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FORENSIC AUDIT ANALYSIS OF RADIOACTIVE URANIUM ORE SAMPLES FROM MINING SITES IN PARTS OF NORTHERN NIGERIA.

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ABSTRACT

Forensic audit analysis investigates the ideal fingerprint of nuclear or radioactive materials within regulatory control, to aid attribution process. It is as fundamental part of a strong nuclear security program as establishment of a nuclear power plant. Fingerprints of uranium and thorium concentration, uranium isotopic and activity ratio, rare-earth elements patterns, trace impurities elements and age is determined to avoid dangerous radionuclides seepages into the environment. They provide specific information on the origin and production process of uranium bearing materials. This paper evaluate the audit processes in the investigation of the fingerprints and their applications in four uranium ore mined samples from parts of northern Nigeria (XR, M1, MII and MK), using integrated Inductive Couple Plasma Mass Spectrometric (IIC - PMS) analytical techniques . Results showed concentration range for uranium as 0.084±0.003 ppm to 73.965±1.371 ppm, equivalent to 1.053±0.033 Bq/kg to 924.566 Bq/kg; thorium had 0.055±0.006 ppm to 5.410±0.318 ppm, equivalent to 0.224±0.027 Bq/kg to 21.966±1.289 Bq/kg. The values for the locations vary significantly hence serve as the fingerprint of the areas. $^{235}U/^{238}U$ and $^{232}Th/^{238}U$ ratios had comparable values with standard of 0.047 and 0.001±7.96E-06 – 1.333±0.039 respectively. Both were analyzed by ANOVA and level of statistical significance of the variations identified as unique fingerprints. Isotopic ratios of $^{87}Sr/^{86}Sr$ (0.15126 ± 7.8505E-17), $^{143}Nd/^{144}Nd$ (0.71429 ± 7.85E-17) and $^{208}Pb/^{206}Pb$ (2.17427) had invariant but comparable values not distinct for fingerprint but can serve as supplementary information. The $^{232}Th/^{238}U$ isotopic ratio was applied to the chronometry of the samples. Age range of 4.506E+06 ± 5.126E+04 to 6.094E+09 ± 1.317E+08 years is comparable with the age of the Earth (4.543E+09 years). Study of viable fingerprints using other set up and technique such as LA-ICP-MS to differentiate between mines in the study area is recommended. This study is important for informed decision making and policy formulation on nuclear energy in Nigeria.

Keywords: Isotope, Forensic Audit, Radioactive Materials, Thorium, Uranium

INTRODUCTION

The threat to global nuclear security, it's devastating effects and consequences on human beings and the environment is a topic of international interest. It is still receiving global attention, especially by member states in the United Nations (Mayer, Wallenius & Ray 2005; Balboni et al., 2016). This is informed by the fact that in recent years, criminal acts that involves nuclear materials (i.e. uranium or plutonium) and radioactive sources by way of illicit trafficking and smuggling have caused havoc thereby raising growing public concern (Mogenstern, Apostolidis & Mayer, 2002; Stanley, 2012). Nuclear forensic science was developed over three decades ago, as a crucial component of the nuclear security strategy (Keegan et al., 2016), to work on the proposition of the inherent nature of certain characteristics of materials, which could be utilised to trace the source of confiscated nuclear material and foil nuclear smuggling (Hutcheon, Kristo & Knight, 2015). Subsequent to the dissolution of the Soviet Union in the early 1990s, there was massive shut down of plants that produce nuclear and radioactive materials, including research facilities (Hutcheon et al., 2015). The countries Russia, Belarus, Ukraine and Kazakhstan witnessed the relocation of the nuclear arsenals from these nuclear facilities, with attendant lost and theft of quite large quantity, resulting in problem of orphan sources (Moody, Grant & Hutcheon, 2014; Keegan et al., 2016). Due to loss of tight regulations and control over personnel, inadequate safeguards in place, these relocated facilities were not prevented from diversion and incessant theft. During that period, a kilogram of highly enriched uranium (HEU) cost tens of thousands of pounds to have it produced in a well-established enrichment programme, thereby the wide spread and sale of such materials out of regulatory control (Moody et al., 2014; Reading, 2016).

