

**Comparative Study of Uranium and Thorium Content of Some Selected Nigerian and Nigerian Cereals Using Neutron Activation Analysis.**

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*Abstract*

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*The need to know the level of contamination of radioactive elements, especially uranium and thorium, in the common foods we eat is highly significant. In this study, 7 food samples, mainly cereals were collected from some parts of Katsina State in Nigeria and Maradi in Niger Republic. The cereals sampled were beans, millet and sorghum. Nigerian rice was analyzed as the seventh sample because there is no commercially grown rice in Niger Republic for comparison. The sampled cereals were analyzed for Uranium and Thorium content. The work was performed with both short and long irradiation protocols of Instrumental Neutron Activation Analysis (INAA) at the Nigerian Research Reactor-1 (NIRR-1) of the Center for Energy Research and Training (CERT) Ahmadu Bello University, Zaria- Nigeria. INAA was chosen due to its advantages over other analytical techniques. Thorium was detected at concentrations ranging from 0.3 to 0.6  $\mu\text{g g}^{-1}$  while Uranium concentrations were below detection limit in all the seven samples. Among the samples, Nigerian millet has the highest concentration (0.6  $\mu\text{g g}^{-1}$ ) of Thorium, while Nigerian beans and Nigerian rice have the lowest (0.3  $\mu\text{g g}^{-1}$ ). Generally, with the exception of Nigerian sorghum, Nigerian cereals have higher concentrations of Thorium. The results compare favorably with those of other workers using different versions of INAA on related cereals. Quality control and Quality Assurance of the method was tested by analyzing an analytical quality control service (AQCS) reference material (lichen) from International Atomic Energy Agency (IAEA).*

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**Keywords:** Key words: Uranium, Thorium, neutron activation analysis, Cereals, Katsina, Maradi.

**1.0 Introduction**

Radioactivity was discovered almost accidentally, by a French scientist Henri Becquerel, in 1896, while working with phosphorescent materials [1]. The results of his experiments were all negative until he used Uranium salt [2].

The dangers of radioactivity and radiation were not immediately recognized. As early as 1546, and for centuries afterwards, it was reported that underground miners in Schneeberg, Germany, suffered an unusually high incidence of fatal lung disease. In 1879, it was demonstrated both clinically and anatomically that half of these miners were dying of lung cancer [3]. The ores in question were particularly rich in uranium. Similar cases of lung cancer incidence have occurred among iron, lead and zinc miners in Sweden, in fluorspar miners in Newfoundland, and especially among Uranium miners in all parts of the world. Scientific papers published in the 1930s, even before the outbreak of World War II, clearly indicated that airborne radioactivity in the mines was the most likely cause of this lung cancer. The principal culprits are Radon gas and its solid by-products, the so-called "Radon daughters" [3].

Biological effect of radiation from sources external to the body can either be acute or chronic [1]. A body experiences relatively acute effect, when it receives a relatively large dose of radiation within a short time. This may be caused by sudden inadvertent exposure to beams of radiation coming out from nuclear reactors, accelerators etc, or due to an

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accident. The chronic exposure, on the other hand, refers to frequent (e.g. daily) exposure to small dose of radiation by workers connected with the operation of nuclear reactors or accelerators or with the handling of radioactive substances, such as radioactive fission products (waste) in a reactor [1]. Radiation in large doses can produce cancer, cause kidney and blood disorders and induce cataract of the eyes. Other effects include lesions, sterility, abnormal pregnancies and malformed off-springs.

The concentration of radioactive elements in foods is generally very low [4]. By far, the largest source of natural radiation exposure comes from varying amounts of Uranium and Thorium in the soil around the world. These contaminations posed significant hazardous effects on man. Research conducted in 2009 [5] from collected samples of some 8 European countries indicated the presence of these radioactive elements in their native food. In view of the above, the quest to obtain the level of contaminations of Thorium and Uranium in our locally cultivated foods is warranted. Uranium and Thorium can be present in food, water and air in varying concentrations through leaching from natural deposits such as soil or rocks, emission from nuclear industry, nuclear weapons, dissolution in fertilizer and combustion of coal and other fuels [5,6]. The need to obtain data on levels of trace elements in foods and beverages has recently become a national challenge in many countries [7]. The major challenges are the determination of elemental concentrations with improved accuracy and precision [7, 8].

