Multi-Elemental Analysis of Local Millet and Wheat by Instrumental Neutron Activation Analysis Using NIRR-1 Facility

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Abstract– **The nutrient value of local millet and wheat in terms of minor and trace element content has been evaluated by Instrumental Neutron Activation Analysis (INAA) using the Nigerian Research Reactor (NIRR-1). Two locally cultivated millet and wheat samples were obtained directly from the farmers and two millet and wheat samples grown under surveillance condition were collected from Institute of Agricultural Research (IAR) of the Ahmadu Bello University, Zaria-Nigeria. Multi-Elemental analyses using the relative technique were adopted. Twenty one elements were determined and analyzed (Na, K, As, Br, La, Sm, Np, Sc, Cr, Fe, Co, Zn, Se, Rb, Sb, Ba, Eu,Yb, Lu, Hg and Pa) in these cereals foods.**

Keywords– **NIRR-1, Millet, Wheat and INAA**

I. INTRODUCTION

Nigeria is a predominantly agricultural country. The multi-elemental determination in staple food especially millet and wheat is of great importance for its nutritional value as well as potentially toxic effects. For food safety, it is necessary to keep contaminants below a permissible level. Millet is a staple food for a large part of the world Population, especially in the North East, North West, and North central States of Nigeria, making it among the most consumed cereal grain. Millet cultivation is well-suited to countries. Wheat is another grain that belongs to the family grass. There are a number of species of wheat which are grown as crops.

The most widely produced are *Triticumaestivum* commonly referred to as bread wheat durum or durum wheat, which has particularly hard kernels and is preferred for puffing as well as being used primarily for milling into semolina and flour for macaroni and other pasta products. There are numerous genetic varieties (also referred to as cultivars) within each species. In many countries wheat is classified according to whether it is hard or soft, white or red grained and planted in spring or winter.

In recent years, there has been increasing implementation of multi-elemental techniques for the analysis of food items to establish limits for human exposure to contaminants from the food. The study of elements in millet and wheat are important in searching for contamination or leftover toxic elements because foods might be contaminated by chemical compounds, particularly heavy metals, during cultivation. For example, cadmium contamination in agriculture products was discovered in Thailand [1]. Cereals grains have long been regarded as valuable sources of essentials nutrients. They provide energy, protein, minerals, and vitamins in the human diet [2]. Cereals are the fruit of cultivated grasses, members of the monocotyledonous family gramineae. Global production of cereals grains has been approximately 2000 million tonnes over recent years [3]. They are cultivated primarily for human food, livestock feed, seed and as a source material for starch, biofuel and other industries. Moreover, different research projects have been conducted to develop methods to measure elements in foods which are of interest because of their effect on human health [4], [5], [6]. Neutron activation analysis (NAA) has the potential to determine multi-elements in all types of samples including millet and wheat.

Multi-elemental studies have recently become a reality and with the development of sensitive and sophisticated instrumentation like the NAA, most elements can be determined in a routine manner. Because of the interactive nature of some elements, their determination is essential to provide data on their pattern of association and their composition in food stuffs. There is therefore, a need to know their levels in samples drawn from different chemical environments of the world. As has been noted by [7], "the concept of speciation applies not only to metals of nutritional importance, but also to potentially toxic elements, such as selenium, arsenic, cadmium, mercury and lead. A better understanding of the predominant chemical forms of such contaminants in food would, therefore, seem to be essential for those who have to make decision concerning dietary requirements and related legislation".

The study of human nutrition and health requires more information about trace elements species in food [7]. Proper dissemination of accurate information gives consumers informed choices, allows industry to make the best use of foods, supplements and processing (which might affect chemical species), and provides governments with the basis for good advice and legislation. Both essential minerals and heavy metals would be useful for the assessment of safety in the consumption of these foods.

It may be that one day essential trace element species will be listed on food composition labels or that legislation for potentially toxic elements will be based on chemical species present rather than the total concentration.

The purpose of this paper is to determine the elemental concentrations in local millet and wheat by instrument neutron activation analysis (INAA) in Cereals obtained from Zaria area of Kaduna state, Nigeria, using NIRR-1 facility.

II. MATERIALS AND METHOD

A) Facility Description

In this work NIRR-1 facility was utilized (Fig. 1). The NIRR-1 swimming pool-type reactor (30 kW) at the Centre for Energy Research and Training, Ahmadu Bello University, Zaria, is a nuclear research reactor, which uses high-enriched uranium as fuel and light water as moderator and coolant. The reactor is used for neutron irradiation in the study; high resolution gamma-ray spectrometers were used in this study.

