

*Full Length Research Paper*

# Determination of heavy metal concentration in canned beer and its effect on human health in Owerri, Nigeria

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Evaluation of metal concentrations in selected canned beers consumed in Owerri, Imo State, Nigeria was conducted using atomic absorption spectrophotometer (AAS) after  $\text{HNO}_3/\text{H}_2\text{O}_2$  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 show 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 health, 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.

**Key words:** Canned beers, risk, metals, human health, Nigeria.

## 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 (Wyrzykowska et al., 2001; Benova et al., 2007; Korenekova et al., 2007; Bellido-Milla et al., 2004). 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 (Svendson and Lund, 2000). 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 (Milacic and Kralj, 2003; Viñas et al., 2002; Wyrzykowska et al., 2001;

Asfaw and Wibetoe, 2005; Nascentes et al., 2005; Llobat-Estelles et al., 2006; Onianwa et al., 1999; Iwegbue, 2010; Soliman and Zikovsky, 1999). 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 levels (Abou-Arab et al., 1996; Dahiya et al., 2005). 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 (Sharpe and Williams, 1995), moreover, lead can cause reduced intelligence quotient, learning difficulties, slow growth, behavioral abnormalities, hearing difficulties and cognitive functions in humans (Donadini et al., 2008).

It should be 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 (Adekunle and Mojisola, 2007; Milacic and Kralj, 2003; Viñas et al., 2002). 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 (Viñas et al., 2002). The project then focuses on the determination of heavy metal concentrations in canned beer and its effect on human health in the study area.

## MATERIALS AND METHODS

### Study area

Owerri Municipal is located between latitudes 8° 30' and 7° 15' N and longitude 50 15' and 5° 30'E. It has a mean annual rainfall that varies from 2000 - 2500 mm, and a mean temperature of 26 to 28°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 called by their names. The samples were obtained from a local store and they represent the types of beers readily available to consumers. Also, identification of the hotels was done randomly for the purpose of picking types of beer for analysis. Made of the beer for human consumption was 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 least 2 to 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 to 7.5% (World Health Organization (WHO), 1989). 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 h (100°C) until complete clarification and allowed to cool, and filtered and diluted to 25 ml with ultra pure water (World Health Organization (WHO), 1989). 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<sub>3</sub> for 48 h 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 was presented as mean and standard deviation and subjected to Pearson's correlation analysis, while one-way analysis of variance (ANOVA) ( $P < 0.05$ ) was used to assess whether heavy metals varied significantly between canned and bottled beer consumed.

## RESULTS AND DISCUSSION

Here, the results from the composition of sampled beers in Owerri Municipal are given. Table 1 presents the mean concentration metals from sampled canned beers ( $\pm$  SD). Tables 2 and 3 present "estimated provisional tolerable intake of metals" and "estimated daily intake of metals" in canned beers sampled for analysis.

From the results in Table 1, the mean concentrations of Aluminium in the different brands of beers that are canned varied between 0.002 and 0.005 ( $\mu\text{g/ml}$ ), with the brand 'F' having the highest mean concentration value of 0.005 ( $\mu\text{g/ml}$ ), and brand 'J' having the lowest mean concentration of 0.001 ( $\mu\text{g/ml}$ ). Also, Tables 1 and 2 show information on the estimated daily intake and provisional tolerable daily intake respectively, based on average per capita consumption of 10 L of beer. The estimated provisional tolerable daily intake of aluminium in this study ranged from 0.001 to 0.002  $\mu\text{g/kg bw/day}$ , which is far lower than the WHO value of 1,000  $\mu\text{g/kg bw/day}$  (Soares and de Moraes, 2003). The NAFDAC and WHO maximum permissible limits of aluminium in drinking water are 0.5 and 0.2  $\mu\text{g/L}$  respectively (Amelia and Mariana, 2011). 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

