Analysis of Metal Concentrations in Selected Canned Beers Consumed in Owerri Urban, Imo state, Nigeria.

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Abstract:
Evaluation of metal concentrations in selected canned beers consumed in Owerri, Imo State, Nigeria was conducted using atomic absorption spectrophotometer(AAS) after HNO_3/H_2O_2 digestion process. Considered Metals in selected canned beers include: Al , Cd, Cr, Cu, Fe, Ni, Pb , and Zn to ascertain the quality and standards as it affect beer consumers. The results of the laboratory analysis shown that the concentrations Cr, Fe, Ni, Cd and Pb in the selected canned beers were above the permissible levels concentration stipulated for potable drinking water, while the metals Zn, Al and Cu were below the permissible limits in the potable drinking water respectively . Ultimately, there is clearly a need to improve quality control in the processing of this and other canned beers. From the risk assessment of canned beers on human heath, it is ascertained that metal concentrations in the selected canned beers do not pose a risk to consumer's health since the estimated metal daily intake per kg bodyweight is below the provisional tolerable intake of these metals as stipulated by the World Health Organization (WHO) .Based on this result, quality monitoring and control by standard organization of Nigeria (SON) were suggested for beer production.

KEYWORDS: Canned Beers, Risk, Metals, Human Health, Nigeria.

1. INTRODUCTION:

Determination of the total metal composition of beer, including major, minor and trace metals, is of particular interest to brewers and consumers. Depending on the concentration and type, metals may be essential or toxic to the human body and can also affect the brewing process and beer quality in view of flavor stability and haze [1, 2,3,4].Trace metals in beers may originate from natural sources _soil, water, cereal, hops and yeast. as well as from environmental contamination, fertilizers, pesticides, industrial processing and containers. Beer drinking has been steadily increasing in recent decades even in countries where alcoholic beverages are not traditional. Beer has indeed become an international drink, especially

among young people [5] . Depending on the concentration and type, metals may be essential or toxic to the human body and can also affect the brewing process and beer quality in view of flavor stability and haze formation [7 ,8,1 , 9, 10,11,12, 13,14]

The study of metal contents in foodstuffs is of growing concern because some of these metals are required for normal growth while others cannot be tolerated at low [15,16]. The hazards of metals to humans from consumption of contaminated foods depend on the relative levels of the metal and its speciation. Lead, for instance, can injure the kidney and cause symptoms of chronic toxicity, including impaired kidney function, hepatic dysfunction and poor reproductive [17],moreover, lead can cause reduced intelligence quotient, learning difficulties, slow growth, behavioral abnormalities, hearing difficulties and cognitive functions in human [18]. However, it should be also noted that although the information on the total metal content in beer is advantageous for the estimation of the metal nutrient uptake source, metals bioavailability from beer to humans and their absorbability in the gastric system crucially depends on speciation forms in which they are present in beer [19, 7, 8]. The knowledge of concentrations of trace metals in food is of significant scientific interest because some of these elements are essential for human health, while others, if present even at low concentrations, can be toxic[8]. The project then focus on the determination of heavy metal concentrations in canned beer and its effect on human health in the study area.

2 MATERIAL AND METHODS

***Study Area*:**

Owerri Municipal is located between latitudes 8^0 30' and 7^0 15' N and longitude 50 15' and 5^0 30'E. It has a mean annual rainfall that varies from 2000 -2500 mm, and mean temperature of 26 to 28 0 C and a humidity that also varies from 70 – 80% . Many hotels are located within Owerri where different types of beer in cans and bottles are sold to the public for consumption.

