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Prevalence of some metals in native and branded factory-based lager beers within Jos metropolis

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Abstract: *Ethyl alcohol toxicity is implicated in disease conditions such as cirrhosis, hepatitis and these ailments among drinkers are high even after seeking medical attention. This work was therefore undertaken to analyse for zinc, iron, lead, cadmium, and manganese as contaminants in samples of beers. Atomic absorption spectrophotometric technique was applied to achieve the objectives of the work. Although the results indicated contamination of the samples with the metals, the magnitude of the contamination was higher in native, relative the factory-based lager beers. In burukutu, the level of Zn was above that in pito and goskolo. Compared to the maximum reference levels in drinking water, level of Fe was lower just as for Pb ($P > 0.05$). Goskolo had the highest burden of Cd followed by burukutu and pito. In burukutu and pito, Mn was high ($P = 0.05$) compared to reference values. In the case of the factory-based lager beers, levels of Zn, Mn and Fe were below the reference values for all the brands. Levels of Cd and Pb were above the maximum values ($P = 0.05$). In Guinness, Harp, and Star, the content of Cd and Pb were significantly ($P = 0.05$) above reference values for drinking water, but other metals were not significant ($P > 0.05$). Extent of contamination with Pb was highest in Gulder ($P = 0.05$). Alcoholic drinks are contaminated with metals whose toxicities could aggravate ailments, usually ascribed to alcohol alone, in drinkers.*

Key Words: *Burukutu, Goskolo, Pito, Lager beers, Lead, Cadmium, Iron, Zinc, Manganese.*

I. Introduction

Native beers constitute rich sources of the B vitamins, calories and lysine [1], they also increase the level of high density lipoproteins, a scavenger of cholesterol and therefore reduce risk of cardiovascular diseases, also have antidiuretic attributes for treating kidney stones. The conditions under which native beers are brewed affect the proximate, mineral elements and antinutritional factors composition of *burukutu;* however, beers fermented at 30^0C for 24 hours are generally acceptable to drinkers [2].

II. Materials and Methods

2.1 Materials

Hot plates, Pyrex beakers, Atomic Absorption Spectrophotometer (AAS-HITACHI 180-80 Polarized Zeeman model. HITACHI Group, Tokyo. Air/acetylene gas was used. Air flow rate was 9.4 l/min; acetylene was 2.3 l/min.

2.2 Chemicals and reagents

Concentrated trioxonitrate (v) acid (HNO_3) was of the British Drug Houses (Koch Light Lab Ltd, Pate, England) grade, purity: 99.5% whereas concentrated tetraoxochlorate (VII) acid ($HCLO_4$) was of the Analytical grade (AnalaR): purity (min assay): 99%.

2.3 Experimental Design

In all, 28 samples (4 samples each of both native and factory-based beers) were analysed. The levels of Zn, Fe, Cd, Pb and Mn were determined. Similarly, the pH *of goskolo* and the factory-based lager beers was determined.

Collection of Samples

Samples of *pito* and *burukutu* were purchased from local drinking parlours located in different parts of *Jos* and kept in plastic sample bottles at 20^0C in a refrigerator until when needed for analysis. In the case of factory-based bottled larger beers, samples were purchased randomly at bars and restaurants within the study area.

Digestion of Samples

A 45ml portion of each native and factory-based lager beer sample in Pyrex Petri dish was digested. Prior to digestion, the samples were dried in an oven at 60^0C over 48 hour period until a constant weight was obtained. The digestion mixture used contained concentrated trioxonitrate (v) acid and concentrated tetraoxochlorate (vii) acid in the ratio 6:1 v/v respectively. Native and factory-based beer samples were digested by adding 3ml digestion mixture intermittently until white precipitate was obtained. The resultant white precipitate was dissolved in 2ml of distilled water and thereafter made up to 10ml each in 20ml measuring cylinder.

2.4 Atomic Absorption Spectrophotometric Analysis of Samples

Each of the digested samples was diluted x10 by pipetting 1ml each of the solution into respective plastic test tubes and made up to 10ml with de-ionised water. Iron, Zinc, Manganese, Lead and Cadmium concentration in the samples were analysed using automated Hitachi 180-80polarised atomic absorption spectrophotometer [3].

2.7 Determination of pH of Samples

Mean pH values of *Goskolo* and some selected brands of proprietary lager beers within the study area and results are as indicated in table 1.

Beer brand	pH
Goskolo	7.9±0.2
Gulder®	5.2±0.1
Star®	5.1±0.3
Guinness®	5.4±0.2
	5.3±0.7
Harp®	

Values are mean (±SEM) for three determinations; n = 4
® = registered trade mark.

Table 2: Mean Levels of Zinc, Iron, Lead, Cadmium and Manganese in native beers obtained from the field within the study area.