Nuclear forensics science encompasses both SNM and radioactive materials as they have many applications, such as radioisotopes, which are widely used in medicine-for treatment, diagnosis or sterilisation of medical facilities, in industry-for gauging or radiography (Ho et al., 2015). Nuclear forensics is applied either through point-to-population comparison, where a sample is connected of a known population of materials, like uranium oxide from a given mine, or point-to-point comparison, where a sample is matched to a source. Also by point-to-model comparison, where possible origins of material being considered are explored in events of non-availability of data (Hutcheon et al., 2015). Nuclear forensics involves a combination of technical data, relevant databases and specialised skills as well as knowledge to generate, analyse and interpret the data (Hutcheon et al., 2015). This analysis consists of categorisation, characterisation and complete nuclear forensic analysis. By categorisation, which is onsite, non-destructive analytical tool is used to find the bulk constituents of the material while determining its level of threats ensued. That leads to differentiating naturally occurring radioactive material (NORM) from SNM as well as radioactive contaminations and sources of commercial radioactive base (Kristo et al., 2016).

A 'National Nuclear Forensics Library' is a database system comprising of reference information and subject matter expertise on nuclear and other radioactive materials produced, used or stored in the State utilised to identify the materials out of regulatory control. It makes possible, comparisons of information on known materials and data obtained from analytical measurement of nuclear or other radioactive materials found outside regulatory control. The ability of subject matter experts to formulate nuclear forensic findings and support investigations is strengthened by the timely availability of nuclear forensics reference information (Varga et al., 2015). Conclusions from nuclear forensics are usually arrived at using information inherent to nuclear and other radioactive material, which include physical properties, chemical and elemental composition and isotopic ratios emanating from geological or manufacturing process. Otherwise referred to as fingerprints or signatures, these material characteristics form the basis for nuclear forensic comparisons and are the information at the center of a Library (IAEA, 2018). The prevention and response to nuclear incidents by countries have deployed the use of nuclear forensic science as a strategy. Meanwhile, all forms of information on nuclear incident are being integrated into data whose analysis and interpretation is made easy providing a solid base of confident response to the incident (L'Annunziata, 2012). Nuclear and other radioactive materials such as uranium, plutonium and other radioisotopes, serve some useful important role in the life of humans with wide applications in diverse fields (Lee et al., 2018). For instance, uranium used as fuel for electrical energy source in pressurised heavy water nuclear reactors as well as its usage in production of nuclear weapons and depleted uranium (World Nuclear Association, 2018). 238U, 235U and 234U are the only three occurring naturally at concentrations (having natural abundance composition of 99.274%, 0.7204% and 0.0055%, respectively) that are significant (Aggarwal, 2016).

Therefore, building a nuclear signature involves identifying parameters measured from the raw material or nuclear fuel fabrication process, as most useful in attribution process (Hutcheon et al., 2015). These parameters and their respective signature as identified by many researchers across the globe over the years, include Appearance (Material type), Uranium, Plutonium content (Chemical concentration), Isotopic composition (Enrichment), Impurities (Geolocation), Age (Production date, origin), Surface roughness (Production facility) and Microstructure (Production process) (Kristo et al., 2016). The development of nuclear forensics is however not without militating factors as global efforts to evolve and strengthen nuclear forensic capabilities have some issues (Moody et al., 2014), such as the ability to interpret data, still in a developmental stage and the need for expanded database with information on nuclear and radioactive material globally. Others include the need for a greater understanding of how materials change while undergoing processing, reprocessing and other processes, no single material provides the required information for all or even any material and the need for a focused international cooperative effort on Non-Proliferation nuclear forensics.

MATERIALS AND METHOD.

For the purpose of this paper, the instruments used both in the field and laboratory analyses with their specifications are presented in Table 1.

