COMPARATIVE ANALYSIS OF CYANIDE CONCENTRATION IN PROCESSED CASSAVA PRODUCTS

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Abstract

Human consumption of cyanide in cassava food products above the threshold has detrimental effect on the body system. This study investigated ten (10) different cassava products purchased to determine their levels of cyanide content. The residual cyanide in the cassava processed products were used as obtained without any pre-treatment, fermented for 36 hours and filtered. Titration was then carried out using the extract with silver trioxonitrate and the result of the HCN obtained are; dry white gari 4.63 ± 0.2 mg / kg, dry yellow *gari* 4.59 ± 0.1 mg / kg, *abacha* or tapioca 3.38 ± 0.4 mg / kg, *lafun (akpu, grated cassava paste)*6.21 ± 0.3 mg / kg, raw *fufu (uncooked cassava flour)*6.35 ± 0.2 mg / kg, cooked *fufu* 4.01± 0.05 mg / kg, cassava chips 6.44 ± 0.4 mg / kg, *eba* white gari 3.20 ± 0.1 mg / kg, *eba* yellow gari 3.65± 0.2 mg / kg and fresh raw cassava tuber 12.29 ± 0.3 mg / kg respectively. The result revealed that the levels of HCN in all the cassava products assessed falls within the stipulated FAO/WHO safety limit except the fresh raw cassava tuber sample. Tapioca or abacha has the lowest cyanide concentration to minimum level. Thus, it implies that the different processing methods for various cassava products effectively influence the level of residual cyanide in the cassava products with varying impacts. There is therefore a need for periodic and constant check and monitoring of the concentration of cyanide in cassava products to ensure quality and safety of food consume by humans.

Keywords: Cassava, Cyanide, Toxicity, *Akpu, Garri, Tapioca, Fufu*

Introduction

Cyanide occurs naturally in many edible plants such as almonds, sorghum, cassava, lima beans, stone fruits and bamboo shoots (Ndubudi and Chidiebere, 2018) as cyanogenic glycosides (Nambisan, 1993). Cyanogens are found in three forms: cyanogenic glucoside, cyanohydrins and free cyanide. Cyanogenic glucoside is a ß-glucoside of acetone cyanohydrin and ethyl-methyl-ketone-cyanohydrin. Depending on their precursor amino acid, they may be aromatic, aliphatic, or cyclopentenoid in nature. The ß-linkage can only be broken under high pressure, high temperature and use of mineral acids, while its enzymatic breakage occurs easily (Younoussa *et al.,* 2014). If the enzyme and substrate are joined, a good detoxification occurs. Cassava (*Manihot esculentacrantz*) is an important cyanogenic food crop for humans, and also referred to as tapioca, manioc, and yuca. Each parts of the cassava plants (leaves, stem, root) contains high levels of cyanogenic glycosides: linamarin, lotaustralin, and amygdalin with linamarin been the most predominant cyanogen. Linamarin is rapidly hydrolyzed by linamarase to glucose, acetone cyanohydrin, and hydrogen cyanide (Cereda and Mattos, 1996).Different varieties of cassava are generally classified based on the levels of cyanide levels into two main types: sweet cassava and bitter cassava. Sweet cassava roots contain less than 50 mg per kilogram hydrogen cyanide on fresh weight basis, whereas that of the bitter variety may contain up to 400 mg per kilogram (Muiru, 2013). The concentration of cyanide varies considerably between varieties and climatic conditions (Famurewa and Emuekele, 2014). The processed bitter cassava can be used in various ways such as glucose, syrup, glue, production of ethanol, *tapioca*, composite bread, starch production among others (Burns *et al.,* 2010). About ten million tonnes of cassava are produced per annum in Nigeria alone while the African continent account for more than 90% of the global cassava production, being the largest producer of cassava in the world today (Etsuyankpa *et al.,* 2013a). Cassava is the third most important food source in the tropics after rice and maize and it is a staple food for at least 600 million people (Famurewa and Emuekele, 2014). The high energy and carbohydrate content suggest that cassava could be utilized as a reliable food and energy security crop as proposed by FAOSTAT, (2013). The processing parameters such as mode, time and cooking temperature have potentials to decrease the cyanide content levels in different cassava products. Traditional processing methods such as grating, soaking and boiling have been suggested to reduce the concentration of cyanide in the process foods. However, the reduction level in every process would depend on sample quality, processing technology and the part of plant used (Younoussa *et al.,* 2014).

