IJASST
International Journal of
Applied Sciences and Smart Technologies

Volume 07
Issue 02

p-ISSN 2655-8564, e-ISSN 2685-943, pp. 253-264, 2025

Determination of Cyanide Content and Heavy Metals (Cu, Ni, Cd, & Pb) in Different Processed Cassava Meal in Abraka Metropolis, Delta State, Nigeria

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(Received 16-02-2025; Revised 20-04-2025; Accepted 26-04-2025)

Abstract

Cassava is a tuberous plant in Nigeria that can be processed into different meal but its various forms contain a trace concentration of cyanide, cadmium, nickel, lead and copper that are not only essential for man but toxic if their concentration levels are high. This study determined the cyanide content and some heavy metals in different processed cassava meal sold in markets at Abraka and its environs. Samples of fufu, garri, starch, and fresh cassava were collected from five selected markets in Abraka. Cyanide concentration was determined using AOAC (1990) method of alkaline titration steam distillation of the sample using silver nitrate. While copper, cadmium, nickel and lead were determined using the atomic absorption spectrophotometer. Results for the cyanide levels were 7.56 mg/kg for fresh cassava, 5.4 mg/kg for starch, 3.24 mg/kg for garri, 2.16 mg/kg for fufu. The levels were in the order, fresh casava > starch > garri > fufu. The heavy metals concentration of copper (Cu), were (mg/kg) 2.04 for fresh cassava, 1.62 for garri, 1.44 for fufu, and 1.02 for starch. The levels were in the order, fresh cassava > garri > fufu > starch. The concentration of cadmium (Cd) were (mg/kg) 3.14 for fresh cassava, 1.03 for garri, 1.47 for fufu, 2.84 for starch. The levels were in the order, fresh cassava > starch > fufu > garri. The concentrations of nickel (Ni) were (mg/kg) 2.46 for fresh cassava, 1.89 for garri. 1.94 for fufu and 1.73 for starch. The levels were in the order, fresh cassava > fufu >garri > starch. Lead (Pb) was not detected in all the samples. From the results obtained in this study, fufu is the safest for consumption due to the low contents of cyanide and heavy metals. Garri is also considered to be safe as they fall within the WHO permissible limit for those metals. Hence, proper processing of cassava products should be encouraged to reduce bioaccumulation of cyanides levels in them.

Keywords: Cassava processed meal, heavy metals, cyanide concentration, sample.

1 Introduction

The extreme toxicity of cyanide is due to CN^- complexing with metal enzymes and hemoglobin in the body, thus preventing normal metabolism [1]. Cyanide is a chemical compound that contains the cyanogroup C=N which consist of a carbon atom triple bonded to a nitrogen atom [2] Most commonly, cyanides refer to as anion. Most cyanide is highly toxic [3]. In organic chemistry compound containing a C=N group are known as nitriles and compounds which contain the NDC groups are known as isocyanides, organic nitriles and isocyanides are far less toxic because they do not release cyanide easily. Heavy metals absorption is governed by soil, characteristics such as pH and inorganic matter content, thus high levels of heavy metals in the soil do not always indicate similar high concentration in plants. The extent of accumulation will depend on the plant and heavy metal species under consideration [4] Heavy metals are persistence contaminants of soil coastal water and sediments. They can affect both the yield of crops and their composition [5] the term heavy metal refers to any chemical element that has relatively density and is toxic and poisonous at low concentration [6]they are present in the earth crust in minute quantities. Most states in the Niger Delta indulge in indigenous farming and fishing as their major occupation. According to federal office of statistics 1995 in Delta State about fifty percent (50%) of the active labour force is engaged in one form of agricultural activity or another with cassava, yam, maize, cocoyam, plantain, and vegetable as predominant food crops in the area. Nigeria is one of world's largest producers of cassava./ cassava is the third largest sources of carbohydrates for meals in the world [7] Cassava (manihot esculenta) is one of the major food crops cultivated in Delta State. Cassava is a source of flour called garri in West Africa and of toasted granules normally called tapioca; it can process into marconi and rice like food, in the form of dried chips. Cassava root is an important animal feed in spite of popularity; its protein content is extremely low and its consumption as a staple food associated with protein deficiency disease kwashiorkor. In addition, part of the plant contains glycosides of hydrocyanic acid substance which on decomposition yield poison hydrocyanic acid (CHCN) prussic acid. chronic diseases including goiter are common in regions where cassava is a staple food [8].