Table 1: Materials and their specification

S/N	Materials	Qty	Specification
1	Inductively Coupled Plasma Mass Spectrometer	1	Table top Agilent 7700 series Inductively Coupled Plasma Mass Spectrometer (ICP-MS) of Agilent Technologies, Inc. USA.
2	Digital Microwave Digestive System	1	Table top Anton Paar Multiwave, PerkinElmer Germany, and rotor of 10 vials of ~ 20mL sample volume.
3	Rock crusher and Milling machines	2	Dickie and Stockler TS-250 Rock crusher and Milling machines.
4	Electronic and Analytical Balance	2	Labocon Analytical balance Lab-200 series 0-200 g, 0.1 mg.
5	Global Positioning System (GPS)	1	eTrex 10 Garmin USA Global Positioning System (GPS)
6	Map of Nigeria	1	Google Map of Nigeria
7	Sampling container	8	High Density Polyethylene Zip Lock Plastic Bag
8	Permanent Marker and Masking adhesive tape	2	Permanent waterproof ink marker and paper adhesive for sample ID
9	Chisel and Mallet	2	Pro hard rock chisel-8'' long with 5/8'' sharp, flat cutting tip. 10'' rubber 2/6'' mallet wooden handle.
10	Disposable Hand Glove and nose mast.	2	Soft rubber disposable hand glove and soft suspended nose mast.
11	Fume cupboard	2	2.5×1.5×3 m wooden and glass technically installed fume cupboard in analytical lab.
12	Analytical container	25	Teflon sample container (Plate.3.5)
13	Dilute Internal standards (ISTD) solution	Mix-4	Multielement mix - 4, 6Li, Sc 50 μg/mL, Ge, Te 25μg/mL, In, Tb, Bi 10 μg/mL, in 5% HNO3, trace HF 100 mL, 103Rh. (P/N 5188-6525) 200 times.
14	Reagents and chemicals	3.5 mL	Concentrated Nitric acid (HNO3), Hydrochloric acid (HCl), Hydrogen per oxide (H2O2), Hydrogen

		each	Fluoride (HF), distilled water, Aqua regia.
15	Dissolved sample filtering device	20	Polyvinylidene difluoride (PVDF) 0.22 μm membrane filtering device

The study area in this work covers accessible locations in parts of northern Nigeria where mining activities of uranium ores are obtainable, which includes Adamawa (Michika), Kano (Riruwai) and Taraba (Mika) areas. The geology and other parameters of the different sampling area considered under this study are illustrated in Table 3.2. The samples analysed were collected according to uranium ore sample collection standard. The sample sites were so chosen due to their geology and mineralisation, following previous prospecting of uranium (Martin & Bowden, 1981; Bute, 2013; NGSA, n.d,; Oruonye & Ahmed, 2017) in the sampling location. About 2.0 kg each of the uranium ore rock samples were collected (using chisel and mallet) at the pit-mining site and immediately transferred into a zip-lock plastic bag to avoid contamination. Four samples of uranium ore rocks were collected from open pit mine sites of similar to varied mineralogy based on the geological location of the sites, as discussed in study area section. One sample each from Riruwai and Michika and two samples from Mika mine sites. The choice of a sample each from Riruwai and Michika mine sites respectively was due to the focus of the study, which was to characterise the samples for nuclear forensic application, looking out for variation between mines with less emphasis on variation within mine. Two samples were collected from Mika mines sites (at a distance of about 200 m apart) based on the variation in its mineralogy and geological settings.

Table 2: Samples location, geology and collection information

Parameter/Sample Location-ID	XR UNGRKR (001)	MI UNGRTMI (002)	MII UNGRTMI (003)	MK UNGRAM (004)
Coordinate	N10o 43.340'; E008o 47.007'	N8o 58' 46''; E11o 36' 23''	N8o 58' 47''; E11o 36' 23''	N10o 39' 51''; E13o 29' 20''
Sample collection date	11/01/2018	01/03/2018	01/03/2018	03/03/2018
*Geology	Uranium bearing mineral is Pyrochlore in Peralkaline Granite	Uranium mineralisation in Pan-African granites	Uranium mineralisation in Jurassic Rhyolite Dykes	Uranium in Brecciated, Silicified and Mylonitized rocks

*Average grade (ppm)	540	114	215	2000
Depth (m)	3.0	5.9	1.3	4.0
*Deposit type	Vein	Vein	Vein	Vein
Mass of Sample collected (Kg)	2.5	2.0	2.5	2.7

