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Advances in Applied Science Research, 2011, 2 (6):370-378

ISSN: 0976-8610
CODEN (USA): AASRFC

Evaluation of trace elements in clay sediments products of tatiko locality using x-ray fluorescence technique

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ABSTRACT

Clay products in Tatiko village, Paikoro local government area in North central part of Nigeria with coordinates 9°26′N 6°38′E / 9.433°N 6.633°E have been major instruments of cooking, drinking of water, eating of meals, decorations and exportations for decades, thus the need to ascertain the level of trace heavy elements. Samples of red clay sediments were taken at a vertical depth of 150 cm and a horizontal depth of 100cm beneath the earth surface at site 1, and labeled Tat. A1. Also, Brown clay sediments were taken at a vertical depth 200 cm and horizontal depth of 100cm beneath the earth surface at site 2 and labeled Tat. B1. Clay sediments products with sample identification: Tat. A2, Tat. M2, Tat. F3 and Tat. M3 were analyzed using Energy Dispersive X-Ray Fluorescence (EDXRF) technique (mini pal 4 PW 4030 X-ray Spectrometer) for the determination of sixteen elements of interest; Al, Ba, Ca, Cr, Cu, Fe, Ga, K, Mn, Mo, P, Rb, Si, Ti, V, and Zn. The concentration of Al, Si, and Fe which were the major elements in the samples ranged from 6.56% to 11.1%, 18.77 to 29.43% and 8.39 to 17.04% respectively for all the analyzed samples. The concentration of the following which constitute the trace elements; Ba, Ni, V, Cu, Ga, P, Ti, and Zn were within the range of 0.15% to 0.47%, 0.011% to 0.0463%, 0.03% to 0.066%, 0.008% to 0.0567%, 0.0005 to 0.0896%, 0.1264% to 0.2005% , 0.6591% to 1.049% respectively. The concentrations of elements obtained were outside the range of toxic and hazardous permissible criteria recommended by Federal Environmental Protection Agency (FEPA) of Nigeria 1998.

Key Words: X-ray fluorescence (XRF) method, Si (Li) detector, Clay sediments, Trace Elements.

INTRODUCTION

Tatiko village in the North central part of Nigeria is located in Paikoro local government area of coordinates 9°26′N 6°38′E / 9.433°N 6.633°E. The village is covered all over with clay minerals that were formed over long periods of time by the gradual chemical weathering of rocks, usually silicate-bearing, by low concentrations of carbonic acid and other diluted solvents. The clays in this village exhibit plasticity when mixed with water in certain proportions. When dry, they become firm and when fired in a kiln, permanent physical and chemical reactions occur [17]. These reactions, among other changes, cause the clay to be converted into a ceramic material.

The X-ray fluorescence (XRF) method is fast, accurate, non-destructive, and usually requires only a minimum of sample preparation [15]. Applications are very broad and include the metal, cement, oil, plastic food industries, along with mining, mineralogy, and environmental analysis of water and waste materials [16]. XRF is also a very useful analysis technique in pharmaceutical chemistry and material physics research. Trace metals (heavy elements, minor elements, micro elements, or micronutrients) are sets of elements which are required or exist in only small amount in ordinary soil, water, air, plant and animals [3]. Trace metals are present in the environment from both natural and anthropogenic (man's activities) process [4]. The accumulation of trace metals in both agricultural product and sea food causes various form of pollution [5].

The term trace metals have been variously referred to as common pollutants, which are widely distributed in the environment with source mainly from the weathering of minerals and soil. However, trace metals are define as those metallic elements, low in the periodic table with high atomic number (weight) > 100, or a relative density greater than five [6].

Some traces metals may be important in the nutrition of plant and animals or humans (e.g. Cu, Cd, Zn, Mn, Ni, V), while others are known to possess virtually negative nutritional effect (e.g. Pd, Cd, Hg). All these trace metals over large territories and long time periods may cause gradual damage of organisms which now necessitate careful assessment of their input. Thus, this work seeks to analyze these groups of trace heavy metals relative to our health [7, 14].

