

Use of k_0 -ENAA technique for Evaluation of Th, U and K in Sediments for Archaeometry Studies

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ABSTRACT

The Evaluation of Th, U and K in Sediments for archaeometry studies using k_0 -ENAA Technique and k_0 -IAEA program has been implemented in NIRR-1. The samples were irradiated at a thermal power level of 15.5 kW which correspond to a neutron flux setting of $5.0 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ for approximately 6 hours. The results of the IAEA Lake sediment-SL-1 and NIST Coal Fly Ash 1633b Standard Reference Material (SRM) showed good agreement with the certified (or literature) values using the k_0 -IAEA program. Within the ten archaeological sediments samples, the concentration of K was found in ranged of $(0.0041 \pm 0.024 \text{ to } 3.31 \pm 0.025) \%$, Th/Pa $(4.38 \pm 0.037 \text{ to } 10.08 \pm 0.15) \text{ mg/kg}$ and U/Np $(2.00 \pm 0.077 \text{ to } 2.71 \pm 0.076) \text{ mg/kg}$. Among the samples analyzed; sample-E (2nd Tat.AHM3), sample-I (4th Tat.1HYS), and sample-J (3rd Tat.2YS), had very low concentration of Th, U and K. These low concentrations are attributed to signal resetting or signal zeroing due to serious application of heat. However, the concentration values of Th, U and K were obtained within a waiting period of three to five days compared to twenty to twenty four days using k_0 -INAA technique.

Keywords: k_0 -IAEA program, NIRR-1, Archaeological sediments, Reference Standard sample material, k_0 -ENAA and k_0 -INAA technique.

1. INTRODUCTION

Over the last three decades, sediments and ceramics analyses have become central to archaeological investigations, partly due to the concurrent advances in computer technology and instrumental chemistry, and partly as a result to the recognition by archaeologists that archaeometry provides much more than mere measurement [1]. Because of the abundance and variety, clays/ceramics provide one basic fundamental tool used to derive archaeological information and further the understanding of how different civilizations lived [2]. This study (k_0 -ENAA) is very fundamental to archaeologists, anthropologists, and ethnoarchaeologists, as well as to physicists, chemists and geologist since it provide accurate concentrations of Th, U, and K found within the samples after excitation.

Ceramic fragments make up a large portion of the materials usually recovered from excavations and can appear to be very similar even under microscopic examination, but clay, sand and other natural materials from which they were fashioned can have a chemical composition that is unique and diagnostic for the local source from which they were taken [3]. The composition of any ceramic fragment depends on the types and proportions of the clay paste and mineral, rock, grog (e.g. crushed pottery or firebricks) and organic tempers used in its manufacture [4]. This work revealed the exploitation of

k_0 -IAEA program and the use of Nigeria Research Reactor-1 (NIRR-1) for the analysis of Th, U and K in Sediments from Tatiko Locality, Paikoro local government area in North central part of Nigeria with coordinates $9^{\circ}26'N \ 6^{\circ}38'E / 9.433^{\circ}N \ 6.633^{\circ}E$ for Archaeometrical Studies using k_0 -EpiCd-NAA Technique.

The emission of gamma radiation from naturally occurring radioisotopes, such as ^{40}K and the radionuclides from the ^{232}Th and ^{238}U series and their decay products also called terrestrial background radiation, which exist at trace levels in all ground formations especially sediments, represents the main external source of irradiation to the human body [9]. The parents ^{238}U , ^{235}U , and ^{232}Th are the three fundamental natural decay series normally called the uranium (U) series, the actinium series and the thorium (Th) series, respectively. Each of these series consists of many daughter products generated through successive decay of parent radionuclides [4].

The naturally occurring radioisotopes are present in different concentrations in sedimentary rocks reflecting the origin of the sediments, the depositional environment and the evolution of the host basin. Furthermore, weathering, interaction with surface and ground waters, secondary mineral precipitation and ion adsorption by clay minerals are some of the many geological processes

that can continuously change the radioisotope distribution in the sediments [5].