(Fieldwork, 2018; *Bute, 2013; *Nwegbu, 2014; *Obaje et al., 2014)

An important part of analytical work is the sample preparation. The type of sample being studied determines the choice of correct preparation method. The ICP-MS technique however, requires that samples be introduced in liquid form, as it cannot analyse solid samples directly. Hence, solid uranium ore samples needed to be dissolved. Homogenous samples guarantee reliable and representative results. Therefore, homogeneity was ensured by first crushing and milling the uranium ore rock samples shown in Plate 3.3a, using Dickie and Stockler TS-250 Mill. The crusher jaws are cleaned after every sample using brush and acetone, to decontaminate the equipment from cross mixing. Uranium ore samples as collected from the mine sites.

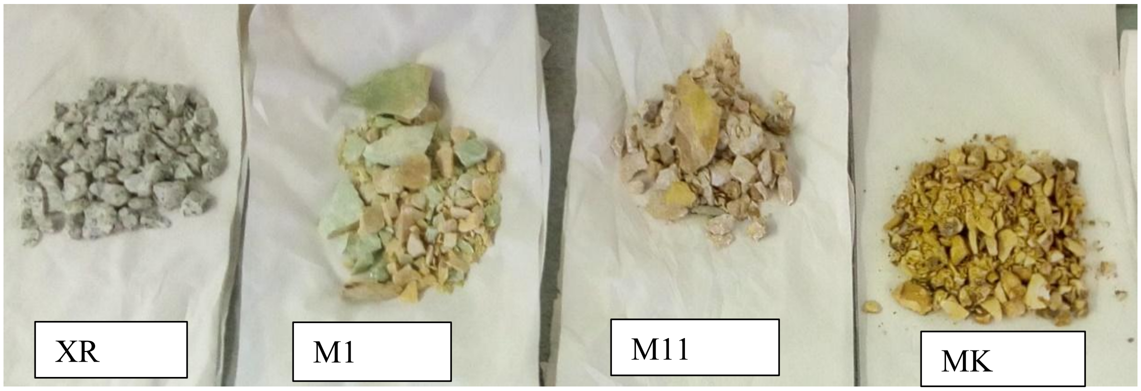

Figure 1: Crushed uranium ore samples from the crusher set for milling

Key: UNGRKR-001 (XR Sample); UNGRTMI-002 (MI sample); UNGRTMI-003 (MII sample); UNGRAM-004 (MK sample).

The dissolution of the milled uranium ore samples was performed using Anton Paar Multiwave, PerkinElmer Germany, and digital Microwave Digestive System, illustrated in Fig. 3.1. Sample preparation using microwave under such conditions have the following benefits: Complete sample dissolution is achieved using hydrofluoric acid and with nitric acid; An improved detection limits were obtained due to the use of lower sample to solution ratio; The volatilisation of certain elements are prevented due to the use of high pressure. The sample dissolution and digestion was carried out in two stages, firstly, a quick test for silica was done which was followed by, sample digestion for ICP-MS analysis.

QUICK TEST FOR SILICA

A quick test for the presence of silica was done, as it can form precipitate during sample preparation and tend to absorb the element thereby making difficult for their detection at the ICP-MS. It can also affect the nebulizer, by making it difficult for sample to get into the plasma for further process to detection, counting and identification of the major and minor elements. About 0.25 g of the sample was added into microwave heating vessel (made of Teflon material). 1 ml of concentrated HNO_3, 4 ml of concentrated HCl and a few drops of H_2O_2 are added. The vessel was then sealed tightly enough and placed on a rotor into the microwave, after sample pre-digestion. The microwave set to a method ASTM D4 309 (Half-scale), 4 vessels, 9 ml sample per vessel at temperature of 180oC and powered for a maximum period of 50 minutes as shown in Fig. 3.1. The cooled digested sample solution was observed to be clear without silicate precipitate. It implied that silicates are not present in the sample to the quantity that can require further action using Hydrofluoric acid (HF) to remove the silicate – which could take longer time. The samples were equally observed to be high in Iron (Fe) after the digestion process.