2 Materials and Method

Sampling: the samples fufu, Garri, starch, and fresh cassava were collected from five selected market in Abraka. Each of the samples were bought in little quantity from five selected market and composites were collected that is (the samples from each market were added together). Samples were packaged in polythene bag.

Preparation of akpu(uncooked): freshly harvested cassava tubers were peeled, washed and soaked in water for five (5) days. During this period the tubers were fermented and softened. The retted chunks were then disintegrated manually in clean water sieved and allowed to settle for about an hour. The sediment was then packed into a bag, tied, squeezed and pressed with hand to produce a semi compact meal which can further be cooked and pounded into a paste (akpu) called fufu.

Preparation of starch: fresh cassava tubers were peeled, washed and grated. The grated cassava was put in a cloth bag and the pressed for the extraction of starch, after which the residue was ruptured to produce small, translucent irregular mass which further dried. The starch was dried on the sun and ready for analysis.

Preparation of Garri: the tubers were peeled, washed and grated. The mashed was placed in bag and then squeezed by tying it up to stick with heavy wood. This was allowed to stand for proper drying and allow detoxification by fermentation. The dewarted mass was sieved using traditional sieve. After which the dough was fried and ready for analysis.

Determination of cyanide: The AOAC (1990) [9] method of alkaline titration of steam distillation of the sample using silver Nitrate as described by Anigboro(1990) was adopted. 20g of mashed cassava samples was placed in $1000cm^3$ round bottom flask and mixed with $100cm^3$ of distilled water. The flask with its content was connected to steam distillation apparatus and allowed to stand for three hours. After three hours, the set up was steam distilled until 100ml of the distillate was collected. $20cm^3$ of 0.02 NaOH from Sigma Aldrich (St. Louis, MO, USA) and were used without further purification was added to the distillate and the mixture diluted to $250cm^3$, from the diluted distillate, two aliquots ($100cm^3$) each was obtained. To each of the aliquots $8cm^3$ of 6M NH_4OH solution prepared from Sigma Aldrich chemicals (St. Louis, MO, USA) and $2cm^3$ of **5%** KI (potassium iodide) provided by Sigma Aldrich (St. Louis, MO, USA) were added. The mixture was then titrated with 0.02M $AgNO_3$, the end point was reached when the mixture changes from clear solution to faint turbid solution. A blank titration was also carried out using distilled water in place of distillate. The cyanide content of the sample was determined by the relation.

$1cm^3$ of 0.02m $AgNO_3$ = 1.08mgHCN.

Heavy metals determination: 2g of the sample were weighed into a conical flasks previously rinsed with distilled water. A mixture of 1000ml of 50% per chloric acid ($HClO_4$), 40ml of trioxonitrate (v)acid (HNO_3) and $1cm^3$ of tetraoxosulphate (vi)acid (H_2SO_4) was added and the flask were heated for about three (3) minutes, then the content was filtered through the filter paper into $100cm^3$ volumetric flasks after cooling. The solutions were made up of $50cm^3$ marks with more deionised water used for washing the conical flasks and later transferred to the $125cm^3$ plastic cans (all Pyrex equipment) and labeled for atomic absorption spectrophotometer (AAS) analysis. The metal content of each digested cassava sample was determined using atomic absorption spectrophotometer (AAS) (Pyeunicam model sp. 2900) in an air acetylene flame starting with blank followed by the samples to determine the metals.

Microwave digestion was used for inductively coupled Plasma Mass Spectrometry (ICP-MS) analysis of copper (Cu), cadmium (Cd), Nickel (Ni), lead (Pb). Roughly, 1 g of each sample was weighed into Teflon vessels that have been acidified, washed in a microwave digester for 1 h and cooled. Five milliliter (5 mL) concentrated nitric acid (63.01 % analytical grade) and 3 mL of 30 % concentrated hydrogen peroxide were added. The vessels were tightened into their respective shields and packed accordingly with their numbers into the microwave digester (Milestone) and digested for 1 h at a temperature of 170 °C and a pressure of 5 MPsi. After digestion the samples were allowed to cool completely and were poured into a 50 mL centrifuge tubes and topped up to 25 mL mark with deionized water. Chemical analyses of Cu, Cd, Ni, and Pb were carried out using Agilent ICP-MS 7700. The ICP-MS was calibrated using 0.5 µg/L, 1.0 µg/L, 5.0 µg/L and 10.0 µg/L standards solution prepared from Sigma Aldrich stock solution of concentration 100 mg/L.