High-purity Germanium HP(Ge) detector (model GEM 30P4 - 76) with a resolution of 1.74keV FWHM at 1332.5 keV of Co- 60, H.V. biased supply model 659 ortec, 5kV, spectroscopy amplifier model 672 ortec, acquisition interface card with computer and basic spectroscopy software (Winspan 2003) was used in this work; the spectroscopy modules is from ORTEC, USA.

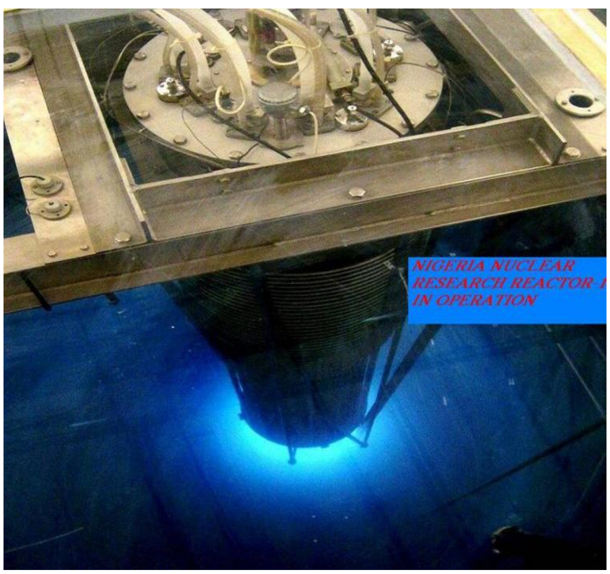

Figure 1: Sectional view of NIRR-1

B) Sample Collection

A total of four samples were collected of which two were directly from the farmers and the other two were of hybrid crops (Table 1) grown under surveillance condition (millet and wheat) collected from the Institute of Agriculture Research (IAR) of the Ahmadu Bello University, Zaria-Nigeria. The cereals were obtained in a dry uncrushed form labeled by the institute.

Table 1: Samples obtained from IAR

S/N	*Sample Name*	*Sample Source*
1.	Sosait -182-Millet	IAR ABU ZAR
2.	Payen-13-Wheat	IAR ABU ZAR

C) Sample Preparation

The samples were crushed into powder form using agate mortar and pestle. The samples were thoroughly mixed to ensure homogenization and were properly dried and pack in a rabbit capsule for long irradiation in the reactor irradiation channel. A similar procedure was adopted for Standard Reference Materials (SRM) IAEA Lichen-336 (Table 3) which were also weighted and packed together with the samples for long irradiation. The purpose of the SRM is for quality control of the experimental procedure.

D) Analysis Procedure

The samples together with the standard were sealed and irradiated in NIRR-1 at a flux of $5x10^{11}$ ncm^{-2} s^{-1} for 6 hours and counted for 1800s and 3600s after 4 and 14 days of cooling period respectively. The stability of neutron flux throughout the period of long irradiation was checked by monitoring the neutron flux from the computer control display and the activity of the standards after irradiation. Identification of gamma-rays of product radio nuclei through their energies and quantitative analysis of their concentrations were achieved using the gamma-ray spectrum analysis software, WINSPAN 2003.

III. RESULTS AND DISCUSSION

The results of the INAA analysis for millet and wheat are shown in Table 2 together with their uncertainty values. Table 3 presents the result of Lichen-336 Standard for Quality Assurance where the result from this work is compared with certified values. Table 4 however shows the measured Concentrations of Elements (ppm) in IAR Control Samples, in this case the result of this work is also correlated with IAR values. The matrices for the standard reference materials are also presented in Table 5.

The spectra of the samples were evaluated using WINSPAN multi –elemental gamma-ray emulation software. In all, twenty one elements (Na, K, As, Br, La, Sm, Np, Sc, Cr, Fe, Co, Zn, Se, Rb, Sb, Ba, Eu, Yb, Lu, Hg, and Pa) were detected in the samples. The elements were determined using only the long irradiation scheme, since all of them are within the medium and long-lived half radionuclide. Our result shows most of them to be below detection limits except Br, Na, K, and Zn.

Bromine is considered by many authors to be essential for mammals [8].The main source of Br in soil that crops cultivates on. This was attributed to the application of agricultural chemicals such as methyl bromide which is used as fumigant [8]. Another important source of the element is from sea water and brought by rain over a long period of time [8]. The element Br was found to be present in all the samples analyzed. This could not be unconnected with the fact that biological samples are rich in bromine. The concentration of the element is higher in millet (2.4±0.001ppm) than in wheat (1.9±0.05ppm).