Heavy metals normally occurring in nature are not harmful to the environment. This is because they are only present in small amounts. The heavy metals become pollution when they show up in huge amounts primarily due to industrialization. Some heavy metals causing pollution are Mercury, Arsenic, Copper, Lead and Zinc [9, 11, 12, 13].

Within the framework of this study, the concentrations of heavy metals in the clay products produced in Tatiko locality were analyzed. The inhabitants of this area used these products for drinking of water, cooking of food, and even some pregnant women eat these products directly.

MATERIALS AND METHODS

2.0 Sample Collection

A total of six samples were selected as described in the table below:

Table 1: Sample sites ID and descriptions

Sites	Sample ID	Description of sample sites
1	Tat. A1	Red clay sediments obtained at a vertical depth of 150cm and horizontal depth of 100cm called site 1
2	Tat. B1	Brown clay sediments obtained at a vertical depth of 200cm and horizontal depth of 100cm called site 2
3	Tat. A2	Mixture of Red clay sediments with Brown clay sediments with 1litre of water
4	Tat. M2	Mixed clay product during molding before firing
5	Tat. M3	After firing of molded mixed clay product and decorated with red coloured clay sediments
6	Tat. F3	Already finished black clay pot used in cooking for five decades (50years)

3.0 Experiment

The Mini pal 4 version, model PW 4030 X-ray Spectrometer was used for the analysis. It is an energy dispersive microprocessor controlled analytical instrument designed for the detection and measurement of elements in a sample (solids, powders and liquids), from sodium to uranium.

The six samples collected were dried at 110°C until constant weights were obtained. The dried clays were manually grinded, in a porcelain mortar, followed by sieving which was aimed at homogenization in a turbulent mixer. The sample mass were ~1.500**g** and pressure of about 10tons applied to produce pellets of the samples for analysis. The pellets were loaded into the sample chamber of the spectrometer system.

The spectrometer was operated at a maximum voltage of 30kV and a maximum current of 1mA applied to produce the primary X-rays to excite the pellet. A preset time of 10 minutes (for each of the samples) was employed and an inbuilt Si (Li) detector was used for counting the secondary X-rays from the samples and the spectrum from the samples were analysed by a PC running the dedicated Mini pal analytical software.

The high intrinsic resolution (170eV at 5.9keV) and excellent stability of the Si (Li) semi-conductor detector permit a direct measurement of the intensity of the characteristic x-rays of elements of interest with very little interference from other excited or scattered radiation [10]. Thus, the concentration of the elements of interest in each of the collected samples were determined by used of simple comparative X-ray fluorescence analysis technique which consist of comparable fluorescence parameters of an analyte-sample to a second material designated as standard material having accurate predetermined concentration of the appropriate trace element(s) of interest. The standards material sealed sources were manufactured by the Innovative Research University Australia. The results of the trace elements of interest are shown in Table 2.

RESULTS AND DISCUSSION

Results (Table 2) for red clay sediments (Tat A1) obtained at a vertical depth of 150cm and horizontal depth of 100cm called site 1 shows that the concentration of Al, Si, and Fe was high of 9.999, 22.98132 and 17.03674% respectively meanwhile the concentration of K, Ca, Ti, V, Cr, Mn, , Ni, Cu, Zn, Ba, and Ga, were very low within the range of 0.032128% for Zn to 2.522896% for K. The following elements, Mo, P, and Rb where below detection limits. Silicon, which is the highest in concentration of 22.98132% is shown graphically in Fig.1

The results (Table 2) of the brown clay sediments (Tat. B1) obtained at a vertical depth of 200cm and horizontal depth of 100 cm called site 2 shows high concentration of Al (10.5820%), Fe (10.18550 %) and Si (27.0908%) shown in Fig. 2 while K, Ca, Ti, V, Cr, Mn, , Ni, Cu, Zn, and Ga, ranged from 0.00580% for Ga to K (1.89217%). However, Ba, Mo, P, and Rb were below detection limit (BDL).

