Electrostatic Corporation (NEC), USA. This equipment was installed at CERD by the NEC, USA (Inyang *et al*, 2012). A PIXE analysis was done using a 2-3 MeV proton beam generated with the aid of this accelerator. Table 1 below show the mean concentration of the elements detected in the samples.

**Table 1: Showing elemental Symbols, atomic number and Mean concentrations in part per million (ppm).**

Elemental Symbols	Atomic number	MEAN CONCENTRATION (ppm)
Si	14	398260.04
K	19	10305.82
Ti	22	3299.68
V	23	346.6
Cr	24	1158.22
Mn	25	250.9
Fe	26	111296.54
Ni	28	13.4
Cu	29	197.74
Zn	30	101.67
Rb	37	86.65
Zr	40	284.7
Pb	82	1628.025

The mean concentration of the element obtained from the samples is in order of Si> Fe>K>Ti>Pb> Cr>Zr>Mn>V> Cu> Zn>Rb> Ni. The Si and K content in the leftover samples studied were found remarkably high. Si concentrations varied from 287099.5 to 550376.7 ppm with average concentration of 398260.04 ppm and K Si concentrations varied from 3120.5 to 41904.2 ppm with average concentration of 17848.62 ppm. Humans and animals need to obtain an adequate supply of potassium from their food and feed to be healthy and grow normally. Silicon constitutes approximately 1g in human body which is present in various tissues and body Fluid (Vasanthi *et al*, 2012). The source of silicon is water, foot and anthropogenic. Plant food contains a higher quantity of silica while animal food contains a low quantity (Vasanthi *et al*, 2012). Therefore its requirement to animals and humans becomes important for the development of bone, fairness of hair and also prevention of certain cardiovascular diseases even though it is a serious health hazard causing silicosis of lungs upon inhalation (Vasanthi *et al*, 2012). Yet silicon products have emerged for use in food, cosmetics and computers which men and women use in day today life (Vasanthi *et al*, 2012). Beside the benefits derived from silicon, it contributes to the serious health problems of animals and human. Silicosis is a progressive occupational lung disease caused by the inhalation, deposition, and retention of respirable dust containing crystalline silica. There is no effective specific treatment, and patients with silicosis can be offered only supportive care (Schleiff, 2016). The Occupational Safety and Health Administration (OSHA) estimates that >2 million workers are currently exposed to respirable crystalline silica in industries where exposure might occur, including 1.85 million workers in the construction industry and 320,000 workers in general industry and maritime workplaces (Schleiff, 2016). Typically a disease of long latency, silicosis usually is diagnosed through a chest radiograph after  $\geq 10$  years of exposure to respirable crystalline silica dust. Nodular silicosis also can develop within 5–10 years of exposure to higher concentrations of crystalline silica (Schleiff, 2016). Respiratory

impairment is severe, and the disease is usually fatal within a year of diagnosis. In addition, occupational exposure to respirable crystalline silica puts workers at increased risk for other serious health conditions, including chronic obstructive lung disease, kidney and connective tissue disease, tuberculosis and other mycobacterial-related diseases, and lung cancer (Schleiff, 2016). In 1997, the International Agency for Research on Cancer (IARC) classified crystalline silica as carcinogenic to humans, and this classification was reconfirmed in 2012 (Schleiff, 2016). The major implications of the findings of this research is to create awareness among the people of kebbi state especially zumerate, that the left-over of gold matrix is not just a waste but contained a significant amount potassium and silicon with other trace elements. Secondly, it allow the miners and dwellers of the area to know the likely health effects caused by the inhalation, deposition, and retention of left-over containing crystalline silicon.

The presented PIXE technique is known for its sensitivity, accuracy, precision, simplicity of the target preparation and the ability to perform multielemental analysis of a large number of samples, sometimes quickly, requiring small amounts of materials (Ene *et al*, 2010).

## CONCLUSION

An analysis of potassium and silicon concentration in the leftover samples collected from maga mining area has been performed using PIXE. The analysis of data obtained from five samples using this method shows that potassium and silicon are the highest concentrated major elements among others. Cu, Zn, Br, Pb, Ti, V, Sr and Zr are detected as heavy metals. According to this result, it can be concluded that potassium and silicon are of commercial deposit in the area, alongside with the other elements such as Iron (Fe) which appear to be deposited in commercial quantities in the area.

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