Sample Preparation for ICP-MS

The complete dissolution of the ore samples was done in duplicate with control as presented in Fig. 3.4. A maximum of 0.5 g (with acceptable error mass range by standard of 0.4997 g – 0.5003 g) of the sample was weighed into microwave heating vessel and 2.0 ml of distilled water was added to moisten it in order to avoid possible explosion. 2.0 ml of concentrated HNO_3, 6.0 ml concentrated HCl and 0.5 ml H_2O_2 (as catalyst) were added. The control vessel contained the same measurement of acids but with no sample in it. The vessels containing the sample and reagents are sealed into rotor then placed into the microwave. The same settings and conditions were applied as in the case of quick test for silica. The purpose of sample digestion besides dissolution (in a closed vessel digestion process) was to produce an aqueous solution in acidified matrix. The digested samples were then filtered using a filtering device, polyvinylidene fluoride PVDF 0.22 μm, (a highly non-reactive thermoplastic, used in applications requiring the highest purity). A diluent – composed of 5 % (50 ml) HNO_3 and 1 % (10 ml) HCl acids was added to the filtrate in two sets: Firstly, by 10 % to reduce the total dissolved solids (TDS) to very low level due to sensitivity of the ICP-MS as well as to cater for the trace elements. Secondly, by 50 % to cater for metals such as magnesium if present in high concentration, which could impend on the system. An internal standard (ISTD) to monitor the stability of the instrument as well as sample is also applied. Rhodium (Rh), a good and commonly used ISTD of value 0.02 ml, equivalent to 20 ppb is utilized for this analysis.

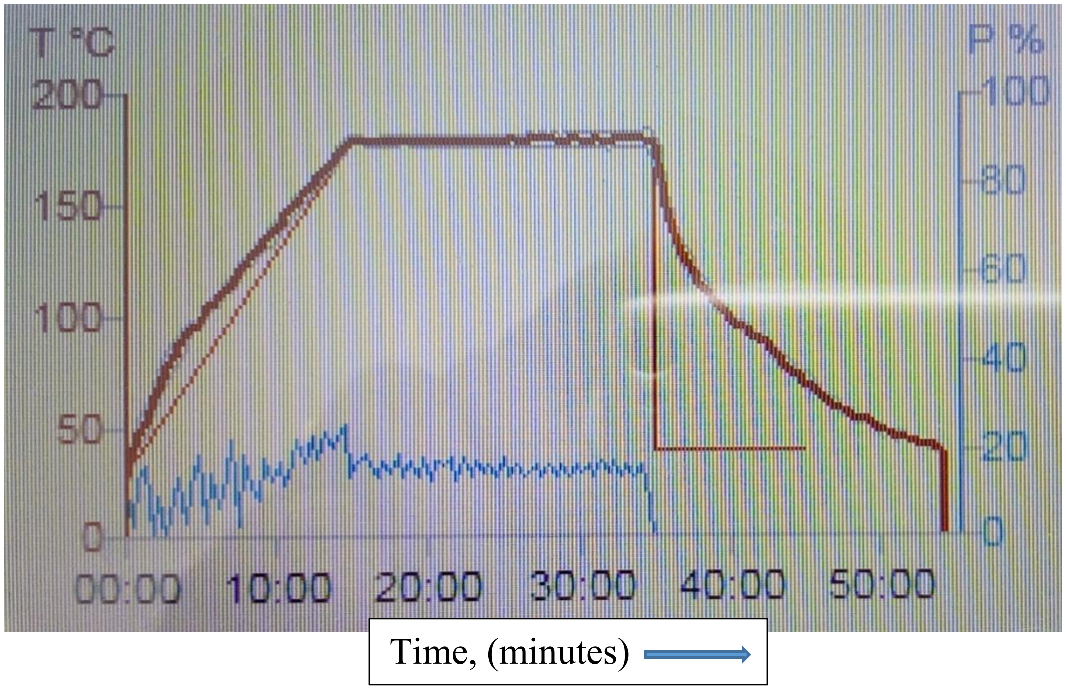

Figure 2: Digestion curve of the sample preparation for ICP-MS Uranium Ore Sample Measurements using ICP-MS