The mixture of red clay sediments with brown clay sediments (Tat. A2) with 1litre of water showed that Rb (11.86330%), Al (6.560840%), Si (18.77740%), and Fe (16.31000%) were high while Mo and P were BDL as seen in Fig. 3. The other set of elements K, Ca, Ti, V, Cr, Mn, , Ni, Cu, Zn, Ga, and Ba, were observed to be low within the range 0.00414% (Ga) to 2.74697% (K).
For the mixed clay product (Tat. M2) during molding awaiting firing, the concentration of Al (11.1111%), Si (27.74570%), Fe (8.78392%) was high while K, Ca, Ti, V, Cr, Mn, , Ni, Cu, Zn, and Ga, range from 0.01101% for Ni and 2.00836% for K. The element Rb was BDL as shown in Fig. 3.

In the already finished black clay pot used in cooking for five decades (50years) with sample ID Tat. F3 shows Al (9.68253%), Si (29.42730%) and Fe (8.78392%) were high while Ba and Rb were below detection limit. The elements K, Ca, Ti, V, Cr, Mn, , Ni, Cu, Zn, and Ga, were less within 0.00803% for Cu and 2.18014% for Ca shown in Table 2 and Fig. 5.

Finally in the case of the after firing of molded mixed clay product, decorated with red coloured clay sediments (Tat. M3) Al (8.295230%), Si (25.31682%) and Fe (14.898416%) were high while Mo, P, and Rb were BDL. However, the other elements of interest K, Ca, Ti, V, Cr, Mn, Ni, Cu, Zn, Ga, and Ba, ranged from 0.039071% for Ga and 2.47820% for K as shown in Table 2 and Fig. 6.

Table 2: Concentration of Elements Determined in this work

S/N	Element	Tat A1	Tat B1	Tat A2	Tat M2	Tat F3	Tat. M3	Range
1	Al (%)	9.9999	10.582	6.5608	11.111	9.6825	8.0952	6.5608-11.111
2	Si (%)	22.981	27.091	18.777	27.745	29.427	25.316	18.777-29.427
3	K (%)	2.5228	1.8921	2.7469	2.0083	1.0456	2.4482	1.0456-2.7469
4	Ca (%)	0.5461	1.2723	2.4231	1.4224	2.1801	2.0729	0.5461-2.4231
5	Ti (%)	1.0066	0.8508	1.0486	0.6591	0.5195	0.9407	0.6591-1.0486
6	V (%)	0.0659	0.0526	0.0559	0.0330	0.0300	0.0559	0.0300-0.0659
7	Cr (%)	0.0581	0.0328	0.0636	0.0266	0.0273	0.0526	0.0266-0.0581
8	Mn (%)	0.0774	0.1400	0.1780	0.0874	0.0897	0.1315	0.0774-0.1780
9	Fe (%)	17.036	10.188	16.3100	8.7839	8.3856	14.898	8.3856-17.036
10	Ni (%)	0.03852	0.0141	0.0463	0.0110	0.0135	0.0369	0.0110-0.0463
11	Cu (%)	0.05111	0.0167	0.0567	0.0175	0.0080	0.0503	0.0080-0.0567
12	Zn (%)	0.03212	0.0080	0.0626	0.0152	0.0592	0.0618	0.0080-0.0626
13	Ga (%)	0.04855	0.0005	0.0041	0.0177	0.0896	0.0390	0.0005-0.0896
14	Ba (%)	0.40324	BDL	0.4659	0.1523	BDL	0.3494	0.1523-0.4659
15	Mo (%)	BDL	BDL	BDL	0.1667	0.1867	BDL	0.1667-0.1867
16	P (%)	BDL	BDL	BDL	0.1264	0.2005	BDL	0.1264-0.2005
17	Rb (%)	BDL	BDL	11.883	BDL	BDL	BDL	0.0000-11.883

(BDL=Below detection limit)