3 Results and Discussions

The result of the experiments carried out on the cyanide level in cassava are presented the Table 1. From the result of the experiments shown in the table above, the cyanide content found in fresh cassava is extremely high due to the presence of cyanide in the soil. The content of cyanide in fufu is lower compared to starch and garri, this is as a result of fermentation. In starch, the cyanide content (5.4mg/0.1kg) is a bit lower than the fresh cassava because it undergoes some process before the extraction and level of cyanide content in garri (3.14mg/0.1kg) reduces due to the application of heat in frying the dried ground cassava thus cyanide contents tend to reduce.

From the result of the experiments shown in the Table 1, the cyanide content found in fresh cassava is extremely high with cyanide content of (7.56/ 0.1kg) due to the presence of cyanide in the soil. The content of cyanide in fufu is (2.16/ 0.1kg) lower compared to starch and garri, this is as a result of fermentation. This value obtained is in line with with published data [10]. The cyanide concentration was below the NIS standard for cassava flour of 10mg/kg [11].In starch, the cyanide content (5.4mg/0.1kg) is a bit lower than the fresh cassava because it undergoes some process before the extraction and level of cyanide content in garri (3.14mg/0.1kg) reduces due to the application of heat in frying the dried ground cassava thus cyanide contents tends to reduce. This value obtained is in line with with published data [10], but reported by [12] to be higher in Enugu metroplolis with a value of 6.87mg/kg. However, cyanide content in different processed meal was also reported in oshogbo to be between 0.03-0.09mg/kg in which tend to be less compared to which is reported in this study and in that reported by [10] from Wukari as well as Ezeh et.al 2018 from Enugu metropolis in Nigeria. The reason for these differences in concentration is attributed to the differences in species, climate condition and soil type [13]; [14a], [14b].

The atomic absorption spectrophotometer, FAO/WHO tolerable limits, and detection limit for heavy metals in cassava products result of the heavy metal analysis are presented in the Tables 2-4.

Table 1. The cyanide levels of different processed cassava meal

sample	starch	Garri	fresh cassava	Fufu
cyanide 2.16mg/0.1kg **content**	5.4mg/ 0.1kg	3. 24mg/0.1kg	7.56mg/0.1kg	

Table 2. Atomic Absorption Spectrophotometer results of the heavy metals.

Heavy metals	Fresh cassava	Garri	Fufu	Starch
Copper(Cu)	2.04	1.62	1.44	1.02
Cadmium(Cd)	3.14	1.03	1.47	2.84
Nickel (Ni)	2.46	1.89	1.94	1.73
Lead (Pb)	ND	ND	ND	ND

Units = ppm

ND =Not Detectable

Table 3. FAO/WHO Tolerable Limits

METALS	FAO/WHO TOLERABLE LIMITS
Copper(Cu)	1.40µg/day
Cadmium(Cd)	1.50µg/day
Nickel (Ni)	0.5mg/day
Lead (Pb)	0.30mg/day

Table 4. Detection Limit Table for Heavy Metals in Cassava Products

Heavy Metal	Detection Limit (AAS) (mg/kg)	Detection Limit (ICP-MS) (mg/kg)	Regulatory Limit (WHO) (mg/kg)
Copper(Cu)	0.01 – 0.05	0.001 – 0.005	≤ 10.0
Cadmium(Cd)	0.001 – 0.005	0.0001 – 0.001	≤ 0.1
Nickel (Ni)	0.01 – 0.05	0.001 – 0.01	≤ 1.0
Lead(Pb)	0.01 – 0.05	0.0005 – 0.005	≤ 0.2

The study also evaluates some selected heavy metals in different processed cassava meal and the result of the metal analysis shown in table 2, shows that the levels of copper ranged from 1.02mg/kg in starch, 1.44mg/kg in fufu, 1.62mg/kg in garri and 2.04mg/kg in fresh cassava. Although, [12] reported 1.34, 2.81 and 1.65mg/kg for abacha, garri and fufu respectively which is line with the study for garri and fufu. A higher value of 3.72mg/kg of copper concentration in garri was reported sold in some major markets in Yenogua metropolis [15], While a much higher mean value of 10.18□0.73mg/g for copper in cassava flour processed by road side drying along Abuja Lokoja highway, Nigeria, was reported by [16] which is higher than what was obtained in all the processed cassava meal in this study. The uptake of heavy metals by plants depends on several factors. These elements include biological parameters like membrane transport kinetics, ion interactions, and the metabolic fate of absorbed ions, soil acidity, physical processes like root intrusion, water and ion fluxes and their relationship to the kinetics of metals solubilization in soils, and the capacity of plants to metabolically adapt to charging stresses in the environment. [17]. In this study, Only the ranges of garri and fresh cassava fall within the WHO standard of 1.5 -3.01mg. The above ranges of copper from starch to garri can be essential for maintaining good health but accumulation can cause harmful effect such as irritation of the nose, mouth and eyes, vomiting, diarrhea and stomach cramps [18]. The level of cadmium ranges from 1.73mg/kg in starch to 1.94mg/kg in fufu while garri and fresh cassava has the concentration of 1.89mg/kg and 2.46mg/kg respectively. The result shows that there is high concentration of cadmium in fresh cassava but in comparison to the WHO standard of 3mg it is not up to, due to the type of soil in which the cassava is planted, while fufu, starch, and garri is lower compared to the