The activity concentrations of ^{239}U / ^{239}Np , $^{233}\text{Th}/^{233}\text{Pa}$, and ^{42}K both in the archaeological samples and the standard reference material is measured in terms of the photons or gamma rays using HPGe spectrometer after excitation from the research reactor using the k_{α} -EpiCd NAA technique [6, 7]. According to the rule that exposure should be "as low as reasonably achievable", these radionuclides will be assessed from the archaeological sample obtained from Tatiko pottery clay cottage factory raw material source and the clay products production processes including the finished clay pots of various durations. This will provide the specific activity of Th, U, and K in the samples from which concentrations down to ppm will be converted to dose rate for archaeometry analysis.

2. SAMPLE COLLECTIONS

In the framework of studies, a cover of clay profiles was selected at Tatiko locality. The locality 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 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 [4]. These reactions, among other changes, cause the clay to be converted into a [ceramic](#) material.

Six sites were selected for sample collection and were called site 1, 2, 3 ...6. For site 1 of vertical depth of 45cm and horizontal depth of ~100cm, the sample was labeled (45Tat.1st). For site 2 of vertical depth 100cm and horizontal length of ~100cm, the sample was labeled (100Tat.2nd). For site 3 of vertical depth ~200cm and horizontal length of ~100cm the sample was labeled (200Tat.3rd). For site 4 of vertical depth 400cm and horizontal depth of 100cm, the sample was labeled (400Tat.4th). For site 5 of vertical depth ~600cm and horizontal length of ~100cm the sample was labeled (600Tat.5th). Finally for site 6 of vertical depth ~800cm and horizontal length of ~100cm the sample was labeled (800Tat.6th). A summary of the sample collection has been illustrated in Table 1 and the sites views are illustrated in plates 1 to 6.

Table 1: Sample sites ID and Descriptions within ~45cm to ~800cm Depth

Sites	Labeled	Sample ID	Description of sample sites
1	C	45 Tat.1 st	Vertical depth of ~45cm and horizontal length of ~100cm
2	H	100Tat.2 nd	Vertical depth of ~100cm and horizontal length of ~100cm
3	F	200Tat.3 rd	Vertical depth of ~200cm and horizontal length of ~100cm
4	G	400Tat.4 th	Vertical depth of ~400cm and horizontal depth of ~100cm
5	B	600Tat.5 th	Vertical depth of ~600cm and horizontal length of ~100cm
6	A	800Tat.6 th	Vertical depth of ~800cm and horizontal length of ~100cm



Plate1: Vertical of depth ~45cm and horizontally ~100cm (45Tat.1st) at site 1



Plate 2: Vertical depth of ~100cm and horizontally ~100cm (100Tat.2nd) at site 2



Plate 3: Vertical depth of ~200cm and horizontally ~100cm (200Tat.3rd) at site 3



Plate 4: Vertical depth of ~400cm, horizontally ~100cm (400Tat.4th) at site 4



Plate 5: Vertical depth of ~600cm and horizontally ~100cm (600Tat.5th) at site 5



Plate 6: Vertical depth of ~800cm and horizontally ~100cm (800Tat.6th) at site 6

The remaining four samples were collected during and after production process of the clay products. The first sample was obtained during the mixture of deep orange-red and brown clay with water and labeled (1st Tat.MRB). The second sample was obtained after the mixtures of dull grey to deep orange-red clay with water have been molded and is ready for firing labeled (2ndTat.MRB). The

third sample was obtained from a finished clay pot of about two years old and labeled 3rd Tat.THY. The fourth sample was obtained from a pot that was approximately two hundred years labeled 4th Tat. THY and has been employed for cooking all these years. The summary of how the samples were collected and the sample ID are illustrated in Table 2.