The determination of the concentration of uranium, trace elements, rare-earth elements (REE) and others, in the ore is done by ICP-MS technique. A technique that is well known and widely reported in literatures (Kristo et al., 2016) for its very elegant, sensitivity and accuracy. Agilent 7700 series ICP-MS of Agilent Technologies, Inc. USA, at the Environmental Analytical Chemistry, School of Chemistry, University of the Witwatersrand, Johannesburg presented in Fig. 3.1a, was used for the analysis of uranium ore samples in this work. Both the prepared and blank samples, the calibration standards (5 ppb, 20 ppb, 50 ppb, 100 ppb, 500 ppb, and 1000 ppb) and quality control samples (20 ppb and 100 ppb) were placed into the auto-sampler, for ICP-MS measurement. Prior to the upload of the samples into the low flow sample introduction system, nitric acid was used to clean the tubing, to avoid washing of residual memory. The cleaning and rinsing of the tubing is repeated after each sample to avoid cross contamination. The process is automatic and computerised. The control is performed on the computer system via an installed software – ICP-MS MassHunter Workstation software, for running Agilent 7700 series. The samples are introduced into the nebuliser containing plasma (a mixture of ions, electrons and atoms) at atmospheric pressure, with an extremely high temperature – 10,000 oC, which makes for easy transition of most elements from atoms to ions. Mostly, single charged positive ions are formed and because argon plasma is used, it becomes relatively simple for mass spectra to be generated and interpreted. The plasma ionises the samples and then through a vacuum interface, transfer to the mass analyser – A hyperbolic quadrupole mass analyser, which is sequential thereby measures elements in sequence. Due to ICP-MS abundant sensitivity, superior adjacent peak separation was achieved. The separated ions are then detected by the ICP-MS detection system – a fast simultaneous dual mode detector (of 9 orders dynamic range), as shown in Fig. 3.1b, giving rise to data acquisition for data analysis.

DATA ACQUISITION AND METHOD OF ANALYSIS

The Agilent 7700 series ICP-MS MassHunter Workstation software incorporated into the computerised system provides for acquisition of data and analysis, results being presented in an excel spread sheet in the unit of part per billion (ppb). This acquired data was then exported for further quantitative analysis, part of which are unit conversion to part per million (ppm) then to specific activity in Becquerel per kilogram (Bq/kg). In this study, the acquired data are analysed using a combination of Microsoft Excel, the SPSS 21.0 for Windows, SPSS Inc., USA, and the Sigma plot 11.0 softwares. Large amount of data of this nature are analysed by various statistical tools that are available. Some of the multivariate methods that provide a better understanding of data include cluster analysis (CA), principal component analysis (PCA) and discriminant function analysis (DA) (Davis, 2002). In this study, the Analysis Of Variance (ANOVA) was applied to the data at 5% significance level (i.e. $\alpha = 0.05$). The ANOVA was used to determine the level of significant variation between the various rare earth elements (REE) and the trace-impurity elements of the samples as well as their respective origin-sample location. The ANOVA analysis works by breaking into two parts, the total variance of a data set. The variance within the individual sample group (particular mine), is determined using Eq. 3.1 and the variances between the different sample groups (all mines), is also determined using Eq. 3.2 (Davis, 2002; Sawyer, 2009).

$$M\,S_W = \frac{\sum (x_i - x)^2}{(n - 1)} \quad \text{(1)}$$

$$M\,S_B = \frac{\sum (x_i - x_o)^2}{(h - 1)} \quad \text{(2)}$$

Where, n is the number of members in sample group, x_i is the measured value, x is the mean of n measurements; h is the number of sample groups, x_o is overall mean. The F-statistic is a ratio of the Mean of Squares between groups ($M\,S_B$), which is variance due to interaction between the different sample groups and Mean of Squares within a group ($M\,S_W$) which is variance due to differences between the replicates in individual sample group (Massart & Kaufman, 1983).

$$F = \frac{M\,S_B}{M\,S_W} \quad \text{(3)}$$

The F critical value is determined from the F-Table, shown in Table 3, using the degrees of freedom (h – 1 and n – 1) as highlighted in yellow, for this study. Variation between samples are considered statistically significant and not by chance, if the obtained F values are larger than the F critical, with 95% confidence. While no conclusions can be drawn if the F value is less than F critical, for the data set (Sawyer, 2009). The probability (with range 0 – 1) that the observed results in the study could have occurred by chance, gives the P-value. Such that, if $P > 0.05$ then the differences observed is by chance and not significant. If $P < 0.05$ then the differences observed is significant and not by chance (Massart & Kaufman, 1983; Davis, 2002).