WHO standard and it seems safer. The range of cadmium in this study is also similar to that obtained by [12]. with values 0.084, 0.206 and 0.135ppm for akpu garri and abacha respectively. Heavy metals are typically absorbed by plants growing in areas contaminated with them through the absorption of minute deposits on air-exposed parts of the environment and during uptake from contaminated soils. The levels of cadmium and other metals in the samples may have been greatly impacted by the different soil chemistry from which the cassava tubers were processed into the sample products, the levels of heavy metal contamination in such soils, contamination from the water used during the fermentation process, and the overall processing environment. The mean amounts of cadmium in the samples were within the allowed limits for a solid food product. Though much intake of cadmium causes irritation to the stomach assistive in vomiting and diarrhea [19]. Human nephrotoxicity may result from long-term exposure to cadmium, primarily as a result of anomalies in tubular re-absorption. [20] and [21]. [22] reported higher values of 0.55 □ 0.002mg/kg, for cadmium in cassava tubers sold in major markets in Benue State, Nigeria, than that obtained in this research, did not detect cadmium in cassava flour sold in Anyigba market, Kogi State, Nigeria. For Nickel, it ranges from 1.73mg/kg in starch, 1.89mg/kg in garri, 1.94mg//kg in fufu and 2.46mg/kg in fresh cassava. Nickel threshold limit was not specified in the NIS 2004 standard. However, the result in this study is extremely in concentration when high and when compared to WHO standard of 1.037mg/kg for Nickel. The highest concentration of nickel in the samples is due to the soil and environment because nickel is a compound that occurs in the environment only at low level [18]. In small quantities, Nickel can lead to high chances of development of lung cancer, nose cancer, larynx cancer, and prostate cancer, respiratory failure, birth defects, asthma and chronic bronchitis and heart disorders [19]. From the result, lead (Pb) was not determined in any of the samples analyzed, this maybe as a result of the environment and the soil in which cassava were planted [12]. reported a non-toxic level of lead (Pb) to be found in the processed cassava meals with values 0.203, 0.431 and 0.323ppm for abacha, akpu and garri. [21] Obtained a higher mean value of 0.889mg/kg for lead (Pb) in garri sold in two major garri markets in Benue State, Nigeria.

4 Conclusions

This study revealed that high cyanide content in fresh cassava, followed by starch and garri but the content is low in fufu, which makes fufu safer for consumption because it undergo fermentation period and this reduces the cyanide content compared to the other processed cassava meals. Heavy metals occur in rock forming minerals and so there is a range of normal background concentrations of these elements in soil. However, this study revealed high concentration of heavy metal cadmium with correspondingly high level of nickel but less concentration of copper and lead(Pb) in the various cassava samples composites from different market locations in Abraka Delta State compared to the WHO standard, although the essential elements are beneficial to man but when found in excessive amount can prove detrimental to health.

Acknowledgements

The authors acknowledge the technologists of the Department of the Department of Chemistry, for providing technical support during this work, and Dr. Osakwe who supervised this thesis during his active service in the University of Abraka, Delta State for his invaluable support in ensuring the success of this analysis. Your contributions are deeply appreciated.

References

1. [1] J.D Lee. “Concise inorganic Chemistry” *(5th edition). 4443-54. (2009)*

2. Claude Fauguent and Deienis Fargette. “African cassava Mosaic virus: Etiology, epidermiology and control plant diseases” *vol.* **74**(0): 404-11 (1990).

3. N.N Greenwood, and, AA. Earnshaw. “Chemistry of element” (3rd edition) oxford: Butterworth Heinemann. ISBN 0.7506-3365. Quality criteria New York pp. **113.** (2001).