Neutron activation analysis was first proposed in 1936 by G. Von Havesy and H. Levy for the analysis of dysprosium in rare-earths using an experiment. NAA was developed as a highly valuable analytical technique especially since the advent of nuclear reactors, which offer extremely high neutron fluxes [9]. NAA seems to be a favorable method for the simultaneous and sensitive determination of Uranium (and Thorium) in food samples [10]. It is a well known technique for determination of trace elements in a wide range of materials including environmental and biological samples [6]. According to [11], NAA has become a mainstay of geochemical and biochemical trace element research because the technique possesses several important advantages that include high sensitivity, multi-element capacity, substantial freedom from systematic errors, freedom from analytical blank and other problems related to dissolution. Others include qualitatively known precision, complementary to other methods and the fact that results in NAA are independent of the chemical state of elements.

Neutron Activation analysis is a sensitive analytical technique useful for performing both qualitative and quantitative multi-element analysis of major, minor and trace elements in samples from almost every conceivable field of scientific or technical interest. In addition because of its accuracy and reliability, NAA is generally recognized as the “referee method” of choice when new procedures are being developed or when other methods yield results that do not agree [12]. Sequential instrumental NAA allows quantitative measurement of up to about 35 elements in a sample. The lower detection limit is in parts per million or parts per billion, depending on the element [13]. Neutron activation analysis is performed in three main steps: irradiation, detection and interpretation of the result [14]. Samples undergo neutron capture and form a compound nucleus which later decays by emission of gamma rays. Detection of the gamma rays (of specific energy) indicates the presence of a particular element [15].

In this study, concentrations of Uranium and Thorium content were determined in some selected food samples (mainly cereals), cultivated around Katsina and Maradi states of Nigeria and Niger Republic respectively, using instrumental thermal neutron activation analysis. The expected results will also add the elements on the list of trace elements found in cereals of these regions.

### **Important Equations.**

#### **Measurement of Count Rate.**

The measured count rate (R) of the gamma rays from the decay of a specific isotope in the irradiated sample can be related to the amount (n) of the original stable isotope in the sample by the activation equation (1) [15];

$$R = \epsilon I_{\gamma} A = \epsilon I_{\gamma} n \phi \sigma (1 - e^{-\lambda t_i}) e^{-\lambda t_d} \tag{1}$$

Where:

R = Measured gamma-ray count rate (cps).

A = Absolute activity of Isotope  $^{A+1}Z$  in sample.

$\epsilon$  = absolute detector efficiency.

$I_{\gamma}$  = absolute gamma ray abundance.

$\phi$  = Neutron flux ( $\text{ncm}^{-2} \text{sec}^{-1}$ ).

$\lambda$  = radioactive decay constant ( $\text{s}^{-1}$ ) for isotope  $^{A+1}Z$ ,

$t_i$  = irradiation time (s)

N = number of atoms of isotope  $^AZ$  in sample.

$\sigma$  = neutron capture cross-section ( $\text{cm}^2$ ) for isotope  $^AZ$ .

$t_d$  = decay time (s)

**Calculation of Concentration using Gamma Ray Counts.**

The procedure generally used to calculate concentration (i.e. ppm of elements) in the unknown sample is to irradiate the unknown sample and a comparator standard containing a known amount of the element of interest together in the reactor. If the unknown sample and the comparator standard are both measured on the same detector set up then one needs to correct the difference in decay between the two. The equation used to calculate the mass of an element in the unknown sample relative to the comparator standard is [12];

$$\frac{A_{sam}}{A_{std}} = \frac{M_{sam}}{M_{std}} \frac{(e^{-\lambda t_d})_{sam}}{(e^{-\lambda t_d})_{std}} \tag{2}$$

Where;

A= activity of the sample (sam) and standard (std),

M= mass of the elements,  $\lambda$  = decay constant for the isotope and  $t_d$ = decay time.

When performing short irradiation, the irradiation decay and counting times are normally fixed as the same for all samples and standard such that the time dependent factors cancel. Thus equation (2) above reduces to:

$$C_{sam} = C_{std} \frac{W_{std}}{W_{sam}} \frac{A_{sam}}{A_{std}} \tag{3}$$

Where;

C=concentration of the element and W=weight of the sample and standard.

**2.0 Experimental Sample Collection**

A total of 7 samples of guinea corn, millet, beans and rice were collected from cities of Funtua, Katsina and Charanchi Local Governments of Katsina State of Nigeria and Maradi Metropolis and Maigamji Village of Madarumfa Local Government both of Maradi state in Niger Republic. The collection was made between July 14 and August 7, 2010. In order to ascertain the locality of the collected cereals, the purchase was made directly from farmers. The exception was in some parts of Niger Republic where some of the samples like guinea corn and beans were purchased at the market after the best harvest period of the samples. The products were however, purchased with careful selection and confirmation of their native origin from the seller. Since there is no popularly grown rice in Niger, only Nigerian rice was considered, among that variety.