RESULT ANALYSIS AND DISCUSSION

The ICP-MS Mass-Hunter computing data generator converted the pulse of various isotopes energy spectrum peak generated from the detector into well up to 1590 data in unit of part per billion (ppb) on an excel spreadsheet. The data on elemental composition of mined uranium ore samples and characteristic parameters relevant to nuclear forensics obtained in this study are in tables. All the data from this study presented in tables in this section are graphically presented in the analysis section. The mean results for the various locations for the uranium and thorium concentrations (ppm) as measured by the ICP-MS.

Table 3: Thorium and uranium isotopes concentrations in uranium ore samples of different locations from Nigeria as obtained in this study

Sample Location	Thorium and uranium Isotopes Concentrations (ppm)			
	232Th	238U	235U	234U
XR	5.410 ± 0.318	1.318 ± 0.049	0.009 ± 0.000	5.297E-07 ± 2.0E-08
MI	0.055 ± 0.006	0.084 ± 0.003	0.001 ±1.9E-05	3.384E-08 ± 1.0E-09
MII	0.159 ± 0.003	73.965 ± 1.371	0.536 ± 0.009	2.972E-05 ± 5.5E-07
MK	0.061 ± 0.002	7.854 ± 0.293	0.057 ± 0.002	3.156E-06 ± 1.2E-07

It can be observed that from Table 4.1, the concentration range of 232Th, for the entire samples, which 0.055 ± is 0.006 to 5.410 ± 0.318 ppm falls below the average crustal concentration range for 232Th that is 8 to 12 ppm (Nicolet & Erdi-Krausz, 2003). It implies that the study areas have concentrations of uranium and thorium that is lower that the crustal concentration. This therefore forms the basis for identifying the samples as having concentration values less than the average crustal concentrations in ppm. The concentrations of the uranium isotopes presented values less than the average crustal concentration (2 to 3 ppm 238U) for the Riruwai (1.318 ± 0.049 ppm) and Mika-I (0.084 ± 0.003 ppm), respectively. However, Mika-II (73.965 ± 1.371ppm) and Michika (7.854 ± 0.293 ppm) have concentrations way greater than the world average. As for 235U and 234U, their respective concentration ranges across the sample locations are: 0.001 ±1.9E-05 ppm to 0.536 ± 0.009 ppm and 3.384E-08 ± 1.0E-09 ppm to 2.972E-05 ± 5.5E-07 ppm. With values for the lower and higher concentrations being both from Mika-I and Mika-II, respectively. The anomalous concentration within Mika mines suggests variation due to endogenic process (the way the rocks were formed and the process that acted on them since after formation), geological setting and mineralogy of sampling point. The implication of the wide variation however, provides a basis for further research.

Table 4: Thorium and uranium isotopes activity concentrations in uranium ore samples in this study

Sample Location	Thorium and Uranium Isotopes Activity Concentrations (Bq/kg)			
	232Th	238U	235U	234U
XR	21.966 ± 1.289	16.479 ± 0.720	0.765 ± 0.033	0.1228 ± 0.005
MI	0.224 ± 0.027	1.053 ± 0.033	0.049 ± 0.002	0.008 ± 0.000
MII	0.646 ± 0.012	924.566 ± 17.131	42.915 ± 0.795	6.891 ± 0.128
MK	0.246 ± 0.009	98.181 ± 3.661	4.557 ± 0.169	0.732 ± 0.027