Table 2: Sample ID and Descriptions of the Archaeological Samples

Sites	Labeled	Sample ID	Description of sample sites
1	D	1stTat.MRB	Mixture of deep orange-red clay and brown clay with water ready for firing
2	E	2stTat.AHM3	After firing the molted clay pot
3	J	3 rd Tat. 2YS	Finished clay pot of approximately two years
4	I	4 th Tat. 1HYS	Clay pot of about one hundred (100) years old use for cooking

3. EXPERIMENTS

In the process of sample preparation, the following were used; agate mortar and pestle, infrared lamp, acetone, cotton wool, sieve, air blower, disposable gloves, white sheet of paper, polythene bags, vials, analytical balance, marker, marking tape. The preparation of samples started with drying the sediments samples with the infrared lamp at 110°C until constant weights were obtained. The disposable glove was first used to avoid contamination of samples through sweating and the agate mortar washed with soap and water and then cleaned up with cotton wool damped with acetone to remove any further impurity. The sieve was thoroughly cleaned using a brush and ordinary cotton wool to remove any impurity. The dried clays were manually grinded, in a porcelain mortar, followed by sieving aiming at homogenization in a turbulent mixer. The grinding was continued until all material passed through the sieve. The archaeological samples were packed in ultraclean irradiation vials (polyethylene capsule) before transferring it for irradiation in the cadmium lined channel. Each sample was then put into a vial of ~2cm height, diameter of ~15mm locked, sealed and labeled of '2 to 24' inscribed on using the marked. The twelve samples were further divided into two series of six (including standards) each, packaged in a single vial of ~4.5cm of height and diameter of ~2cm.

The samples were irradiated at a thermal power level of 15.5 kW which correspond to a neutron flux value of $5.0 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$ on the control console for 6 hours. After irradiation, the induced activities in the foils were measured using the vertical dip-stick detector ORTEC-GEM-30195 HPGe coaxial, with resolution (FWHM) at 1.33 MeV, ^{60}Co to be 1.85 keV and at 122 keV, ^{57}Co to be 0.85 keV, peak-to-Compton ratio, ^{60}Co to be 60:1 and

relative efficiency of 30 % at 1332.5 keV of ^{60}Co at a geometry of 25cm. With the aid of the Maestro Multi-Channel Analyzer (MCA) emulation software card, which is coupled to the detector through the ORTEC electronic modules, the nuclear spectrum for the samples where acquired for k_0 -EpiCd neutron activation analysis.

Quality control of the k_0 -standardization ENAA method was performed by analyzing standard reference materials, IAEA-SL-1 lake sediment and Coal fly ash (1633b). This was carried out in order to assess the accuracy and precision of the method and the k_0 -IAEA software program. The irradiation of IAEA-SL-1 lake sediment and Coal fly ash (1633b) samples were carried out with the samples at irradiation position A-3 (Cd-lined) for 6hours in the channel A-3 of NIRR-1. The measurement was performed in two geometries after a waiting period of about 3-5 days. The first series of measurements were performed at a sample-detector distance of 15cm after one day cooling time for short lived nuclides. The second series were measured at 2 cm from detector after two days cooling time for medium and long nuclides. The third series were measured at 2 cm from detector after five-six days cooling time for very long half life nuclides. For each sample with respect to the first group of long irradiation (6hrs), measurement time was 1800 seconds for first and second series and 3600 seconds for third series and the dead time did not exceed 6%. The nuclide of interest, ^{42}K (1524.6 keV) was aimed after cooling time of three days. The second short-count was aimed at the nuclides of interest $^{239}\text{U}/^{239}\text{Np}$ (277.6 keV) and $^{233}\text{Th}/^{233}\text{Pa}$ (312 keV). These analyses were evaluated using the k_0 -IAEA software program. A typical spectra for a selected sample (sample 1: NIST Coal Fly Ash 1633b) was interpreted as shown in Figure 1 below using the View/Raw (or Fitted) Spectra option.