Locational Study:

Different hotels where different canned beers are sold were identified and named by their names . The samples were obtained from a local store and represent the types of beers readily available to consumers. Also identification of the hotels will be done randomly for the purpose of picking types of beer for analysis. Made of the beer for human consumption will be identified and used for characterization. The selection was made to reflect the popular brands consumed by different income groups. The brands selected included Cody (A- k), Becks, Dettinger, Guinness Stout, Heineken, Henburg, Hollandia, Olsten, Panther and Tuborg. The samples all had at least2–3 months to the expiration date. The major ingredients in the samples included sorghum, wheat, malt, barley, roasted barley, hops and water. Apart from Guinness Stout, the samples were lager type beers. The percentage of alcohol by volume in the samples ranged from 5.0 to7.5% [20]. The samples were stored at 4°C until analysis was completed.

Heavy Metals Analyzed:

These included Al , Cd, Cr, Cu, Fe, Ni, Pb , and Zn in canned beers .

Laboratory Techniques:

Before the analysis, all beer samples were degassed using an ultrasonic bath for 30 min. A 10-mL aliquot of the degassed sample was mixed with 2 ml of nitric acid and 2 ml of hydrogen peroxide in a digestion tube. The mixture was heated for 1 hour (100°C) until complete clarification and allowed to cool, and filtered and diluted to 25 ml with ultra pure water [20]. Analytical blanks were prepared in a similar manner, but omitting the test sample. The solutions were subsequently analyzed for metals using atomic absorption spectrophotometry (GBC scientific equipment SENS AA, Australia). Appropriate quality assurance procedures and precautions were carried out to ensure reliability of the results. Samples were handled carefully to avoid contamination. Glassware was soaked in 1 M HNO_3 for 48 hours and rinsed with

ultra pure water. The reagents (nitric acid, hydrogen peroxide and water) were of analytical grade. Calibration standards were made by dilution of commercial BDH high purity metal standards for atomic absorption analysis. A recovery test of the total procedure was carried out for the metals by spiking analyzed samples with aliquots of metal standards and then reanalyzing the samples. The results of the recovery studies for the various metals were greater than 93.4%.

Statistical Techniques

Analysis of heavy metals will presented as mean and standard deviation and subjected to Pearson's correlation analysis, while one-way analysis of variance (ANOVA) ($P < 0.05$) will be used to assess whether heavy metals varied significantly between canned and bottled beer consumed.

3 RESULTS AND DISCUSSION

This chapter deals with the results from the composition of sampled beers in Owerri Municipal. Table 1 presents the mean concentration metals from sampled canned beers (± SD).Table 11 and 111 present estimated provisional tolerable Intake of Metals and Estimated Daily Intake of metals in canned beers sampled for analysis**.**

Table 1: Metal Contents in canned Beers in Owerri

Code of Sampled Beers	Metals in Selected Beers (µg/ml) Al	Cd	Ni	Cu	Cr	Fe	Pb	Zn
A	0.003± 0.001	0.003±0.001•	0.08±0.02	0.07±0.02	0.19± 11	**0.56±0.21**	0.021±0.019	0.08±0.02
B	0.004± 0.002	0.006±0.002	0.07±0.02	**0.08±0.03**	**0.34±.18**	0.34±0.12	**0.045± 0.25**	0.09±0.03
C	0.004±0.001	0.005±0.001	0.06±0.02	0.06±0.02	0.23±.11	0.40±0.19	0.036±0.013	0.09±0.03
D	0.003±0.002	0.003±0.001	**0.10±0.04**	0.04±0.02•	0.24±.09	0.51±0.32	0.031±0.011	0.07±0.02•
E	0.003±0.001	**0.008±0.003**	0.08±0.03	0.06±0.03	0.23±.08	0.34±0.15	0.043±0.019	0.09±0.03
F	**0.005±0.002**	0.007±0.002	0.07±0.03	0.06±0.03	0.18±.09	0.45±0.22	0.023±0.012•	0.13±0.03
G	0.004±0.001	0.006±0.002	0.09±0.04	0.08±0.02	0.24±.08	0.32±0.16	0.033±0.011	**0.15±0.05**
H	0.003±0.001	0.004±0.001	0.06±0.02	0.06±0.02	0.21±.07	0.23±0.10•	0.036±0.013	0.12±0.02
I	0.003±0.002	0.005±0.002	0.04±0.02•	0.06±0.02	0.17±.07•	0.45±0.21	0.041±0.020	0.10±0.02
J	0.002±0.001•	0.006±0.002	0.07±0.03	0.05±0.01	0.26±.12	0.34±0.17	0.030± 0.015	0.13±0.03
K	0.003±0.002	0.006±0.002	0.08±0.02	0.09±0.03	0.23±.11	0.54±0.31	0.042±0.021	0.08±.0.02

Source: Laboratory Analysis by An Author, 2012.