The activity concentration of 232Th across sample locations as presented in Table 4.2 has a range of 0.224 ± 0.027 Bq/kg (from Mika-I) to 21.966 ± 1.289 Bq/kg (from Riruwai). The value was lower than the average activity concentrations of 232Th in the continental crust of 44.00 Bq/kg (Maxwell et al., 2013). The activity concentration of 238U across the sample locations also has a range value of 1.053 ± 0.033 Bq/kg (from Mika-I) to 924.566 ± 17.131 Bq/kg (from Mika-II), which is extremely higher than the average activity concentration of 238U in the continental crust of 36.00 Bq/kg. However, Mika-I and Riruwai samples have lower activity concentration values while Michika and Mika-II have way higher values of activity concentrations, compared to the average continental crust value. The isotopic ratios considered in this study include 238U/235U and 235U/234U together with 235U/238U and 234U/238U. The 232Th/238U activity ratio also determined and presented.

Table 5: Uranium concentration isotopic ratios of the uranium ore samples

Sample Location	Uranium composition isotopic ratio			
	238U/235U	235U/234U	235U/238U	234U/238U
XR	137.8812700	130.9113019	7.252617×10-03	5.5400999×10-05
MI	137.8812745	130.9112930	7.252608×10-03	5.5401003×10-05
MII	137.8812735	130.9113012	7.252617×10-03	5.5400996×10-05

MK	137.8812643	130.9113014	7.252615×10-03	5.5400999×10-05

238U/235U isotopic ratio in this study is 137.8812 and shows no significant variation across the sample location, but equals the constant value for natural uranium under the solar system which is 137.88 (Stirling et al., 2007; Weyer et al., 2008). 235U/234U isotopic ratio yielded a value of 130.9113, show no significant variation across the samples. However, it falls within the World's range value of 83.63-164.17, from different geochemical environment (Brennecka et al., 2010).

The standard value for the isotopic ratios 235U/238U and 234U/238U and their variability are well known, as 7.253 ×10-03 and 5.502 ×10-05 respectively (Verga et al., 2011; Mishra et al., 2017). The values measured in this study were 7.252617×10-03 and 5.5400999×10-05, which are identical to the standard values, although, there was no significant variation across the samples locations. The results of the rare earth elements concentrations in ppm and their respective uncertainties, are obtained by applying the dilution factors 10 and 50, thereafter converted from the raw data units of ppb to ppm (by a factor of 1000).

CONCLUSION AND RECOMMENDATIONS

In this paper, four uranium ore rock samples were collected from some parts of northern Nigeria, specifically, Riruwai (Kano), Mika (Taraba), and Michika (Adamawa) respectively. The uranium ore samples were analysed using inductively coupled plasma mass spectrometry (ICP-MS) technique, with Agilent 7700 device, together with the Anton Paar digital multiwave digestion machine. The analysis was performed at the Environmental Analytical Chemistry Laboratory (EACL), University of the Witwatersrand, Johannesburg South Africa. The aim of the study was to characterise the uranium ore samples and obtain signature or fingerprints for nuclear forensic application. To be added to National Nuclear Forensic Library (NNFL), thereby bridging the existing gap in data from Africa, though being among top suppliers of the world's uranium resource. Also in support of peaceful use of nuclear and other radioactive materials and to thwart illicit trafficking and smuggling in nuclear and other radioactive materials. The following can therefore, be used to create nuclear signature for the respective mine samples:The isotopic concentrations of Nd (146Nd, 144Nd and 143Nd), Sr (88Sr, 87Sr and 86Sr) and Pb (208Pb, 207Pb, 206Pb and 204Pb) and their corresponding ratios 143Nd/144Nd, 87Sr/86Sr as well as 208Pb/206Pb and 207Pb/206Pb . The age of samples The ICP-MS measurement of the uranium ore samples provided excellent results for the stable isotopes thereby other isotopes determined from them could not provide distinct variation of their ratios between different mines. Therefore, further work is recommended on direct ratio measurement using ICP-MS without spiking or combination of methods such as Laser Ablation or Multi Collimator Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS, or MC-ICP-MS) with Thermal Ionisation Mass

Spectrometry (TIMS). The scope of the work can further be widened to include other geological locations from different countries and regions of Africa in order to provide a robust and near complete overview of the signature for the continent.