ASSESSMENT OF NUTRIENTS AND TOXIC MINERALS LEVELS IN RICE AND BEANS SAMPLES BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS AND ATOMIC ABSORPTION SPECTROPHOTOMETRY

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ABSTRACT

The aim of this study was to assess the nutrients and toxic minerals levels in rice and beans by instrumental neutron activation analysis (INAA) and atomic absorption spectrophotometry (AAS). Four varieties of rice and six of beans were bought from markets in Jigawa, Kano and Kebbi all in North-Western Nigeria in 2019 were investigated under this study. INAA was used for determination of multiple nutrients and toxic minerals and AAS was used to determine Pb and Cd The range obtained for each of the nutrients and toxic minerals in the rice samples analysed were Pb (3.91 to 5.00), Cd (0.0067 to 0.0233), La, (1.19 to 6.38), Cr (3.31 to 8.09), Co (0.00 to 0.456), Mn (13.5 to 45.4), Cu (2.08 to 19.9), Zn (66.5 to 146), Fe (250 to 700), Sm (0.169 to 0.605) and V (0.27 to 4.49), Mg (709 to 2061), Al (498 to 8636), Cl (151 to 482), Ca (672 to 2037), K (2789 to 4161), Na (517.5 to 2645), Br (0.54 to 4.41) and Sc (0.22 to 1.2) mg/Kg. while for the beans samples the range were: Pb (0.00 – 0.82), Cd (0.01 – 0.02), La (0.06 - 1.11), Cr (2.08 to 4.3), Co (0.19 to 18), Mn (16.1 to 48.1), Cu (0.000 to 5.15), Zn (26.0 to 60.0), Fe (0.000 to 420), Sm (0.006 to 0.132), La (0.060 to 1.11) and V (0.00 to 1.98), Mg (192 to 1998), Al (94.0 to 2799), Cl (152.7 to 195), Ca (624 to 1945), K (8522 to 13970), Na (314 to286), Br (1.33 to 2.98) and Sc (0.018 to 0.23) mg/Kg. The levels of the nutrients and toxic minerals were higher in the rice samples compared to the beans except for Co and Mn. Mean concentration of all the nutrients and toxic minerals analysed were within the limits set by FAO/WHO, except for Pb and Cr which were above the recommended limit. Lead (Pb) has been implicated to cause severe damage to the kidneys, nervous system, brain and reproductive system, whereas, chromium (VI) has been associated with lung cancer.

Keywords: Nutrients, Jigawa, Rice, Bean, INAA

INTRODUCTION

In North-Western Nigeria States agriculture is the main occupation. Rice and bean are among the majorly grown and consumed food items. Rice is a staple food for a large part of Nigerian population, especially in the North-Western region. Beans are important source of protein and it is well sort for, due to its low price. For food safety, it is necessary to keep contaminants below permissible level. Thus, the analyses of rice and beans are of great importance for its nutritional value as well as for its toxic metals levels. Cadmium (Cd) and Pb toxicity have been associated to lung, prostate, and kidney cancers [1]. It has been reported elsewhere that, rice accumulate more metals than other cereals [2].

Furthermore, the study of trace element contents, such as Ca, Na, K, Mg, Al,, Br, Cl, Cu, V, La, Sc, Sm, Fe, Mn, Co, Zn, Cr, Cd and Pb in food samples has attracted worldwide interest. The determination of trace quantities of elements present in these types of matrices is of considerable importance because of their essential and toxicological effect in the human body. Rice growing on soils rich in elements such as selenium (Se), molybdenum (Mo) and cadmium (Cd), has been shown to accumulate these elements up to levels that were of concern to human health. This has triggered the need to use reliable analytical methods capable of

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analysing multiple elements in food samples. In Nigeria there are few information available concerning levels of elements in rice and beans, as such, it is felt that Instrumental Neutron Activation Analysis (INAA) and Atomic Absorption Spectrophotometer (AAS) can give an important contribution in this respect.