From the overall results, the following elements Al, Ba, Cu, Cr, Fe, Ga, Rb, K , P and S were depleted after heat was applied, while Ca, Si, Mn and Zn were enriched after heat was applied. The depleted elements may be due to the mixing of the samples or during the making of the clay product. The results also show that Silicon has the highest percentage concentration in all the samples analysed (Fig. 1-6), Ni, V and Cu do not vary in all the sediments. Some are toxic while others relatively harmless to all organisms. From the report of the committee on substances, Federal Environmental Protection Agency, Nigeria (1998) it was observed that the elements classified as toxic element As, Cr, Pb, and Se while Cd classified as hazardous were not found in the entire clay products sediments analyzed. Thus, the results (Table 2 & 3) shows that the clay sediments might not pose any hazards and are quite suitable for cooking, drinking and decoration purposes.

Table 3: Permissible criteria of substances to human health

S/N	Substance	Permissible criteria (ppm)	Desirable criteria (ppm)
1	Arsenic (As)*	0.05	Absent
2	Calcium (Ca)	20	-
3	Cadmium (Cd)**	0.01	Absent
4	Chromium(Cr)* (hexavalent)	0.05	Absent
5	Copper (Cu)	1.5	Virtually absent
6	Iron (Total Fe)	Less than 0.3	Virtually absent
7	Lead (Pb)*	Less than 0.5	Absent
8	Magnesium (Mg)	150	150
9	Manganese (Mn)	Less than 0.5	Absent
10	Mercury (Total Hg)	0.0001	Absent
11	Selenium (Se)*	0.01	Absent
12	Zinc (Zn)	15	5

** Highly Toxic, ** Hazardous to health*

Source: Report of the committee on substances, Federal Environmental Protection Agency, Nigeria (1998)

The range of the concentration of the elements Cu, Fe, Zn, and Mn for all the samples were far below the permissible criteria indicated in Table 3 recommended by FEPA 1998. Figure 1 shows the percentage concentration of some of the heavy metals of interest present in all the clay samples. Al, Si and Fe have the highest percentage concentration in the clay product production processes which are not necessarily required by humans in large quantity but are all essential to plants. The toxic elements; Ba, Cr, Ga, V and Zn were below the limit recommended by the report of the committee on substances, Federal Environmental Protection Agency (FEPA), Nigeria (1998) for substance in relation to human health.

However, K was found within 1.0456-2.7469 % in the humic compounds which could undergo increased leaching in acid soils and has an antagonistic influence on its bioaccumulation by plants. Fe in the clay sediments occurs within range 8.3856-17.036% in residue form and could be bound to organic matter. Fe has large sorption capacity for other metals. Organic compounds increase mobility of Fe and its bioavailability for plants [17]. Mn concentration was within the range 0.0774-0.1780% where it exists as a large influence on anthropogenic activity. Mn also forms its own oxides and hydroxides, bounds with organic matter and decides about redox reactions of other elements. Excessive pollution of clay sediments by Mn could occur after fertilization with liquid manure as has been the practice in this village for yam production. Zn is an element which could be found mainly in residue was determined within the range of 0.0080-0.0626% may have been introduced to the clay sediments during pollution of the environment with compounds of Zn. This could create stable bonds with organic matter, strong compounds with Fe and Mn oxides. The mobility increases with decreasing pH [1], [17], but in alkaline soils Zn could be mobile, because of its ability to create mineral-organic compounds and anion complexes. Rb observed in Tat. A2 (11.883%) occur mainly in residue form in the mixed sediment products which may be from areas of high pollution, like housing estates, parks, petrol stations of Paikoro main town. Rb over various fractions depends on the origin of the clay soil, the influence of anthropogenic activity (in clay soils from areas of high pollution Rb exists in easy exchangeable form). Increasing Rb content in organic matter fraction could be connected with a large content of organic matter, its acidity and fertilization. Distribution depends on the origin of the soil and the pH value. In the light acid soils Rb is easy leachable while in alkaline soils it could be initiated and bioaccumulated by plants. However, Fe, Mn, Zn, and Rb in acid clay soils are easily leachable and, worse: bioaccumulated by plants. Their organic and mineral-organic compounds are very important in soil-forming processes and influence other elements.