Highest values in bold and the lowest in •

Table 11: Estimated Provisional Tolerable Intake of Metals (µg/kg/bw/day) based on average per capita Consumption of 10 Litres of beer.

Code of Sampled Beers	Metals in Selected Beers (µg/ml)							
	Al	**Cd**	**Ni**	**Cu**	**Cr**	**Fe**	**Pb**	**Zn**
A	0.001	**0.005**	0.04	0.03	0.11	0.22	0.003	**0.07**
B	0.001	0.001	0.02	**0.03**	**0.05**	0.24	**0.02**	0.06
C	0.001	0.004	0.05	0.02	0.12	0.18	0.02	0.04
D	0.001	0.003	**0.03**	0.03	0.10	0.23	0.02	0.04
E	0.001	**0.002**	0.04	0.03	0.11	0.24	0.01	0.04
F	**0.002**	0.000	0.05	0.05	0.13	**0.33**	**0.00**	0.005
G	0.001	0.004	0.03	0.03	0.07	0.25	0.01	**0.005**
H	0.001	0.00	0.04	0.03	0.10	0.26	0.004	0.005
I	**0.001**	**0.00**	**0.02**	**0.02**	0.05	**0.14**	0.00	0.005
J	0.001	0.00	0.04	0.03	0.12	0.21	0.02	0.005
K	0.001	0.00	0.03	0.02	**0.18**	0.18	0.01	0.005

▪High and Low values bolded (adopted from Chukwujindu (2010)

Table 111: Estimated Daily Intake (µg/day) of metals based on average per capita of 10 litres of beer

Code of Sampled Beers	Metals in Selected Beers (µg/ml)							
	Al	**Cd**	**Ni**	**Cu**	**Cr**	**Fe**	**Pb**	**Zn**
A	0.08	**0.27**	2.47	1.64	6.59	13.15	0.16	**4.11**
B	0.08	0.03	**1.10**	1.94	**2.74**	14.52	**1.04**	3.56
C	**0.06**	1.37	**2.74**	1.37	7.40	14.52	0.93	2.19
D	0.08	0.16	2.19	1.92	5.75	13.70	**1.29**	2.19
E	0.08	**0.11**	2.19	1.92	6.30	14.25	0.85	2.19
F	**0.11**	**0.00**	2.74	**2.74**	7.67	**20.00**	**0.00**	0.27
G	0.08	0.22	1.64	1.92	4.38	15.07	0.66	**0.27**
H	0.08	0.00	2.19	1.92	6.03	15.34	0.31	0.27
I	0.06	0.00	1.10	1.10	2.74	**8.49**	0.31	0.27
J	0.08	0.00	2.47	1.64	7.12	12.60	0.92	0.27
K	0.06	0.00	1.92	1.37	**10.96**	10.96	0.82	0.27

▪High and Low values bolded(adopted from Chukwujindu (2010)

From the results in Table 1, the mean concentrations of Aluminum in the different brands of beers that are canned varied between 0.002 – 0.005 (µg/ml), with the brand 'F' having the highest mean concentration value of 0.005 (µg/ml), and brand 'J' having the lowest mean concentration of 0.001 (µg/ml). Also Table 1 and 11 show information on the estimated daily intake and provisional tolerable daily intake respectively, based on average per capita consumption of 10 litres of beer. The estimated provisional tolerable daily intake of aluminium in this study ranged from 0.001 to 0.002 µg/kg bw/day, which is far lower than the WHO value of 1,000 µg/kg bw/day[22]. The NAFDAC and WHO maximum permissible limits of aluminium in drinking water are 0.5 µg/L and 0.2 µg/L respectively [21]. The level of aluminium observed

in the various beer types was below these limits. This is suspected to be due to low temperature in the fridge of storage. The result is consistent with the finding of [23] that Aluminium concentration changes in canned beer depend on storage temperature. Storage in the refrigerator protects against aluminium migration from the can, while storage at 22 °C facilitates aluminium migration from can to beer.