Instrumental Neutron activation analysis (INAA) has the potential to determine multi-elements in rice and beans samples. The aim of this work is to assess the nutrients and toxic elements in rice and beans by instrumental neutron activation analysis (INAA) and atomic absorption spectrophotometry (AAS). INAA is a suitable method for determination of various elements and it is also a powerful tool for the investigation of cereals. Thus, this study employed INAA technique for determination of Ca, Na, K, Mg, Al,, Br, Cl, Cu, V, La, Sc, Sm, Fe, Mn, Co, Zn and Cr in rice and beans samples. However, due to its limitation in the analysis of Cd and Pb, AAS was used for these elements.

MATERIALS AND METHODS

Sampling

Four varieties of rice and six varieties of beans were bought from markets in Jigawa, Kano and Kebbi all in North-Western Nigeria in 2019 were used for this study. The rice samples were labelled as Rice-A, Rice-B, Rice-C, Rice-D, whereas the beans samples were labelled as Beans-E, Beans-F, Beans-G, Beans-H, Beans-I and Beans-J. These rice and beans varieties are commonly consumed by people in this region. Composite samples were collected for each of the variety. After purchasing, the samples were transported to Chemistry Laboratory in Sule Lamido University Kafin Hausa.

Sample Preparation

Samples of rice and beans were cleaned once with tap water, twice with deionised water and then dried in a hot-air oven at 60±2 ^{0}C for 4 h. Subsequently, five (50) g of each sample was ground into fine particles using a high speed blender. The samples were filtered through a No. 60 mesh (250 mm) sieve and packed in acid-washed, plastic bottles. The samples were kept in a freezer at below 4 ^{0}C until analyses of nutrient and toxic elements (Ca, Na, K, Mg, Al,, Br, Cl, Cu, V, La, Sc, Sm, Fe, Mn, Co, Zn and Cr) by INAA and (Cd and Pb by AAS) are carried out.

Instrumental Neutron Activation Analysis (INAA)

Samples were irradiated in an open pool at the Nuclear Science and Technology Section, Centre for Energy Research and Training, Ahmadu Bello University, Zaria. Short and long irradiations were performed.

The samples were introduced with the aid of rabbit carriers into the reactor through the pneumatic transfer system which uses pneumatic pressure. The Nigeria Research Reactor-1 (NIRR – 1) at the Centre for Energy Research and Training (CERT), Ahmadu Bello University, Zaria, Nigeria, irradiated the samples with a thermal neutron flux of 2.5 x10^{11} ncm^{-2} s^{-1} for 5 minutes and 5.0 x10^{11} ncm^{-2} s^{-1} for 6 hours for short and long irradiations, respectively. The whole system was equipped with electronic timers which monitor the exact irradiation and decay time. The samples were

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then taken to a measurement room consisting of a high purity germanium

Atomic Absorption Spectrophotometry (AAS)

Samples were determined for Pb and Cd by wet digestion in a closed digestion system using a mixture of concentrated nitric acid and perchloric acid (10:1, v/v) at 110 ^{0}C until a clear solution is obtained. Pb and Cd from samples were extracted into the chloroform layer by complexion with ammonium-1-pyrrolidine dithiocarbamate (APDC), and then diluted with nitric acid and metal contents were determined by AAS, [3].

RESULTS AND DISCUSSION

Table 1 presents the mean levels of Ca, Na, K, Mg, Cl, Al, Br, Cu, V, La, Sc, Sm, Fe, Mn, Co, Zn, Cr, Pb and Cd) that were determined in four varieties of rice and six varieties of beans samples. Co, Cu, V and Fe were not detected in samples Rice-A, Beans-G, Beans-H and Beans-H respectively. While the following elements, Al, Ca, Cl, Cu, I,a, Mg, V, Br, Cd, K, Na, Mn, Cr, Fe, Sc, Sm and Zn were found in all the samples analysed.

One Way Analysis of Variance (ANOVA) showed that there was a significant difference among the various samples. Meanwhile, the levels of elements in Rice-A sample were significantly lower when compared with other samples. This low concentration observed was because during rice polishing the metal content is greatly reduced, as the metal-rich embryo and bran are removed.

The levels of toxic elements like Pb, Cd, Cr and La were also determined. The concentration of Pb was higher in the rice samples ranging from 3.91 to 5.00 mg/Kg, than in the beans samples which ranged from 0.00 to 0.818 mg/Kg. Lead plays no biological role in the human body. It causes severe damage to the kidneys, nervous system, brain and reproductive system.