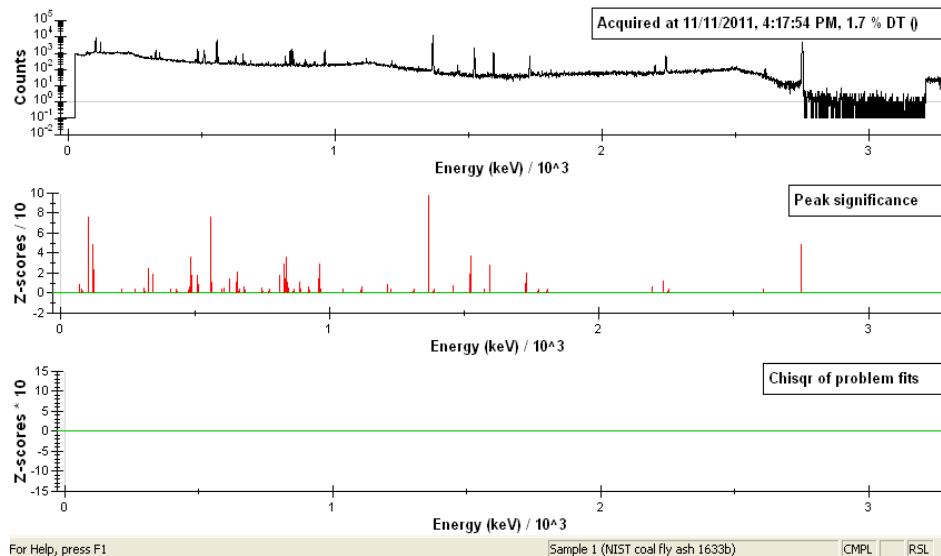


Figure 1: Spectra interpretation for NIST Coal Fly Ash using k_0 -IAEA Program

The samples were considered to be ordinary. All the spectra of the sample were interpreted simultaneously. The flux parameters determined with the Edit/Map fluxes command and the interpretation was performed.

4. RESULTS AND DISCUSSIONS

For quality control, the reference materials are means by which the accuracy of the technique relies on [7]. Assessment of data gives an opportunity to know acceptable elements of interest [8]. Thus, the results of the

IAEA Lake sediment-SL-1 and NIST Coal Fly Ash 1633b reference standard sample material in this work and the certified values are shown in Table 3 and Figure 2. These results show good agreement with the certified (or literature) values. On this basis, the the concentration of Th, U and K values were obtained for the ten archaeological sediments samples obtained from Tatiko village Paikoro local Government Area analyzed with k_0 -IAEA program. These data where obtained within a waiting period of three to five days and are shown in Table 4.

Table 3: Results for Ratio (Experiment/Standard Reference Values) and 95% confidence level Range for IAEA Lake sediment-SL-1

Element	Experiment (k_0 -ENAA) NIST Coal fly Ash 1633b in ppm	Reference value, NIST Coal fly Ash 1633b in ppm	Ratio (Expt/Reference Value)	k_0 -IAEA program, ppm (Lake sediment IAEA-SL-1)	Reference value, ppm(Lake sediment IAEA-SL-1)	Remarks
As	135 ± 2	136.2	0.99	32.4 ± 3	24.7-30.5	NO
Ba	704 ± 12	709	0.99	642.2 ± 131	586-692	YES
Br*	1.9 ± 0.6	2.9	0.66	5.2 ± 2	NA	
Ca	1501 ± 24	1510	0.99	1.33 ± 0.6	NA	
Ce*	ND	190	NA	98 ± 5	100-134	YES
Co*	39 ± 3	50	0.78	18.9 ± 0.5	18.3-21.3	YES
Cr	194 ± 6	198.2	0.97	104.7 ± 8.0	95-113	YES
Cs*	9 ± 0.3	11	0.81	6.8 ± 1.0	6.1-7.9	YES
Eu*	3 ± 0.1	4.1	0.73	2.2 ± 1.1	1.1-2.1	NO
Fe	7781 ± 98	7780	1.00	64400 ± 384	65700-69100	NO
Hf	5.9 ± 0.2	6.8	0.86	4.6 ± 0.7	3.6-4.8	YES
K	1952 ± 57	1950	1.00	11900 ± 458	12400-16600	NO
La*	95 ± 1.2	94	1.01	47.0 ± 0.1	49.5-55.7	NO