Zinc is among the most nutritionally important element [9]. It is a constituent of skin cells, bone metabolism and functioning of taste and eyesight [10]. Zinc is also known to prevent impaired spermatogenesis [11]. Zinc deficiency is characterized by recurrent infections, lack of immunity, growth retardation, skin disease, poor appetite and mental lethargy [11]. Pregnant and lactating women require 20 to 25 mg, while normal adult require 15mg of zinc everyday [11]. The wheat samples analyzed have zinc in substantial concentrations than in millet. Estimated safe and adequate daily intake for Zinc is between 10,000 and 20,000 µg/day [12]. Prolonged consumption of large doses was reported to result in some health complications such as fatigue, dizziness and neutropenia [13].

Just like bromine, the element K was found to be present in all the samples analyzed. This is also connected with the fact that biological samples are rich in potassium and bromine. The concentration of the potassium element is higher in wheat (4428±97.416ppm) than in millet (4324±164.312ppm).

K and Na are somewhat interdependent and it was reported that regulation of potassium involved that of sodium [14]. Sodium is essential for regulation of osmotic pressure of the body and helps to maintain acid – base and water balance of the body. Its deficiency causes loss of body weight and nerves disorder [14]. Potassium is accumulated within human cells by the action of Na^{+}, K^{+} - Atpase, called sodium pump and it is an activator of some enzymes and in particular coenzyme for normal growth and muscle function and helps in the protein and carbohydrate metabolism[14]. Apart from the fact that it is the principle cation of the intracellular fluid, its presence influences muscle activity particularly the cardiac muscle (14). Potassium deficiency causes nervous disorder, diabetes, and poor muscular control resulting in paralysis [14]. Na concentration was found to be relatively low in all the samples analysed. Millet sample has 17.65±0.829ppm and then wheat sample has 6.679±0.28ppm.

Table 2: Concentrations of the elements found in our cereals samples

Nuclide	Millet (ppm)	Wheat (ppm)
24Na	17.65±0.829	19.34±0.83162
42K	4324±164.312	4428±97.416
76As	< 0.0035349	< 0.0026914
82Br	2.412±0.0065	1.938±0.056202
140La	0.05477±0.0134	< 0.056111
153Sm	< 0.017624	< 0.017398
239Np	< 0.00359±0.001	< 0.0053138
46Sc	< 0.026991	< 0.00585±0.005
51Cr	< 1.0467	< 0.62455
59Fe	< 173.36	< 146.09
60Co	< 0.025163	< 0.1409±0.083
65Zn	69.31±6.5844	< 22.672
75Se	< 0.028853	< 0.021145
86Rb	< 4.6491	6.183±1.48392
122Sb	< 0.031845	< 0.0037283
131Ba	< 10.22±5.9684	< 13.269
152Eu	<0.020099	< 0.019655
175Yb	< 0.01437±0.007	< 0.01034
177Lu	< 0.0083456	< 0.0027811
203Hg	< 0.042009	< 0.028127
233Pa	0.1268±0.02028	0.01123±0.0071

Table 3: Result of Lichen 336 Standard for Quality Assurance

Nuclide	This Work (ppm)	Certified Value (ppm) 95% C.I
24Na	320.2±1.9212	280 – 360
42K	1819±78.217	1640 – 2040
76As	0.01206±0.0009	0.55 - 0.71
82Br	11.23±1.426	11.2 - 14.6
140La	0.5918±0.028	0.56 - 0.76
153Sm	0.1183±0.006	0.092 - 0.120
46Sc	0.1846±0.0129	0.15 - 0.19
59Fe	358.2±48.72	380 – 480
233Pa	0.06979±0.01452	0.12 - 0.16
239Np	< 0.0062672	---
51Cr	< 0.7865	0.89 - 1.23
60Co	< 0.09834±0.0322	0.24 - 0.34
65Zn	< 22.45±7.27	27.0 - 33.8
75Se	< 0.021818	0.18 - 0.26
86Rb	< 1.251±0.976	1.54 - 1.98
122Sb	< 0.038016	0.063 - 0.083
131Ba	< 8.557±5.656	5.3 - 7.5
152Eu	< 0.01213±0.007	0.019 - 0.027
175Yb	< 0.044819	0.025 - 0.049
177Lu	< 0.0067947	0.0042 - 0.0090
203Hg	< 0.031468	0.16 - 0.24