The values recorded for rice in this study were higher than those reported by [4], which ranged from 0.16 - 0.92 mg/Kg. However, these values (0.16 - 0.92 mg/Kg) were similar to the concentration of Pb observed for beans samples in this work. This could be attributed to differences in anthropogenic activities in the cultivation sites. The levels of Pb in this study was above the maximum permissible limit of 0.300 mg/Kg set by [5]

Cadmium (Cd), does not play any biological function in the human body and it is very toxic. The levels of Cd were significantly greater in the rice samples (0.0300 to 0.0400 mg/Kg)) than in the beans samples (0.0067 to 0.0233 mg/Kg). This can be attributed to the soil and fertilizer used during cultivation [6]. The level of Cd in this study (0.04 mg/Kg) was less than those reported by [3], which has an average value of 0.130 mg/Kg. The concentration of Cd in this work was in agreement with those reported by [4], which ranged from 0.03 - 0.05 mg/Kg. This agreement in the results may be due to the use of similar pesticides. The level of Cd in this study was below the maximum permissible limit of 0,200 mg/Kg set by [5]. Thus, the levels of Cd, in these samples do not pose immediate health hazards to the consumers.

Furthermore, the level of Cr (3.31 to 8.09), in rice samples was significantly greater than those recorded in beans (2.08 to 4.3 mg/Kg). It

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has been reported by [2] that, rice accumulate more metals than other cereals. Chromium (III) is an essential nutrient. However, an association has been found between exposure to chromium (VI) and lung cancer. The level of Cr in this study was greater than those obtained by [4]

Table 1: Levels of nutrients and toxic minerals in rice and beans samples

Minerals	Rice A	Rice B	Rice C	Rice D	Bean E
Mg	709±52	1266±101	2061±101	950±103	1586±62
Al	498±15	7889±63.1	8636±59	7005±77	447±12
Cl	252±13	482±16	378±18	151±14	153±162
Ca	672±13	2021±254	2037±230	1910±233	624±0.00
V	0.27±00	4.49±0.54	1.93±0.21	2.2±0.20	0.084±0.00
Cu	4.11±00	19.9±5.9	5.12±0.00	2.08±00	3.91±0.00
Mn	27.4±0.2	18.2±0.1	45.4±0.30	13.5±0.2	13.5±0.01
Na	518±1.0.	1282±3.0	1814±2.0	2645±3.0	92.4±0.06
K	2789±39	3336±47	4161±54	3874±58	12860±77
Br	1.35±0.05	1.54±0.07	4.41±0.08	0.54±0.08	1.89±0.04
La	1.19±0.03	3.12±0.05	4.29±0.01	6.38±0.07	0.21±0.02
Sm	0.169±00	0.43±0.01	0.605±0.01	0.916±0.01	0.026±0.00
Sc	0.22±0.01	0.57±0.02	0.85±0.02	1.2±0.02	0.04±0.00
Cr	3.31±0.37	4.43±0.35	8.06±0.48	8.09±0.48	4.3±0.01
Fe	250±30	700±45	635±50	629±42	194.1±38
Co	BDL.	0.315±0.05	0.456±0.05	0.342±0.02	0.245±0.06
Zn	66.5±3.8	112±4.0	111±5.00	146±5.00	43.8±3.20
Pb	4.91±0.01	5.00±0.03	3.91±0.04	4.00±0.02	BDL
Cd	0.04±00	0.03±0.00	0.03±0.00	0.04±0.00	0.02±00
Minerals	**Bean F**	**Bean G**	**Bean H**	**Bean I**	**Bean J**
Mg	192±7.0	1516±61	1385±51	1998±98	1713±74
Al	2350±24	146±7.0	94±3.0	2799±45	2089±31
Cl	195±12	155±9.0	186±11	182±14	172±11
Ca	1459±175	990±115	680±105	1945±228	1078±163
V	0.5±0.11	0.065±0.00	BDL	1.98±0.21	0.69±0.10
Cu	3.52±0.00	0BDL	0.67±0.00	4.01±0.00	5.15±0.00
Mn	20.1±0.0	17.8±0.2	16.1±0.2	48.1±1.0	17.4±0.2
Na	286±1.0	55.1±0.5	49.5±0.8	25.8±0.5	314±2.0
K	12750±90	12520±88	12990±156	8522±128	13970±168
Br	2.28±0.05	1.41±0.01	2.98±0.06	1.77±0.05	1.33±0.05
La	1.11±0.03	0.1±0.01	0.09±0.02	0.06±0.01	0.84±0.03
Sm	0.132±0.00	0.013±0.00	0.012±0.00	0.006±0.00	0.101±0.00
Sc	0.23±0.01	0.02±0.00	0.029±0.00	0.018±0.00	0.12±0.01
Cr	2.58±0.29	2.3±0.32	2.18±0.33	2.08±0.26	3.7±0.31
Fe	420±38	134±28	BDL	29.3±0.00	227±32
Co	0.29±0.03	0.19±0.03	0.11±0.00	0.2±0.03	18±3.9
Zn	40.6±3.2	60±3.40	26±3.00	37.8±2.8	47.5±3.20
Pb	0.36±0.00	0.82±0.03	0.55±0.00	0.64±0.00	0.73±0.00
Cd	0.02±0.00	0.02±0.00	0.01±0.00	0.01±0.00	0.01±0.00