Na	204 ± 12	201	1.01	1638.9 ± 27	1600-1800	YES
Nd*	NA	85	NA	45 ± 6	NA	
Rb*	NA	140	NA	106 ± 19	102-124	YES
Sb*	6.8 ± 0.7	6	1.13	1.3 ± 0.3	1.19-1.43	YES
Sc*	40.4 ± 7.8	41	0.98	16.3 ± 0.03	16.2-18.4	YES
Sm*	19 ± 2.2	20	0.95	8.2 ± 0.12	6.74-9.76	YES
Sr	1040 ± 47.2	104	0.99	NA	37-123	
Ta*	1.7 ± 0.05	1.8	0.94	1.2 ± 0.3	1.00-2.16	YES
Tb*	2.1 ± 0.13	2.6	0.81	1.1 ± 0.4	0.94-1.86	YES
Th	24.9 ± 1.8	25.7	0.96	13.5 ± 0.7	13-15	YES
Tm*	2 ± 0.11	2.1	0.95	2.5 ± 0.9	NA	
U	8.9 ± 0.56	8.79	1.01	4.0 ± 0.6	3.69-4.35	YES
Yb*	7.5 ± 1.5	7.6	0.98	3.2 ± 0.3	2.77-4.07	YES
Zn*	211 ± 98.4	210	1.00	227.4 ± 16	213-233	YES

YES (Within 95% Confidence Level for IAEA Lake sediment-SL-1), NO (outside the 95% Confidence Level range)