Cassava has been earmarked as the crop that can spur rural industrial development and raise income for producers, processors, and traders. Cassava has been used in the production of different types of food most especially in Africa, which are referred to as cassava processed products, including yellow and white *garri, fufu*, cassava flour (lafun), *abacha*, tapioca, wet pulp, smoked cassava ball, fermented and dried cassava pulp, starch, etc in many countries with Africa accounting for 45%, Asia 28% and Latin America and the Caribbean 19%. The five main producing countries are Nigeria, Brazil, Thailand, Congo (DRC) and Indonesia.

Consumption of cassava and its products that contain large amounts of cyanogens may cause cyanide poisoning. Toxicological symptoms include vomiting, nausea, dizziness, stomach pains, weakness, headache, exacerbates goitreand occasionally death. Certain pathological disorders such as konzo disease, thyroid goiter and tropical ataxic neuropathy have been reported (Egbele and Milton, 2013). Cyanide poisoning can kill within seconds or minutes to hours of exposure depending on the route and length of exposure as well as the dose received. Cyanide toxicity can either be acute or chronic. In humans, the clinical signs of acute cyanide intoxication include rapid respiration, drop in blood pressure, rapid pulse, dizziness, mental confusion, twitching and convulsions. It usually halts respiration of the cells by inhibiting *cytochrome C. oxidase* enzyme in the mitochondrion from utilization of oxygen. This makes metabolism of the cells to shift from aerobic to anaerobic. Brain and heart which are among the tissues with highest oxygen demands are affected profoundly by acute cyanide poisoning. According to Alcorta (2004), signs of chronic cyanide poisoning include; altered mental status, seizures or coma, mydriasis, tachypnea, bradypnea, hypertension and cardiovascular collapse.

Indeed, cases of cyanide toxicity from the consumption of inadequately processed cassava products have been reported. According to Adindu and Aprioku. (2006), consumption of poorly processed cassava based meals has caused occasional cases of deaths of families. A ready to eat cassava chips and processed products were found to contain large amounts of cyanide as documented by Anna and Roslyn, (2012). In 2005, twenty seven (27) children died after eating cassava at a Philippine school (China Daily, March 10, 2005). In 2011, two (2) children died in Makueni district hospital in Kenya. One of the children had consumed raw cassava that had cyanide levels of 52.3 mg HCN equivalent/Kg while the other child consumed poorly cooked cassava which had cyanide levels of 73.2 mg HCN equivalent/Kg (Njue *et al.,* 2011). In 2008, it was widely reported ofa family who was nearly wiped out after eating food prepared from fermented cassava flour in Ondo state, Nigeria.

As a result of these, a constant periodic check on the concentration of cyanide in various cassava containing foods is necessary. Manyhighly processed foods contain< 1 ppm total cyanide (Anna and Roslyn, 2012). Cassava products are among the basic foods worthy of attention (Etsuyankpa *et al.,* 2013a). The Food and Agricultural Organization of United Nations (FAO) / World Health Organization (WHO) presented safety limits for cyanide in cassava food as 10 mg / Kg dry weight (Egbele and Milton, 2013).

Food has been a surviving necessity of man for long but of what importance is it if food contains poisonous/deadly substances like cyanide? Consequently, the need for check and motoring of harmful chemical substances in cassava food products is the aim of this study, to ensure human health and safety in cassava processed food products. It has been reported that further outbreaks of these illnesses and disorders can be prevented by having important efficient methods for processing of fresh cassava and its derivate products (Younoussa *et al.,* 2014). This work therefore is focused on assessment of the effects of different ways of processing of cassava on the residual concentrations of cassava in the processed foods.

To consider the effectiveness of the different processing techniques in sequestering cyanogens contents in cassava products in this study, we shall consider the traditional methods used in processing cassava products. Peeling, grating, fermentation, drying, soaking in hot and cold water, grinding, boiling and cooking have been reported to cause significant reduction in the cyanogenic glycosides of processed cassava foods. These process generally leads to disintegration of the cyanogens contents which lead to the production of cyanide. Since cyanide is volatile, further processing techniques, such as roasting and drying will volatilize the remaining cyanide to low level.