	Metal Concentration (mg/litre)				
Beer	**Zinc**	**Iron**	**Cadmium**	**Lead**	**Manganese**
Burukutu	0.184±0.05	2.614±0.15[a]	0.081± 0.03[a]	0.022±0.01	1.11±0.04[a]
Pito	0.051±0.03	2.654±0.33[a]	0.071±0.06[a]	0.041±0.03	0.74±0.13[a]
Goskolo	0.003±0.00	0.171±0.04	1.880±0.22[a]	0.011±0.0	0.032±0.0

Values are means of three replicate determinations (±SEM). P = 0.05 considered significant; (n= 4).
[a] = statistically significant compared to the reference standard values (P = 05).

Table 3: Mean Levels of Zinc, Iron, Lead, Cadmium and Manganese in some brands of factory-based beers within the study area.

	Metal Concentration (mg/litre)				
Beer	**Zinc**	**Iron**	**Cadmium**	**Lead**	**Manganese**
Gulder®	0.001±0.01	0.011±0.01	0.009± 0.01	1.080±0.11[a]	0.012±0.01
Guinness®	0.002±0.01	0.051±0.01	0.864±0.37[a]	0.004±0.00	0.011±0.01
Star®	0.028±0.01	0.319±0.06	0.455±0.21[a]	0.003±0.00	0.04±0.02
Harp®	0.033±0.02	0.340±0.12	0.810±0.37[a]	0.011±0.01	0.05±0.03

Values are means of three replicate determinations (±SEM). P = 0.05 considered significant; (n=4).
[a] = statistically significant compared to the safe level in water (P = 0.05).
Gulder® = Nigeria Breweries PLC
Guinness® = Guinness Nigeria PLC
Star® = Nigeria Breweries PLC
Harp® = Nigeria Breweries PLC

Table 1 gives the various pH values of *Goskolo* and some factory-based beers where all of them have acidic pH values except for *Goskolo* whose pH was found to be weakly alkaline. The pH of *Burukutu* and *Pito* had already been reported in our previous work which is also acidic.

In Table 2, are results for levels of the metals in native beer samples obtained from the field. Levels of Cd, Fe and Mn in both *burukutu* and *pito* were statistically significant (P = 0.05) relatively reference values. As for *goskolo,* only the level of Cd was statistically significant (P = 0.05)

In table 3 are results of the levels of the five metals in bottled factory-based lager beers purchased from the field. The extent of contamination in them was lower than in native beers. Compared to levels in drinking water, the levels of zinc, iron and manganese were not statistically significant (P>0.05) whereas levels of cadmium and lead were significant (P = 0.05) in *Gulder®.* In *Guinness Stout*, cadmium level (P =0.05), other metals (P >0.05). In Star® and *Harp®,* levels of cadmium (P = 0.05), levels in others were not statistically significant (P>0.05) relative levels in drinking water.

III. Discussion

From the results obtained, *burukutu* was the most heavily contaminated with trace/heavy metals relative *pito* and *goskolo*. Although *pito* is consumed in the study area, it is not as popular as *burukutu*. It is also prepared using sorghum, millet and corn. It is a dark brown liquid with sweet taste and in some cases bitter; it contains lactate, amino acids and sugars with alcohol content of 3.0% [4]. [5] reported a pH-dependent increase of iron in *burukutu* and *pito* in each phase of brewing with the final products normally consumed containing highest levels. Similarly, [6] have reported a phase-of-brewing of native beers dependent increase (p= 0.05) in contamination with zinc and manganese. *Goskolo* is another drink whose pH is weakly alkaline (7.9) and contains just 0.002% ethyl alcohol (v/v); drinkers within the study area have lost their lives which led to banning its preparation, sale and consumption by the Government of Plateau State, Nigeria.

The mean pH values of factory-based lager beers ranged from 5.1 to 5.4. Compared to factory-based beers, native beers differ because lactic fermentation occurs during their preparation and are consumed while they are still fermenting which could lead to metabolic shift from a precursor to undesirable and harmful metabolites. Compared to the generally accepted pH of lager beers which is put at 4.1, *burukutu* and *pito* samples are more acidic [7] whereas factory-based beers are less acidic. If there were standard methods of regulating the pH during native beers brewing, this would not be the case. This agrees with the report of [8] where due to a change in pH during the fermentation of xylose by *Clostridium tyrobutyricum*, the desired product, butyrate, was not formed but lactate and acetate were produced instead.

Cadmium is a toxic metal causing injury and necrosis to nephrons, hepatocytes and several other cells. Compared to *pito*, *burukutu* has higher Cd content but the two had much higher levels than the factory-based lager beers. This implies that drinkers of native beers are exposed to cadmium which induces the generation of reactive oxygen species thereby depleting antioxidants, enhance peroxidation of lipids. Furthermore, cadmium is known to deplete magnesium levels; a component of chlorophylls of plants, a cofactor of glucokinase and protects against hepato- and nephrotoxicity of both cadmium and lead toxicity in animals. Cadmium also disrupts the biosynthesis of collagen in the lungs by inhibiting fibroblast procollagen and peptidoglycan production which could adversely affect the integrity and fluidity of cell membranes.