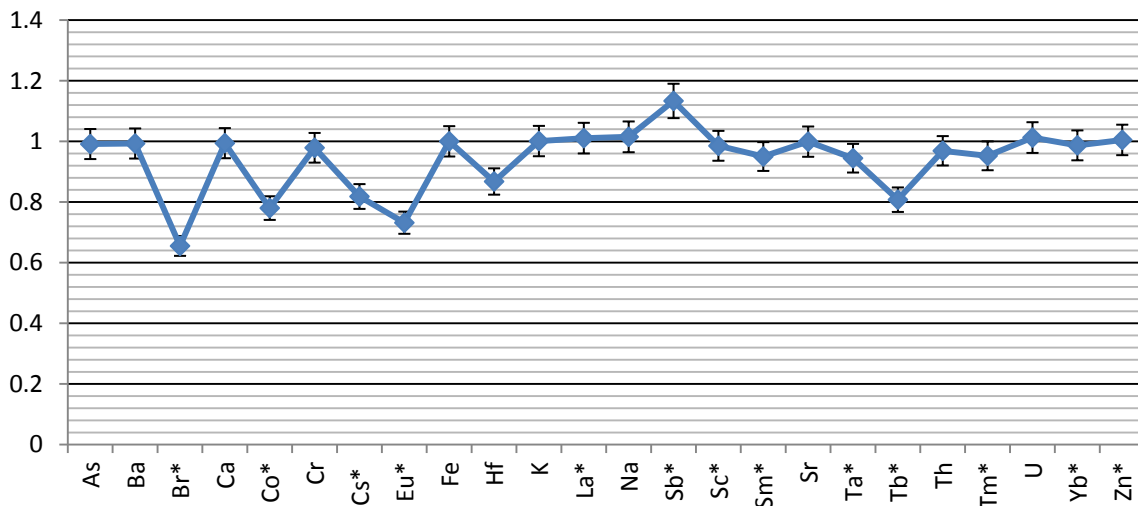


Figure 2: Ratio of Experimental /Reference Value of NIST Coal Fly Ash 1633b

Table 4: Results of K, U and Th Concentration in the Ten Sediments Samples

Sample ID	Sample type	K (%) ±2s	U/Np ±2s	Th/Pa ±2s
A (mg/kg)	800 Tat.5th	3.03±0.017	2.48±0.008	10.08±0.15
B (mg/kg)	600Tat.6th	3.31±0.025	2.45±0.080	8.90±0.15
C (mg/kg)	45 Tat.1st	1.78±0.016	2.00±0.077	9.87±0.15
D (mg/kg)	1st Tat.MRB	2.45±0.017	2.47±0.07	6.67±0.15
E (mg/kg)	2nd Tat.AHM3	0.07±0.017	2.71±0.076	9.96±0.15
F (mg/kg)	200Tat.3rd	1.45±0.025	2.57±0.17	8.42±0.37
G (mg/kg)	400Tat.4th	1.68±0.025	2.55±0.17	5.47±0.37
H (mg/kg)	100Tat.2nd	1.96±0.026	2.47±0.16	6.62±0.38
I (mg/kg)	4th Tat.1HYS	0.0018±0.026	2.50±0.16	8.61±0.38
J (mg/kg)	3rd Tat.2YS	0.0041±0.024	2.64±0.17	4.38±0.37

The concentration of K was found within 0.0041±0.024% to 3.31±0.025 % in the humid compounds which could

undergo increased leaching in acid soils and has an antagonistic influence on its bioaccumulation by plants.

Th/Pa in the clay sediments occurs within range 4.38 ± 0.037 mg/kg to 10.08 ± 0.15 mg/kg while U/Np

occurs within range 2.00 ± 0.077 mg/kg to 2.71 ± 0.076 mg/kg as shown in the Figures 3 to 5 below.