BDL: Below Detection Limit

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which ranged from 0.02- 0.52 mg/Kg and it was similar to that reported by [7]. This could be due in part to the high sensitivity of the INAA used in this study and also to the differences in the anthropogenic activities in the environment where these crops were grown. The level of Cr in this study was above the maximum permissible limit of 2.30 mg/Kg set by [5].

In addition, the levels of lanthanum, La, (1.19 to 6.38 mg/Kg) in the rice samples were significantly greater than those observed in the bean (0.060 to 1.11 mg/Kg) samples. In addition, the levels of lanthanium (La) observed in this work were similar to those reported by [8]. Lanthanum inflicts severe damage to animals and also causes nervous system disorder in humans.

On the hand, sixteen essential nutrients (Co, Mn, Cu, Zn, Fe, Sm, V, Mg, Al, Cl, Ca, K, Na, Br, Cr and Sc), for human and of high interest to nutritionists were also analysed. Form the analysis it was found that these nutrients had the following range of concentrations, Co (0.00 to 0.456), Mn (13.5 to 45.4), Cu (2.08 to 19.9), Zn (66.5 to 146), Fe (250 to 700), Sm (0.169 to 0.605), La (1.19 to 6.38) and V (0.27 to 4.49), Mg (709 to 2061), Al (498 to 8636), Cl (151 to 482), Ca (672 to 2037), K (2789 to 4161), Na (517.5 to 2645), Br (0.54 to 4.41) and Sc (0.22 to 1.2) mg/Kg in the rice samples and in the beans samples the concentration range for these nutrients were, Co (0.19 to 18), Mn (16.1 to 48.1), Cu (0.000 to 5.15), Zn (26.0 to 60.0), Fe (0.000 to 420), Sm (0.006 to 0.132), La (0.060 to 1.11) and V (0.00 to 1.98), Mg (192 to 1998), Al (94.0 to 2799), Cl (152.7 to 195), Ca (624 to 1945), K (8522 to 13970), Na (314 to286), Br (1.33 to 2.98) and Sc (0.018 to 0.23) mg/Kg,

In contrast, the levels of cobalt, (0.110 to 18.0 mg/Kg), in the beans samples were significantly higher than the values obtained for the rice samples (0.000 to 0.456 mg/Kg). Foods high in cobalt content help the body to absorb and process vitamin B_{12}. Also, cobalt helps to enhance the immune system by stimulating activities of the white blood cells to prevent infections and it keeps nerves healthy. However, the levels of Co in this study was within the permissible limit of 50,0 mg/Kg recommended by [5].

Similarly, the concentration of Mn, in beans samples was statistically greater compare to those obtained in rice. The concentrations of elements recorded in this study were similar to those reported by [9]. Mn helps in fat and carbohydrate metabolism, calcium absorption, and blood sugar regulation [10]. However, the level of Mn in this study was within the safe limit of 500 mg/Kg set by [5].