In animals, it preferably accumulates in the liver and kidneys [9] and was reported by [10] to be better absorbed in the presence of ethyl alcohol. Upper safe limit of this metal is 0.003ppb [11] which is lower than the concentration established in this work. [12] reported that the most important metabolic parameter for cadmium uptake is a person's possible lack of iron; people with low iron supplies showed a 6% higher uptake of cadmium than those with a balanced iron stock.

Iron is a nutrient playing vital biological functions such as being the prosthetic group of haemoglobin to which molecular oxygen binds, involved in the electron transport chain when associated with various co-factors such as the cytochrome p450 enzyme complexes. Iron is also a co-factor of aconitase and choline dehydrogenase. There are a number of haem containing proteins involved in the transport of oxygen (hemoglobin), oxygen storage (myoglobin) and enzyme catalysis such as nitric oxide synthase (NOS) and prostaglandin synthase (cyclooxygenase). The magnitude of iron contamination of native beers was higher than that of factory-based bottled beers. The safe levels of iron in lager beers as stated by NAFDAC and Standards Organisation, SON, are 0.030ppm and 0.300ppm respectively. Extent of contamination with iron was higher than the standard reference values. Drinkers of native beers are at risk of iron accumulation although that would be dependent on absorption of iron from the gastrointestinal tract, gastric emptying, and level of fibre in both the native beers drank and the foods consumed (bioavailability). Excess intracellular iron results in formation and deposition of haemosiderin which can lead to cellular dysfunction and damage [13]**.** Iron solubility gradually increases during beer making process of germination and fermentation [1]. Haemochromatosis, a disorder of iron metabolism is characterised by excessive iron absorption, saturation of iron-binding proteins and deposition of haemosiderin in the tissues is of the numerous problems associated with iron metabolism; the primary tissues affected are liver, skin and pancreas.

Lead is a highly toxic metal that particularly deposits in bones and causes severe damage to the nervous system. Occupational exposure to lead is common among workers in paint manufacturing factories, lead smelting works and petrol engines are the major sources of lead pollution of the human environment. *Burukutu*, *pito* and *goskolo* samples had levels of lead higher but not statistically significantly (p>0.05) different compared to the safe level. This could be statistically valid, but changes that are not statistically significant could be biologically significant! Also, drinkers consume these native beers chronically and therefore long term consequences are very significant. Since lead is known to distort calcium homeostasis *in vivo*, especially as it pertains to nerve impulse transmission from axon to dendrite which is dependent on the release of Ca^{2+}at the synapse, cognitive capacity of drinkers, especially children will be impaired leading to mental illness. This agrees with the report of [14] ---in the study area, even infants are in some cases fed native beers!

Zinc is an essential nutrient required in the body for boosting immune functions, a co-factor of several enzymes including carboxypeptidase, DNA polymerase, carbonic anhydrase, Zn-superoxide dismutase, alkaline phosphatase and alcohol dehydrogenase among others; involved in the metabolism of the macromolecules including proteins, lipids, carbohydrate and even nucleic acids. Zinc possesses anti-cold properties and its supplement in infants enhances the action of immune system. Both the WHO and NAFDAC have recommended that when the concentration of zinc in water exceeds 5mg/litre, it becomes gradually toxic. In all instances, levels of zinc in the native beers were marginally higher than reference values.

Manganese is an essential nutrient required by the cell as it is a co-factor of some enzymes including hexokinase, glucokinase, Mn-superoxide dismutase (Mn-SOD), chondroitin sulphate (cartilage) biosynthesis as well as an activator of isocitrate dehydrogenase. Mn-SOD scavenges superoxide anions and catalyses reduction of reactive oxygen radicals to hydrogen peroxide and molecular oxygen [15]. This is similar to the report of [6] where the levels of manganese and zinc were higher than control values. The upper safe levels of manganese in water as established by both NAFDAC and WHO 0.05mg/litre. This is lower than its levels in *burukutu* and *pito* samples. Level in *goskolo* was 0.032mg/litre, which is lower than the reference safe level. Manganese is reported to increase the risk of deficient cognitive performance [16]. Nano scale manganese induces depletion of dopamine and its metabolites: dihydroxyphenyl acetic acid and homovanillic acid in a dose-dependent manner [17].

The trace/heavy metals content in the different brands of factory-based bottled lager beers were high compared to their respective upper safe limits. One brand, *Gulder*, stands out because it did not only contain the highest levels of lead among the factory-based bottled lager beers but also native beers although it had the least level of cadmium. Lead is a component of glass as lead trioxosilicate (v) ($PbSiO_3$) and its reduction by hydrogen peroxide has been reported to cause formation of metallic lead granules [18]. The acidic pH of the brew may have reduced the lead trioxosilicate (v) to metallic lead granules as sediments in the brew. Apart from *Gulder*, the level of cadmium in the other brands of bottled factory-based beers was higher (p= 0.05) compared to safe level of cadmium in drinking water.

IV. Conclusion

It is concluded that ethyl alcohol may not necessarily be the sole causal factor of ailments among drinkers since toxic metallic contaminants are significantly present in the brews.

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