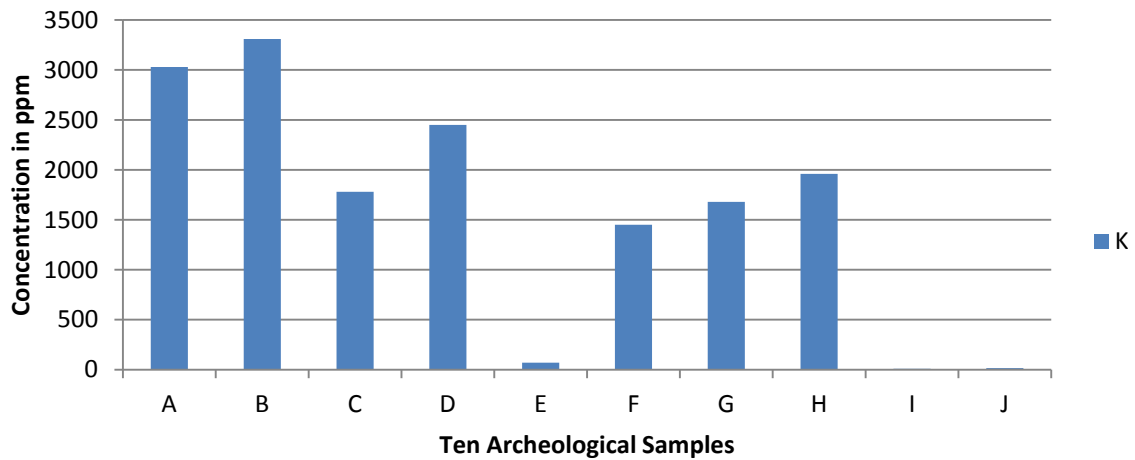


Figure 3: Concentration of K in the ten samples

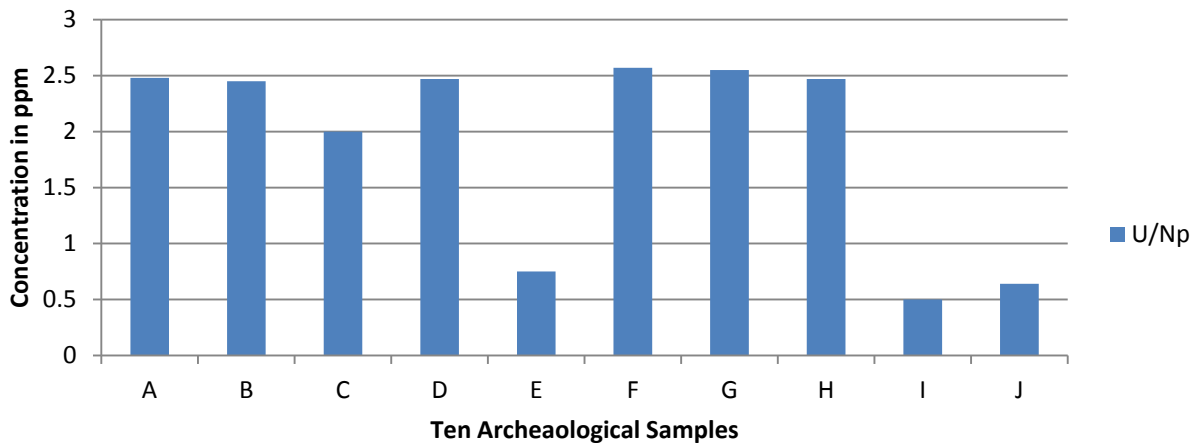


Figure 4: Concentration of U/Np in the ten samples

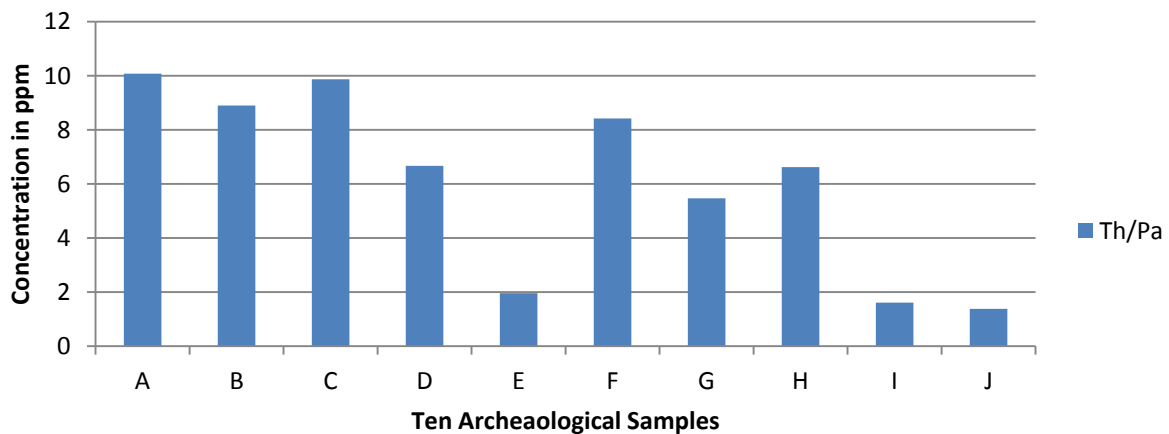


Figure 5: Concentration of Th/Pa in the ten samples

From the graphical interpretations Figure 3 to 5, the concentration of Th, U and K reduced drastically after heat has been applied in samples E (2nd Tat.AHM3), I (4th Tat.1HYS), and J (3rd Tat.2YS) . These drastic reductions are due to signal resetting or signal zeroing as a result heating.

5. CONCLUSION

Evaluations of Th, K and U have been standardized by implementation and dissemination of tools like NIRR-1, k_0 -IAEA program and k_0 -EpiCd-NAA technique. The authenticity of the results and technique was base on the analysis of the reference standard material; IAEA Lake sediment-SL-1 and NIST Coal Fly Ash 1633b which showed good agreement with the certified (or literature) values. The results for the ten archaeological samples showed that the concentration of K was found within (0.0041±0.024 to 3.31±0.025) %, Th/Pa (4.38±0.037 to 10.08±0.15) mg/kg and U/Np (2.00±0.077 to 2.71±0.076) mg/kg. These values turn to be very low for samples that heat has been applied due to signal resetting or signal zeroing. The concentration values of Th, U and K were obtained within a waiting period of three to five days compared to twenty to twenty four days using k_0 -INAA technique. In this work we have evaluated Th, K and U purposely for archeometry studies and improved on the data base profile for future studies around Northern Nigeria.

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