Materials and Methods

Materials

The sample materials used in this study are common local cassava processed products, namely: A = White *gari (dry)*, B = Yellow *gari (dry)*, *C* = Cassava flakes *(Abacha or tapioca)*, D = Uncooked cassava flour (*fufu*), *E* = *Grated*cassava paste*(akpu)*, F = Cooked cassava (*lafun/akpu)*, G = Peeled cassava chips, H = Eba (G*ari* soaked in hot water) I = G*ari* soaked in cold water) J = Fresh Cassava Tuber. The cassava processed products samples (A-J) were purchased in Wukari Central Market in Taraba State, Nigeria. The samples were used as obtained without any pre-treatment.

Methods

The procedure described by Oti and Ngele, (2016), was adopted for the extraction of the cyanide from the samples. For each of the sample, 10g was weighed into a 250 ml conical flask containing 100 ml of distilled water and fermented for 36 hours followed by filtration. To 50 ml of each filtrate (extract), 20 ml of 0.02 M NaOH solution was added and made up to 100 ml with distilled water followed by addition of 2 ml 5% KI. This was mixed properly and then titrated against 0.2 M $AgNO_3$ solution. The end point colour changed was from clear solution to faint yellow. The total hydrogen cyanide (HCN) content/concentration in mg equivalent / Kg of each sample was then determined by calculation as follows:

$$Total\ HCN\ Content = 13.6\ x\ \frac{T_v}{M} \quad (i)$$

Where, M = Mass of sample, T*v* = Average Titre Volume and 13.5 is a constant value

Results and Discussion

The result obtained from the titration of $AgNO_3$ against HCN in cassava products samples concentration of cyanide in mg / kg in each sample is presented in Table 1.

Table 1: Titre Values Obtained from Titration and Concentration of Cyanide in the Samples

Sample Code	Sample Name and Description	Average Titre Value of $AgNO_3$ (ml)	Concentration of Cyanide in Samples (mg/kg)
A	White *Garri* (dry)	3.43	4.63 ± 0.2
B	Yellow *Garri* (dry)	3.40	4.59 ± 0.1
C	*Cassava Flakes (Tapioca, abacha)*	2.50	3.38 ± 0.4
D	*akpu* (Grated Cassava paste)	4.60	6.21 ± 0.3
E	*fufu* (cassava Flour uncooked)	4.70	6.35 ± 0.2
F	*Fufu / akpu* (Cooked)	2.97	4.01 ± 0.05
G	Cassava chips	4.77	6.44± 0.2
H	*Eba* (white *gari*)	2.37	3.20± 0.1
I	*Gari soaked in cold water)*	2.70	3.65 ± 0.2
J	Fresh cassava tuber	9.10	12.29 ± 0.3

The results obtained shown in Table 1 revealed the concentration of hydrogen cyanides in the various cassava products. Fresh raw cassava tuber (sample J) with a mean titre value of 9.10 ml has the highest cyanide concentration of 12.29 ± 0.3 mg/kg among all the samples assessed. This value obtained was in accordance with previously published data (Etsuyankpa *et al.*, 2013a, b). Siritunga and Sayre, (2003) stated that cassava root has a range of 10 to 500 mg cyanide equivalents / kg dry matter, while the range of 15 – 61 mg / kg dry matter was reported by Yeoh and Sun, (2001). The reason given for the differences in concentration has to do with the differences in species, climate condition and soil type (Famurewa and Emuekele, 2014; Etsuyankpa *et al.*, 2013a, b).

As previously stated, the raw cassava tuber has the highest cyanide concentration of 12.29mg/kg followed by cassava chips and cassava flour (*fufu* and *akpu*) with 6.44mg/kg and 6.35 mg/kg, respectively. Next is white gari (dry) and yellow gari (dry) with 4.63 mg/kg and 4.59 mg/kg respectively. The level of cyanide in the samples of the tapioca, and *eba* (gari soaked in hot water) was 3.38 mg/kg and 3.20 mg/kg, respectively. Processing methods have been reported to have the potential to reduce linamarin and cyanide in food, however, improperly processed cassava products would contain some amount of residual linamarin and hydrogen cyanide resulting in the potential toxicity of the cassava products. These results showed clearly that the processing treatment of the cassava products greatly affect the residual cyanide concentrations in the cassava products.

Table 2 depicts the different processes used in the production of each of the cassava products under consideration in this study.