In 2002, Das Bundesamt für Verbraucherschutz und Lebensmittelsicherhei (reported Cd in beers (n = 251) from the German market, in the period 1995–2002, as 0.0017 µg/mL with a 13.5 share of the samples having a quantifiable residue level. Most of the beer cans and refreshments are made of aluminium. In comparison with the steel the aluminium and the recipients made of it are lighter more resistant to corrosion easier to mold less resistant in general and more expensive[23].

From Table 1, cadmium concentrations in canned beers sampled ranged between 0.003 – 0.008 µg/ml, with brand beer 'A' having the highest value of concentration of 0.008 µg/ml, and the lowest brand being 'E' with the value of 0.003 µg/ml [20] in 2007 reported the average content of Cd in beers from the Italian market as 0.16 - □0.15 µg/L. Similarly, [24] reported a Cd content varying from 12.9 to 14.3 µg /L in Brazilian beers. The levels of Cd reported in the present study were similar to levels reported in different beer types in other regions of the world[24, 25]. The JECFA limit for Cd is 1 µg /kg bw/day [26]. The estimated provisional tolerable daily intake of Cd in this study ranged from 0.0 to 0.005 µg /kg bw /day

Results in Table 1 indicates that , the mean concentration of Nickel (Ni) in sampled beers ranged between 0.004 – 0.10 (µg/ml), with brand 'D' having the highest mean concentration of 0.10 (µg/ml), and brand 'I' having the lowest mean value. The WHO maximum permissible limit of Ni in drinking water is 0.02 µg/mL [27]. The concentration of Ni in the different brands was above the WHO maximum permissible limit of Ni in drinking water. The tolerable daily intake (TDI) of Ni is 5 µg/kg bw/day [28, 29]. The estimated provisional tolerable daily intake of Ni in this study ranged from 0.02 to 0.05 µg/kg bw/day

The Copper (Cu) content of the sampled canned beers varied between 0.05 – 0.08 (µg/ml), with the brand 'B' having the highest concentration value of (µg/ml), and the lowest being brand 'D' with the mean value of 0.05(µg/ml). The permissible limit for Cu in the drinking water in Nigeria is 1.0 mg/L (Standard Organization of Nigeria [30]. The Cu content of the beer samples was below the permissible limit [21]. The JECFA provisional maximal tolerable daily intake of Cu is 500 µg /kg bw/day and a safe upper limit of 160 µg /kg bw/day has been recommended by the Expert Group on Vitamins and Minerals . The estimated provisional tolerable daily intake of Cu from the consumption of these brands of canned beer ranged from 0.005 to 0.05 µg /kg bw/day, which is within the safe daily intake limits.

From Table 1, the mean Chromium (Cr) content in sampled canned beers ranged between 0.17 – 0.34 (µg/ml), with brand 'B' having the highest mean value of 0.34 (µg/ml), and brand 'I' having the lowest value of 0.17 (µg/ml). The average daily intake of chromium in this study ranged from 2.74 to 10.96 µg per day, which is below the recommended dietary allowance of 130 µg/day/person . The permissible limit of chromium in drinking water is 0.05 mg/L [29,29]. All the samples examined had chromium concentrations above the permissible limit in drinking water. However, the EVM guidance level for chromium is 150 µg/kg bw/day for total dietary intake of trivalent chromium;[30] . The estimated provisional tolerable daily intake of chromium in this study ranged between 0.05 and 0.18 WHO µg/kg bw/day.