Some of them have a good mobility in alkaline clay soils because of their ability to create mineral-organic compounds and anion complexes.

A large precipitation of carbonate and oxide fraction could be connected with acidity of used reagent, which could cause releasing of metals from clay, which are then associated with other fractions, like carbonates and oxides. Occurrence of larger association of metals with humic compounds could be connected with the presence of clay high content and with advanced processes of mineralization, forming humic compounds. In some clay sediments product samples, a larger content of organic matter fraction was ascertained, which could be connected with a high content of organic matter and with the ability of some elements to create stable bonds with organic compounds. However, occurrence of a large residue in examined samples is possible in mineral soils with high content of clay where elements (Zn) have the ability to penetrate crystal structure of silicates.

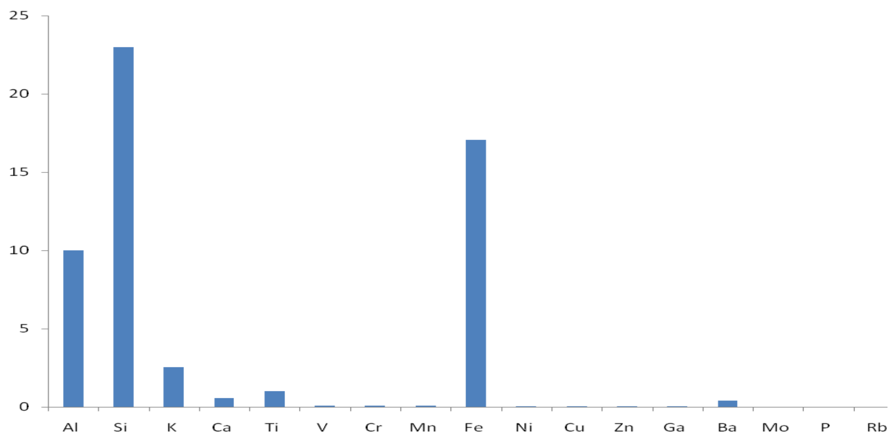

Figure 1: Percentage Concentration of Elements in the red Clay (Tat A1)

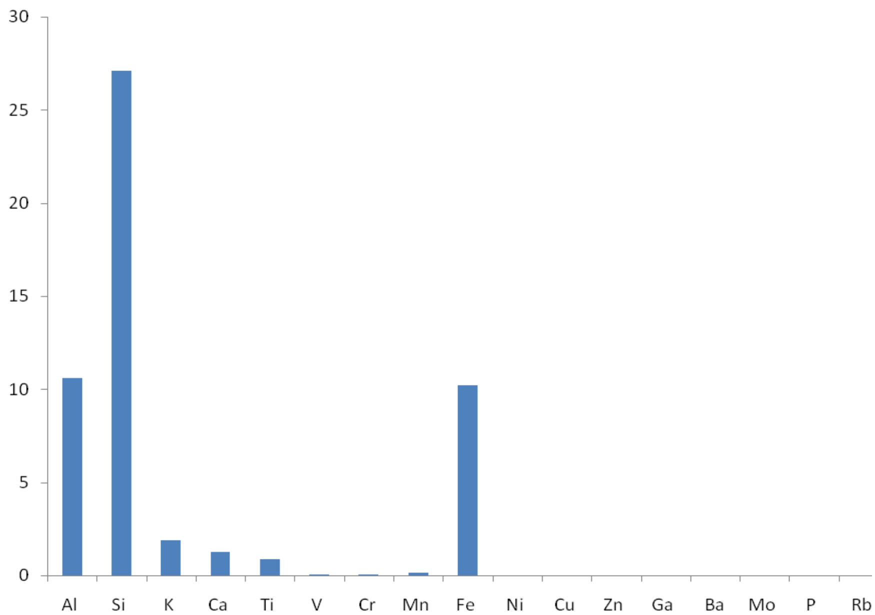

Figure 2: Percentage Concentration of Elements in the Brown Clay (Tat B1)