**Table 1:** Samples collection locations.

S/N	Sample Level and Name (Botanical/Scientific)	Collection Area (Locality)	Method of Collection	Quantity- measure(Tiya)
1	S1- Guinea Corn (Sorghum)	Dutsenreme, Bakori L.G, Katsina State-Nigeria	Direct from farmer	¼
2	B1- Beans (Vigna sunensis)	Funtua L.G, Katsina-Nigeria	Direct from farmer	¼
3	M1- Millet (Pennisetum typhoides)	Charanchi L.G, Katsina-Nigeria	Direct from farmer	¼
4	R- Rice (oriza sativa)	Kurami-Bakori L.G, Katsina-Nigeria	Direct from farmer	¼
5	S2- Sorghum	Maradi- Niger Rep.	Maradi –market	¼
6	B2- Beans	Maradi-Niger Rep.	Maradi market	¼
7	M2- Millet	Maigamji, Madarumfa L.Govt. - Niger Rep.	Direct from farmer	¼

### Sample Preparation

Samples were taken to analytical chemistry laboratory, Umaru Musa Yar’adua University, Katsina State for grinding. Using the available ceramic mortar and pestle, the samples were crushed into fine powder. In order to avoid any form of mixture of the samples methanol was used to wash the mortar and pestle before and after preparation of each sample. The dried grinded samples were then replaced back into their respective polythene bags.

The packaged samples were then taken to sample preparation department, Center for Energy Research and Training (CERT), Ahmadu Bello University, Zaria, Nigeria. A small portion of the powdered samples were then prepared, weighed using precision balance and packed into 8ml polyethylene vials. An air dryer was used to heat seal the vials.

**Table 2:** Exact masses of samples used.

S/N	Sample Level	Sample Name	Mass (g)
1	S1	Sorghum	0.2772
2	B1	Beans	0.2641
3	M1	Millet	0.2668
4	R	Rice	0.2588
5	S2	Sorghum	0.2602
6	B2	Beans	0.2663
7	M2	Millet	0.2642

### Irradiation, Counting and Analysis.

Using rabbit carriers, the samples and standard were sent into the reactor through a pneumatic transfer system which uses pneumatic pressure. NIRR – 1 at A. B. U. Zaria, irradiated the samples with a thermal neutron flux of  $5.0 \times 10^{11} \text{ ncm}^{-2} \text{ s}^{-1}$  for 6 hours of long irradiations protocol. The whole system is equipped with electronic timers which help in monitoring the exact irradiation and decay times.

At the end of irradiation the vials were returned from the reactor with the help of pneumatic pressure to an ejector. It is then allowed to decay, by allowing the activity of the sample to fall down. Sample is usually handled when its activity is within the acceptable handling limit. The acceptable limit is about  $30 \mu\text{Sv/h}$ , which is well below the activity of several  $\text{mSv/h}$  it comes with when removed from reactor.

The samples were then taken to a detecting set up consisting of a high purity germanium (HPGe) detector, connected to a PC-based Multi-Channel Analyzer (M.C.A.). The samples were then allowed to decay further for the analysis of long life elements. Counting after the first 3 days is referred to as first long count and is done in 30mins. The samples were then further cooled for another 7 days after which they were ready for second long count in a period of 1 hour.

## 3.0 Results and Discussion

### Results

Tables 3 and 4 give the results of elemental concentration of various elements obtained in the samples and reference material analyzed for Quality control. Uranium and Thorium concentrations in Nigerian and Nigerien food samples were also compared in separate tables.

**Table 3:** Uranium Concentration in samples

S/N	Sample name	Concentration ( $\mu\text{g g}^{-1}$ )	
		Nigerian (1)	Nigerien (2)
1	Sorghum	BDL	BDL
2	Beans	BDL	BDL
3	Millet	BDL	BDL
4	Rice	BDL	-

**Table 4:** Thorium Concentration in samples

S/N	Sample name	Concentration ( $\mu\text{gg}^{-1}$ )	
		Nigerian (1)	Nigerien (2)
1	Sorghum	0.4	0.5
2	Beans	0.4	0.3
3	Millet	0.6	0.4
4	Rice	0.3	-