4. I. Hughes, F. Carvello, and M. Hughes, “Purification characterization and clonning of Alpha hydroxynitrile Lyase from cassava (manihot esculenta crantz).” *Arch Biochemistry.* Biophys 311:496-502 (1994).

5. C.C Ndiokwere, and C. A Ezehe, "The occurrence of heavy metals in the vicinity of industrial complexes in Nigeria." *Environment International 16:291-295. (2000)*
6. Osakwe, S.A (2009). "Heavy metal distribution and bioavailability in soil and cassava (manihot esculenta) grantz along warri Abraka expressway, Delta State", *Nigeria, Journal of Chemical Society of Nigeria, 34:211, 235-245*.

7. T.P. Philips., "An overview of cassava consumptions and production in cassava tooxicity and thyroid." Pp 83-88. (2001).

8. L. Dul., M. Bokangs, B.L Moller, and B.A Halker, "The Biosynthesis of cyanogenic glycosides in roots of cassava" photochemistry. **39**: 323-326. (1995).

9. AOAC (1990), Official method of analysis, association of official analytical chemist. Horwitz (Ed). Washinton DC.

10. R.O.A. Adelagun, F.E. Aihkoje, O.J. Igbaro, J.O. Fagbemi, E.P. Berezi, O.M. Ngana, M.S. Garba, and G. Osondu, "Comparative analysis of cyanide concentration in different proccessed cassava product." FUW Trends in Sci & Tech.;8(1):210-213. E-ISSN: 24085162. 2023

11. L.O. Sanni, B. Maziya-Dixon, J.N. Akanya. "Standards for cassava products and guidelines for export." IITA. 2005.

12. E. Ezeh, O. Okeke, C.M Aburu, O.U. Anya, "Comparative Evaluation of the Cyanide and Heavy Metal Levels in Traditionally Processed Cassava Meal Products Sold Within Enugu Metropolis". Int J Environ Sci Nat Res. 2018; 12(2): 555834. DOI:10.19080/IJESNR.2018.12.555834

13. J.A.V. Famurewa, and P.O. Emuekele, "Cyanide reduction pattern of cassava (Manihot esculenta) as affected by variety and air velocity using fluidized bed dryer." AJFST 5(1): 75 – 80.2014.

14. M.B. Etsuyankpa, C. E. Gimba, E.B. Agbaji and K.I. Omoniyi. "Determination of Cyanide and Saponins in the Products of Selected Cassava Varieties from Three Sampling Sites in Nigeria State." CSN Book of Proceedings. 1(36): 247-250. 2013a

    M.B. Etsuyankpa, C.E. Gimba, E.B. Agbaji & K.I. Omoniyi, "Evaluation of Proximate Composition of 'Fufu', 'Lafun' and 'Gari' Through Microbial Fermentation of Four Varieties of Cassava." CSN Book of Proceedings. 1(36): 251-256. 2013b.

15. L,.T. Kigigha, P. Nyenke, S.C. Izah: "Health risk assessment of selected heavy metals in garri (cassava flakes) sold in major markets in Yenegoa metropolis, Nigeria." Moi Toxicology 4(12); 47-52. 2018

16. A.A. Audu, M. Waziri, T.T. Olasinde. “Proximate analysis and levels of some heavy metals in cassava flour processed by roadside drying along Abuja-Lokoja Highway, Nigeria.” IJLS 2(3);55-58. 2012.

17. D.A. Cataldo, R.E. Wilding, “Soil and plant factors influencing the accumulation of heavy metals by plants.” EHP 27;149-159. 1978.

18. FAO/WHO: “Adverse health effects of heavy metals in Human. Human Health for health sector” Geneva 77p.

19. World Health Organisation: “Heavy Metals, Safety evaluation of certain food additives and contaminants. 55 meeting of the joint FAO/WHO. Expert committee in food additives, Geneva, WHO food additives series,” Geneva, 46p. 2014

20. G. Nordberg, “Excursions of intake above ADI: case study on cadmium.” Regul Toxicol Pharmacol. 30:57-62. 1999.

21. I.O. Ogbonna, B.I. Agbowu, Agbo, “Proximate composition, microbiological safety and heavy metal contaminations of garri sold in Benue, North-central, Nigeria.” Afr. J. Biotechnol. 16(18); 1085-1091. 2017..

22. J.E. Emurotu, U.M. Salehedeen, O.M. Ayeni, “Assessment of heavy metal in cassava flour sold in Anyiba market, Kogi State, Nigeria.” J. Adv. Sci. Res. 3(5): 2444-2448. 2012

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