The Iron (Fe) content in the sampled canned beers varied between 0.23 – 0.56(µg/ml), with the highest concentration of Fe in sampled canned beers being 0.56(µg/ml) in brand 'A', and the lowest concentration with the value of 0.23(µg/ml) in brand 'H'. The National Agency for Food, Drug Administration and Control (NAFDAC) maximum allowed limit of Fe in drinking water is 0.30 mg/L [21]. The concentrations of Fe in the different brands of canned beer were above the limit for drinking water. The estimated provisional tolerable daily intake of Fe from consumption of any brands ranged from 0.14 to 0.33 µg /kg bw/day. The estimated daily intake of Fe is below the recommended dietary allowance of 35–700 µg /gd–1 person.

From the results in Table 1, Lead (Pb) concentration in the sampled canned beers ranged between 0.021- 0.045 µg/ml), with the brand 'B' having the highest concentration of Pb in sampled canned beers of 0.045 µg/ml), and brand 'A' having the lowest value of 0.0.021 µg/ml). The concentrations of Pb in the canned beers were all below the permissible limit of Pb in alcoholic beverages (0.5 mg/L) but exceeded the guideline value for Pb in drinking water [29]. A survey of bottled beers in 1986 indicated that the majority of beers packaged in the United Kingdom contained Pb concentrations from 10–200 mg /L [31]. [32] reported Pb content varying from 13 to 52 mg /L in Brazilian beer samples. In 2003, [24] reported Pb levels ranging from not detected to 290 mg /L. Similarly, [33] reported Pb levels varying from 3 to 15 mg /L in Spanish beers. Pb concentrations less than 30–120 mg/L were reported for Italian beers [34]. [20], in a 2007 survey reported that the average content of Pb in beers from the Italian market was 1.83- □3.24 µg /L. The concentrations of Pb in the present study are comparable to the levels reported in beers from other parts of the world [20, 24, 32, 33, 34,35] . The estimated dietary intake of Pb from the Table I. Metal content (□/mL) in a mix of canned beers available in the Nigerian market.

Zinc (Zn) concentration in sampled canned beer ranged from 0.07 – 0.15 µg/ml), with the brand 'G' having the highest concentration of 0.15 µg/ml) and brand 'D' having the lowest value of 0.07 µg/ml) in sampled canned beers respectively. The estimated provisional tolerable daily intake of Zn in this study ranged from 0.005–0.07 µg /kg bw/day. The Joint FAO/WHO Expert Committee on Food Additives (JECFA) provisional maximal tolerable daily intake of Zn is 1,000 µg /kg bw/day [35]., the EVM safe upper limit (SUL) for Zn is 4.2 mg/day (equivalent to 700 µg /kg bw/day in a 60 kg adult) for total dietary intake [30]. The estimated intake of Zn from canned beer constituted less than 1% of the safe upper limit for Zn.

4. CONCLUSION AND RECOMMENDATIONS

In view of excellent beer quality assurance, knowledge concerning metal composition in beer and brewing liquors at various steps of beer production is very important to the brewers and the consumers. The results confirmed that metals concentration in finished beer differs among samples of different brands and also among samples of the same brand because heavy metals in beer is derived from various raw materials, equipment and brewing processes[36] . It was assumed that during upside down storage more prominent migration could occur due to the fact that beer is in contact with the edges of the can body and its lid on which more corrosion points could arise. The results of the present survey indicate Cr, Fe, Ni, Cd and Pb were present at concentrations above the permissible levels in drinking water, while the metals Zn, Al and Cu were present at levels below the permissible limits in drinking water. Ultimately, there is clearly a need to improve quality control in the processing of this and other canned beers. Non-compliance with an established standard per se is not an offence except where the standard is mandatory. Offences Relating to Mandatory Standards: Section l2(b) impose a duty on every manufacturer of any item in respect of which -a mandatory standard has been declared to ensure that the item complies with the standard.

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