Table 4: Measured Concentrations of Elements (ppm) in IAR Control Samples

Elements	**Millet** (This Work)	**Millet** (IAR Values)	**Wheat** (This Work)	**Wheat** (IAR Values)
Na	17.6±0.8	16.±1.2	19.3±0.8	20±1.1
K	4324±164.3	4132±152.1	4428±97.4	3400±20.0
As	BDL	BDL	BDL	BDL
Br	2.41±0.0065	3.11±0.3	1.93±0.056	0.8±0.08
Zn	69.31±6.5	71.25±0.2	BDL	BDL
Rb	BDL	BDL	6.183±1.4	6.36±0.1

Table 5: Standard Reference Materials

Standard Reference Material	**Matrices**	**Mass Fraction (mg/kg)**
IAEA-16336	Lichen	0.22
SRM 1572	Citrus leaves	0.025
SRM 1515	Apple leaves	0.050±0.009
IAEA-155	Whey powder	0.064
IAEA-359	Cabbage	0.12

IV. CONCLUSION

Twenty one elements (Na, K, As, Br, La, Sm, Np, Sc, Cr, Fe, Co, Zn, Se, Rb, Sb, Ba, Eu,Yb, Lu, Hg and Pa) were analyzed in all the samples. IAEA 336 lichen standards was also analysed, as well as control millet and wheat collected from Institute of Agricultural Research (IAR), ABU Zaria Nigeria together with the samples for quality control and assurance. Results for the IAEA 336 standards agree well with its certified values. Most of the elements found in the cereals samples were below detection limits except Br, Na, K and Zn. Our results were compared with recommended permissible limits and found to be within the acceptable values.

The data showed that amounts of toxic elements in local cultivated millet and wheat vary to certain extents, these possibilities due to many factors especially from cultivation, post-harvest and storage processes. Elemental composition of soil, fertilizer and agricultural chemicals (herbicides, fungicides and insecticides) usually plays a significant contribution to the elemental composition in grains [6], [15]. The INAA method selected for the study proved to be simple, accurate with minimal sample processing for the simultaneous determination of toxic and nutrient elements in millet and wheat samples.

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REFERENCES

[1]. Kent, N.L and A.D Evers (1994).Technology of cereals, 4th ed. Pergamonpress, Oxford.
[2]. FAO. (Food and Agricultural organization) (2007).The state of food insecurity in the world (report). FAO/UN, Rome.
[3]. Simmons, R.W., Ponhsakul, P., Saiyasitpanich, D., Klinphoklap, S. (2005). Elevated levels of cadmium and zinc in paddy soils and elevated levels of cadmium in rice grain downstream of a zinc mineralized area in Thailand: implications for public health.Environ. Geochem. Health 27, 501–511.
[4]. Das, P., Raghuramulu, N., Rao, K.C. (2005).Determination of in vitro availability of iron from common foods. J. Hum. Ecol. 18, 13–20.
[5]. Demirbas, A. (2005).*b*-Glucan and mineral nutrient contents of cereals grown in Turkey. Food Chem. 90, 773–777.
[6]. Acar, Z., Ayan, L., Gulser, C. (2001): Some morphological and nutritional properties of legumes under natural conditions. J. Biol. Sci. 4, 1312–1315.
[7]. Reilly, C. (2002). Metal contamination of food: its significance for food quality and human health, 3rd ed., *Blackwell Science Ltd*., Oxford, UK
[8]. Yamada,Y. Talanta. (1968). Occurrence of bromine in plants and soil. Faculty of Agriculture, Kyushu University, Fukuoka Japan.Nov; 15(11):1135-41.
[9]. Paulchoudhury,R.,Kumar,A.,Reddy, A.V. R, Garg, A.N.(2007).Thermal neutron activation analysis of essential and trace elements and organic constituents in Trikatu: An Ayurvedic formulation journal of radio analytical and nuclear chemistry,274:411-419.
[10]. Thunus, L., Lejeune, R. (1994). Handbook on metals in clinical and analytical chemistry. Marcel Dekker, New York.
[11]. Charturvedi,V. C,Shrivastava,R.,UpretiR.K. (2004).Viral infections and trace elements: a complex interaction. CurrSci 87:1536-1554.
[12]. NRC (National Research Council) (1989).Diet and health implications for reducing chronic disease risk.Report of the committee on diet and health, Food and Nutrition Board, *National Academy Press*, Washington D.C. 750.
[13]. Hess, R Schmid,B., (2002). Zinc supplement overdose can have toxic effects J.PoehartHaematoonoel. 24:532-584.
[14]. Birch, N. J., Padgham C. (1994). Handbook on metals in clinical and analytical chemistry. Marcel dekker New York. 71-73.
[15]. D'Ilio, S., Alessandrelli, M., Cresti, R., Forte, G., Caroli, S. (2002):Arsenic content of various types of rice as determined by plasmabased techniques. Microchem. J. 73, 195–201.