Copper is both an essential nutrient and a contaminant. The levels of Cu, in rice were statistically higher when compared to those recorded in beans. However, the level of Cu in this study was within the recommended range of 73.3 mg/Kg set by [5]. Also rice samples had a higher concentration of Zn than beans samples. The level of Zn recorded by [3], (21.8 mg/Kg) was lower than those obtained in this study. Zn is an essential trace element that functions as a cofactor for certain enzymes that take part in metabolism and cell growth [11]. However, the level of Zn in this study was within the recommended limit of 99.4 mg/Kg

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set by [5]. Furthermore, rice samples analysed had a high levels of Fe compared to the beans samples. Fe is an essential component of myoglobin, a protein that provides oxygen to muscles [12]. However, the level of Fe in this study was above the maximum permissible limit of 425.5 mg/Kg set by [5]. This indicates the rice and beans samples were safe for human consumption.

More so, the levels of samarium Sm, in rice samples (0.169 to 0.916) were significantly greater than those reported for the beans (0.006 to 0.132 mg/Kg). Samarium has no biological role and it is not that toxic. It is observed that some of its soluble salts are mildly toxic but cannot affect human life. The levels of vanadium ranged from (0,000 to 4.49 mg/Kg). Its level in the rice samples was higher than those obtained for the bean samples. One of the main roles played by vanadium is to reduce the level of cholesterol and triglyceride in the blood.

Furthermore, the levels of chlorine in the rice samples ranged from (151 to 482), while in beans its ranged from 155 to 186 mg/Kg). The high levels of chlorine recorded may be as a result of the use of preservative chemicals containing chlorine.

Pearson correlation analysis was performed. Rice-A shows a strong positive correlation with Rice-C, Rice-D, Beans-E, Beans-F, Beans-G, Beans-H, Beans-I and Beans-J at a significance level of 0.05 (2-tailed). Positive correlations were also recorded for rice-B, with rice-C and rice-D. Similarly, Beans-E is correlated to Beans-F, Beans-G, Beans-H, Beans-I and Beans-J at a significance level of 0.05 (2-tailed). Thus, indicating the differences in varieties of samples did not significantly affect the levels of elements in the rice and beans samples.

Potassium has the highest concentration among all the analysed elements in the samples, which agreed with values reported from other studies. In this study, the order of levels of elements for the rice samples was K > Al > Ca > Na > Mg > Fe > Cl > Zn > Mn > Cu > Cr > Pb > La > V > Br > Sc > Sm > Co > Cd, while the order reported for samples collected from Talad-Thai and Yoawarat markets by [3]; was K > Mg > Zn > Mn > Cl > Al > Br. More so, in the beans samples, the sequence of the levels of elements was in this order Mg > Al > K > Ca > Cl > Fe > Na > Zn > Co > Cu > Cr > Br > V > Pb > La > Sc > Sm > Cd while [13], reported this order K > Mg > Cu > Ca > Zn > Mn > Br > Cl for beans in India.

In addition, the values obtained for V, Br, Co and Cd were the lowest in all the samples. The variation observed in the levels of minerals in the different samples might be associated to the soil parent bed composition, agrochemical used during cultivation and anthropogenic activities prevalent in the areas under study.

CONCLUSION

In this study, sixteen nutrients (Ca, Na, K, Mg, Al, Br, Cl, Cu, V, Sc, Sm, Fe, Mn, Co, Zn and Cr) and three toxic minerals (Pb, Cd and La), were determined in four varieties of rice and six varieties of bean.

Furthermore, it was found that these elements had the following range of concentrations, Ca

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(624 to 2,037), Na (25.8 to 2,645), K (2,789 to 13,970), Mg (709 to 2061), Al (94 to 7889), Br (0.54 to 4.41), Cu (0.00 to 19.9), Cr (2.08 to 8.09), Co (0.00 to 0.456), Mn (13.5 to 48.1), Cu (0.000 to 19.9), Zn (26.0 to 146), Fe (0.000 to 700), Sm (0.006 to 0.605), La (0.600 to 6.48) and V (0.00 to 4.69) mg/Kg.

The levels of the nutrients and toxic minerals were higher in the rice samples compared to the beans samples except for Co and Mn. Mean concentration of all the nutrients and toxic minerals analysed were within the limits set by FAO/WHO, except for Pb and Cr which exceeded the standard recommended limit set by FAOWHO. Lead plays no biological role in the human body. It causes severe damage to the kidneys, nervous system, brain and reproductive system. Moreover, chromium (VI) had been implicated to cause lung cancer.

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