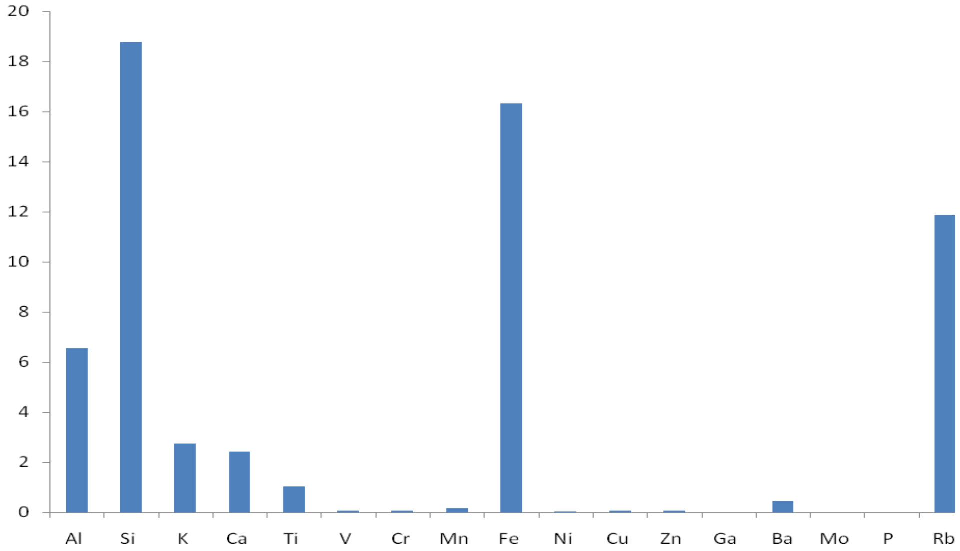

Figure 3: Percentage Concentration of Elements in the Mixed Clay sediments (Tat A2)

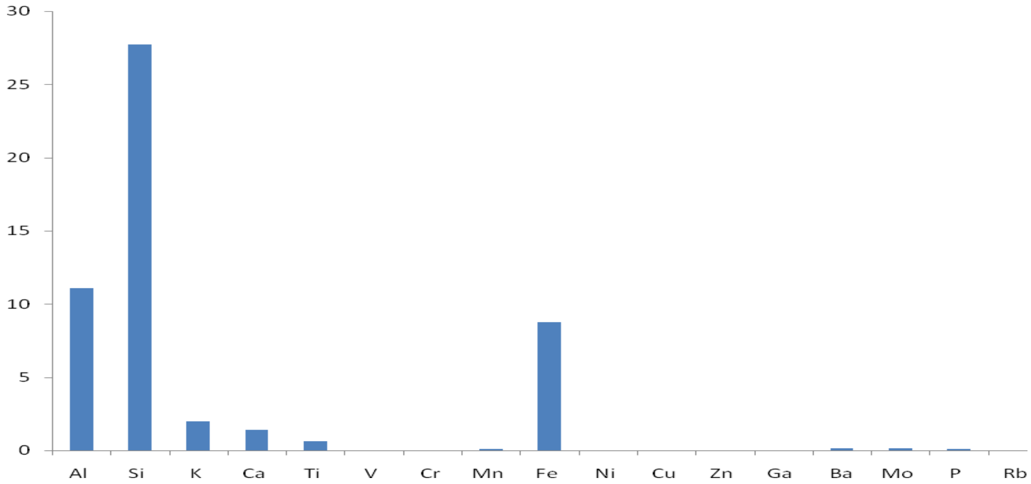

Figure 4: Percentage Concentration of Elements in the Molded Clay sediments (Tat M2)