Table 2: Processes Used in the Production of each of the Cassava Products

Processing Techniques	Cassava Tuber	Cassava Chip	Grated cassava Paste	Cassava Flour	Cooked Cassava Flour	Gari (Dry)	Gari soaked in cold water	Eba (Gari soaked in hot water)	Tapioca
Peeling		✓	✓	✓	✓	✓	✓	✓	✓
Cutting		✓	✓	✓	✓	✓	✓	✓	✓
Crushing			✓	✓	✓	✓	✓	✓	✓
Air drying				✓	✓				
Rinse in water			✓		✓	✓	✓	✓	✓
Fermentation			✓		✓	✓	✓	✓	✓
Roasting						✓	✓	✓	✓
Cooking		✓							
Soaking in cold water							✓		
Soaking in hot water								✓	✓

Peeling and using small small-sized cassava pieces was reported to result in 25%reduction in cyanide content, and a 75%reduction by soaking in water. This is because cyanogenic glycosides are water soluble, as such a higher percentage of cyanides are removed when cassava products are processed in water as seen in Samples C, F and I in comparison with samples A,B and D. Solubilization of cyanogenic glucosides from the small cassava chips into the large volume of water seemed to better explain the cyanogen removal than enzymatic degradation. .Boiling is not as effective as soaking in water for cyanide removal (50%) because of the increase in temperature. At100°C, linamarase, a heat-labile β-glucosidase, is denatured and linamarin cannot then be hydrolyzed into cyanohydrin. Fried cassava products has higher levels of cyanide as it is not soluble in lipids/oil, hence less cyanide is lost during frying (relatively higher levels in Samples A and B compared to Samples H and I)).The same reason apply for weak loss of cyanide resulting from steaming, baking, or frying (temperatures) of over 100°C (Egbele and Milton 2013).

Drying process could be via mechanical drying, such as in an oven, and natural drying by the sun. Generally, sun drying is not an efficient means of detoxification, especially for cassava varieties with high initial cyanogen glucoside content (Sample G). Cyanogenic glucoside breakdown during sun-drying depends on enzymatic hydrolysis and on gradual root cell disintegration. The fermentation method by lactic acid bacteria is a processing method commonly used in Africa. Fermentation is done with grated or soaked cassava roots and results in a decrease in pH value. The fermentation of grated cassava roots is efficient at removing cyanogen glucosides. The process of roasting after fermentation of grated cassava, which is used for *gari*, is relatively efficient as free HCN and cyanohydrin are steadily removed into the atmosphere leaving little free HCN. The cyanogen removal process can be improved by increasing by peeling and grating cassava roots followed by the soaking and fermentation many times. Sample H (*eba*; *gari* soaked in hot water) has a reduced cyanide concentration of 3.20 ± 0.1 mg / kg compared to sample A (4.59mg/lg) as a result of having been soaked in hot water. The drastic reduction in the cyanide concentration in Sample H can be attributed to the effectiveness of the processing method by soaking in hot water and cooking in addition to its been already processed as white *gari* from cassava which further decreases the residual cyanides (Echeribi and Edaba, 2008).

The result obtained for the raw cassava tuber was the highest among all the samples assessed. This is because no processing was done or carried out to reduce or remove the poisonous cyanide content. This suggest the presence of large content of cyanide in fresh raw cassava tubers beyond normal of any variety, specie or cultivar of cassava processed products. Consequently, raw, unprocessed and /or insufficiently processed cassava product is dangerous and unfit for consumption by both humans and animals. From the result of this study it can be observed that processing is necessary to reduce cyanide content. The increasing order of the results of cyanide concentration in cassava products analyzed are *eba* < *abacha /tapioca* <*soaked gari* < cooked *fufu* < dry yellow *gari* < dry white *gari* < grated cassava paste < *lafun* (cassava flour) < cassava chips < fresh cassava tuber.

Conclusion

Cyanogenic glycosides occur in all cassava products at varying concentrations. Consumption of improperly processed cassava can lead to chronic and acute health problems as a result of cyanide poisoning. Appropriate and adequate processing methods of cassava products will help in mitigating and reducing cyanide toxicity. The various processing methods (e.g. peeling, washing, fermentation, frying, heating, drying, boiling etc) have great significance and very effective in the reduction of cyanide concentration in cassava and products at different levels.

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