**Table 5** Analytical result of Lichen-336 reference material used for quality control.

ELEMENTS	ANALYZED IAEA – 336 (LICHEN) ( $\mu\text{gg}^{-1}$ ) FOR THIS RESEARCH	CERTIFIED IAEA – 336 (LICHEN) ( $\mu\text{gg}^{-1}$ ) 95%	
Mg (ppm)	NA	NA	
Al (ppm)	680 ± 12	680	570-790
Cu (ppm)	BDL	3.6	3.1-4.1
Ca (ppm)	NA	NA	
Ti (ppm)	NA		
V (ppm)	1.47 ± 0.19	1.47	1.25-1.69
Mn (ppm)	63 ± 0.3	63	56-70
Dy (ppm)	BDL		
Na (ppm)	320 ± 1	320	280-360
K (ppm)	1840 ± 28	1840	1640-2040
As (ppm)	0.63 ± 0.03	0.63	0.55-0.71
La (ppm)	0.66 ± 0.03	0.66	0.56-0.76
Sm (ppm)	0.11 ± 0.005	0.106	0.092-0.120
U (ppm)	NA		
Sc (ppm)	0.17 ± 0.009	0.17	0.15-0.19
Cr (ppm)	BDL	1.06	0.89-1.23
Fe (ppm)	430 ± 37	430	360-480
Co (ppm)	0.29 ± 0.05	0.29	0.24-0.34
Zn (ppm)	30.4 ± 2.7	30.4	27.0-33.8
Br (ppm)	12.9 ± 1.1	12.9	11.2-14.6
Rb (ppm)	BDL	1.76	1.54-1.98
Sb (ppm)	BDL	0.073	0.063-0.083
Cs (ppm)	NA	0.11	0.097-0.132
Ba (ppm)	BDL	6.4	5.3-7.5
Eu (ppm)	0.023 ± 0.007	0.023	0.019-0.027
Yv (ppm)	BDL	0.037	0.025-0.049
Lu (ppm)	BDL	0.0066	0.0042-0.0090
Hf (ppm)	NA		
Ta (ppm)	NA		
Th (ppm)	0.14 ± 0.04	0.14	0.12-0.16

**Key:** PPM – Part per million, BDL – below detection limits, NA – not analyzed, PPM =  $\mu\text{gg}^{-1}$

**Discussion**

Tables 3 and 4 show the analytical results of thermal neutron activation analysis of 7 biological samples comprising sorghum, beans, millet and rice from Nigeria and Niger republic.

Table 3 shows that concentration of Uranium in both Nigerian and Nigerien cereals is less than detectable amount using thermal NAA.

This result is similar to the result of a study [4] in which uranium was not detected in the cereal (corn) used in their experiment. A study conducted [6] at Nuclear Engineering Teaching Laboratory, University of Texas at Austin, U.S.A., on some 8 Nigerian foods which includes sorghum, however, were able to detect Uranium. The major differences are the

*Journal of the Nigerian Association of Mathematical Physics Volume 20 (March, 2012), 239 – 244*

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combination of epithermal neutron activation analysis and Compton suppression methods.  $^{238}\text{U}$  has a much larger epithermal neutron absorption cross-section, as compared to its thermal absorption cross-section. In addition to the epithermal cross-section, there is also drastic reduction in the  $^{24}\text{Na}$  and  $^{38}\text{Cl}$  background interferences when epithermal neutrons are used over thermal neutrons [6].

Table 4 gives the thorium concentrations in various Nigerian and Nigerien foods. Close observations of the table show that Nigerian millet has highest concentration ( $0.6\ \mu\text{gg}^{-1}$ ) of thorium, while Nigerian rice contains the least ( $0.3\ \mu\text{gg}^{-1}$ ). Both Nigerian sorghum and Nigerian beans have same concentration of  $0.4\ \mu\text{gg}^{-1}$ . In same table for Nigerien cereal, Nigerien beans has however the least concentration of thorium ( $0.3\ \mu\text{gg}^{-1}$ ) while Nigerien sorghum has the highest of  $0.5\ \mu\text{gg}^{-1}$ .

Concentrations of these radioactive substances are thus attributed to cultivation sites.

## Conclusion

Elemental concentrations of various elements were determined in all the 7 samples. The presence of thorium was verified and compared in all the 7 samples from Nigeria and Niger republic. These selected samples form the staple food cereals in Nigeria and Niger republic. Uranium concentration was however below detection limit of the setup used. Neutron activation analysis is a non-destructive method, requiring no dissolution or addition of any chemical and about 35 elements can be readily analyzed, depending on the sample type and the detection limit of elements in the sample in question. It is also considered that Thorium may be regarded as one of the trace elements in our foods. It is recommended that future work could employ epithermal NAA and Compton suppression methods to determine more accurately Uranium concentration in the samples, as Uranium has a higher epithermal neutron absorption cross section. The occurrence of these elements in appreciable concentrations in food samples could litigate the need for a policy on controlling the massive consumption of the affected samples.

**Quality Control** – This was ensured by the agreement observed between the analyzed standard reference material and certified values of lichen obtained from AQCS of IAEA.

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