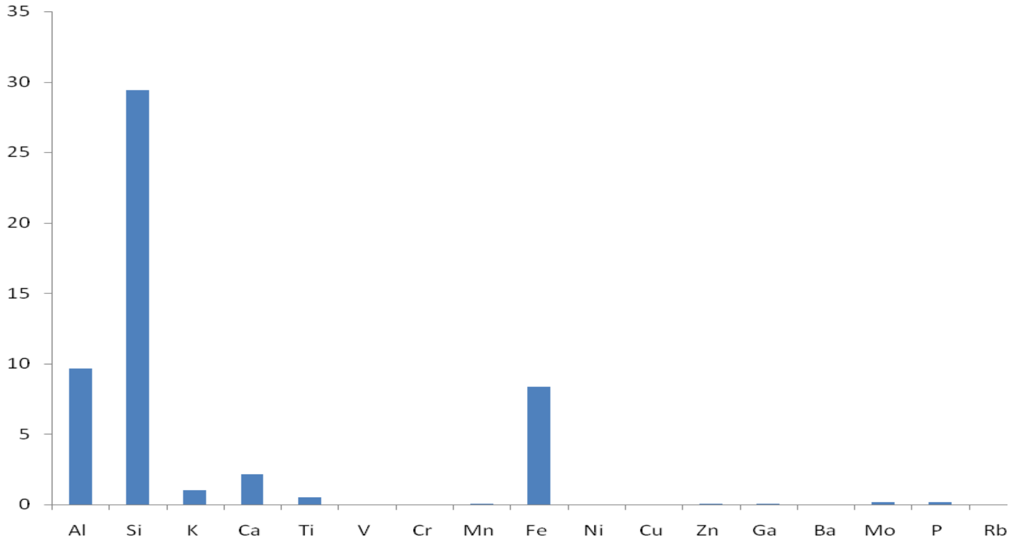

Figure 5: Percentage Concentration of Elements in the Black Clay Pot used for 50 years (Tat F3)

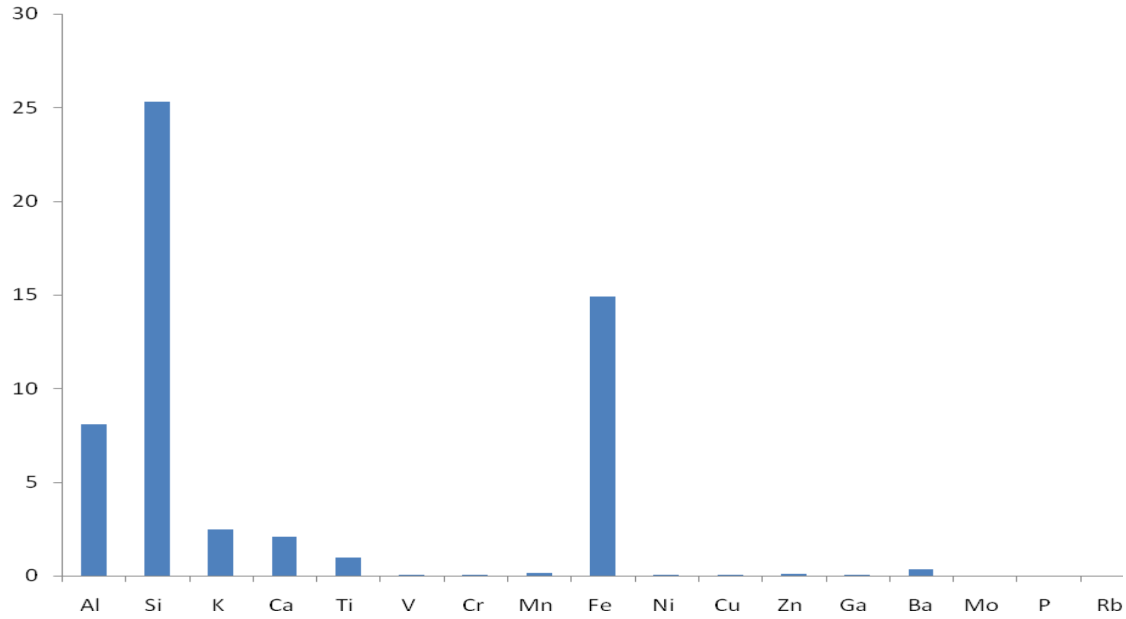

Figure 6: Percentage Concentration of Elements in the Clay Finished Product after firing (Tat M3)

CONCLUSION

The obtained results have shown that application of the XRF method gave an array of the elemental composition of clay sediments product in Tatiko village, Paikoro local government Area, Niger State-Nigeria. This work showed seventeen different elements which were neither toxic nor hazardous to humans as classified by the reports of the FEPA, Nigeria, [2]. This work showed clearly that the toxic elements; Ba, Cr, Ga, V and Zn were below the limit recommended by the report of the committee on substances in relation to human health, by Federal Environmental Protection Agency (FEPA), Nigeria [2]. These results gave the information on the main contents of the clay products, anthropogenic activities which influence clay sediments, natural clay-forming processes and hazards, connected with changes of elements chemical form under environmental conditions and their influence on living organisms.

REFERENCES

[1]. Alex Nii Moi Pappoe, Ernest K.A. Afrifa and Frederick A. Armah (**2011**). *International Journal of Applied Science and Technology Vol. 1 No. 41*

[2]. Federal Environment Protection Agency (**1998**) *Report of the Committee on Water Quality Criteria*, Federal Water Pollution Administration PP. 9 – 10.

[3]. X-Ray Fluorescence: A Discussion (**1979**). *Clays and Clay Minerals*, Vol. 27, No. 4, p. 305,

[4]. Fergusson, J.E. (**1990**). *The heavy elements: Chemistry, environmental impacts and health effects*, Pergamon press: Oxford, U.K. pp 22-31

[5]. Springer-Verlag Berlin Heidelberg Jankiewicz, B., Ptaszynski, B., Turek, (**2002**). *Polish Journal of Environmental Studies* 11(6):745-749

[6]. Assessment of Arsenic enrichment of cultivated soils in Southern Poland. *Polish Journal of Environmental Studies*, 2: 187–192. Malhi, Y. *et al*. (**2004**). *Global Change Biology* 10: 563–591.

[7]. Teng Y G, Tuo X G, Zhang C J, **2002**. *Environmental Science and Technology* 2: 7–9, 48.

[8]. Germany: Springer. Yahaya, M. I., Ezeh, G. C., Musa, Y. F. and Mohammad, S. Y. (**2009**). *African Journal of Pure and Applied Chemistry* 4 (3): 022-030.

[9]. Baranowski R, Rybak A, Baranowska I (**2011**). Ajibola, V. O. Rolawanu, R. *J. Sci. Industry Res*. **2000**, 59(2) 132 - 136.

[10]. Baranowski R, Rybak A, Baranowska I (**2002**). *Polish Journal of Environmental Studies Vol. 11, No. 5 (***2002***), 473-482*
[11]. D'Hoore Jl (**1968**). The classification of tropical Soils. The soil resources of Tropical Africa. Cambridge University Press. London, 7 - 26.
[12]. Ewa, I.O.B., Oladipa, M.O.A Dim, L.A., Mallam S.P (**2000**) *Journal of Trace and Microprobe Techniques*, 18 (3), 398-395.
[13]. Ewa. I. O. B, Dim. LA (**1989**) *J. Environmental Sci. Health* A24, 243 - 254.
[14]. Ewa. I. O. B, Ebel, S. Umar, I. M. Molnar, Z. S (**2002**). *Journal of Trace and Micro probe Techniques*, 20 (3) 385 - 393.
[15]. S. K. Kulshreshtha, D. N. Wagh and H. N. Bajpei (**2005**). X-ray Spectrometry, 34, 200–202.
[16]. M. Huber, G. Angloher, C. Hollerith, A. Ruedig, J. Jochum, W. Potzel and F. von Feilitzsch (**2004**). X-ray Spectrometry, 33(4),
[17]. Ghildyal, B.P. and Tripathi, R. P. (**1987**). Soil Physics, Wiley Eastern Limited, New Delhi.
[18]. Oladipo .M.O.A (**1987**) Studies on Trace Element Analysis of Corinthian Pottery and related clays. Published Ph.D thesis Manchester University.