**Table 1.** Metal contents in canned beers in Owerri.

Code of sampled beers	Metals in selected beers ( $\mu\text{g/ml}$ )							
	Al	Cd	Ni	Cu	Cr	Fe	Pb	Zn
A	0.003 $\pm$ 0.001	0.003 $\pm$ 0.001*	0.08 $\pm$ 0.02	0.07 $\pm$ 0.02	0.19 $\pm$ 11	<b>0.56<math>\pm</math>0.21</b>	0.021 $\pm$ 0.019	0.08 $\pm$ 0.02
B	0.004 $\pm$ 0.002	0.006 $\pm$ 0.002	0.07 $\pm$ 0.02	<b>0.08<math>\pm</math>0.03</b>	<b>0.34<math>\pm</math>0.18</b>	0.34 $\pm$ 0.12	<b>0.045<math>\pm</math>0.25</b>	0.09 $\pm$ 0.03
C	0.004 $\pm$ 0.001	0.005 $\pm$ 0.001	0.06 $\pm$ 0.02	0.06 $\pm$ 0.02	0.23 $\pm$ 0.11	0.40 $\pm$ 0.19	0.036 $\pm$ 0.013	0.09 $\pm$ 0.03
D	0.003 $\pm$ 0.002	0.003 $\pm$ 0.001	<b>0.10<math>\pm</math>0.04</b>	0.04 $\pm$ 0.02*	0.24 $\pm$ 0.09	0.51 $\pm$ 0.32	0.031 $\pm$ 0.011	0.07 $\pm$ 0.02*
E	0.003 $\pm$ 0.001	<b>0.008<math>\pm</math>0.003</b>	0.08 $\pm$ 0.03	0.06 $\pm$ 0.03	0.23 $\pm$ 0.08	0.34 $\pm$ 0.15	0.043 $\pm$ 0.019	0.09 $\pm$ 0.03
F	<b>0.005<math>\pm</math>0.002</b>	0.007 $\pm$ 0.002	0.07 $\pm$ 0.03	0.06 $\pm$ 0.03	0.18 $\pm$ 0.09	0.45 $\pm$ 0.22	0.023 $\pm$ 0.012*	0.13 $\pm$ 0.03
G	0.004 $\pm$ 0.001	0.006 $\pm$ 0.002	0.09 $\pm$ 0.04	0.08 $\pm$ 0.02	0.24 $\pm$ 0.08	0.32 $\pm$ 0.16	0.033 $\pm$ 0.011	<b>0.15<math>\pm</math>0.05</b>
H	0.003 $\pm$ 0.001	0.004 $\pm$ 0.001	0.06 $\pm$ 0.02	0.06 $\pm$ 0.02	0.21 $\pm$ 0.07	0.23 $\pm$ 0.10*	0.036 $\pm$ 0.013	0.12 $\pm$ 0.02
I	0.003 $\pm$ 0.002	0.005 $\pm$ 0.002	0.04 $\pm$ 0.02*	0.06 $\pm$ 0.02	0.17 $\pm$ 0.07*	0.45 $\pm$ 0.21	0.041 $\pm$ 0.020	0.10 $\pm$ 0.02
J	0.002 $\pm$ 0.001*	0.006 $\pm$ 0.002	0.07 $\pm$ 0.03	0.05 $\pm$ 0.01	0.26 $\pm$ 0.12	0.34 $\pm$ 0.17	0.030 $\pm$ 0.015	0.13 $\pm$ 0.03
K	0.003 $\pm$ 0.002	0.006 $\pm$ 0.002	0.08 $\pm$ 0.02	0.09 $\pm$ 0.03	0.23 $\pm$ 0.11	0.54 $\pm$ 0.31	0.042 $\pm$ 0.021	0.08 $\pm$ 0.02

Source: Laboratory analysis by an Author in 2012. Highest values are in bold and the lowest in \*.

**Table 2.** Estimated provisional tolerable intake of metals ( $\mu\text{g/kg/bw/day}$ ) based on average per capita consumption of 10 L of beer.

Code of sampled beers	Metals in selected beers ( $\mu\text{g/ml}$ )							
	Al	Cd	Ni	Cu	Cr	Fe	Pb	Zn
A	0.001	<b>0.005</b>	0.04	0.03	0.11	0.22	0.003	<b>0.07</b>
B	0.001	0.001	0.02	<b>0.03</b>	<b>0.05</b>	0.24	<b>0.02</b>	0.06
C	0.001	0.004	0.05	0.02	0.12	0.18	0.02	0.04
D	0.001	0.003	<b>0.03</b>	0.03	0.10	0.23	0.02	0.04
E	0.001	<b>0.002</b>	0.04	0.03	0.11	0.24	0.01	0.04
F	<b>0.002</b>	0.000	0.05	0.05	0.13	<b>0.33</b>	<b>0.00</b>	0.005
G	0.001	0.004	0.03	0.03	0.07	0.25	0.01	<b>0.005</b>
H	0.001	0.00	0.04	0.03	0.10	0.26	0.004	0.005
I	<b>0.001</b>	<b>0.00</b>	<b>0.02</b>	<b>0.02</b>	0.05	<b>0.14</b>	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	<b>0.18</b>	0.18	0.01	0.005

\*High and low values are bolded (adopted from Chukwujindu, 2010).

**Table 3.** Estimated daily intake ( $\mu\text{g/day}$ ) of metals based on average per capita of 10 L of beer.

Code of sampled beers	Metals in selected beers ( $\mu\text{g/ml}$ )							
	Al	Cd	Ni	Cu	Cr	Fe	Pb	Zn
A	0.08	<b>0.27</b>	2.47	1.64	6.59	13.15	0.16	<b>4.11</b>
B	0.08	0.03	<b>1.10</b>	1.94	<b>2.74</b>	14.52	<b>1.04</b>	3.56
C	<b>0.06</b>	1.37	<b>2.74</b>	1.37	7.40	14.52	0.93	2.19
D	0.08	0.16	2.19	1.92	5.75	13.70	<b>1.29</b>	2.19
E	0.08	<b>0.11</b>	2.19	1.92	6.30	14.25	0.85	2.19
F	<b>0.11</b>	<b>0.00</b>	2.74	<b>2.74</b>	7.67	<b>20.00</b>	<b>0.00</b>	0.27
G	0.08	0.22	1.64	1.92	4.38	15.07	0.66	<b>0.27</b>
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	<b>8.49</b>	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	<b>10.96</b>	10.96	0.82	0.27

\*High and low values are bolded (adopted from Chukwujindu, 2010).

Bundesamt für Verbraucherschutz and Lebensmittelsicherheit (1995-2002) 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 and Lebensmittelsicherheit reported Cd in beers ( $n = 251$ ) from the German market (in the period of 1995 - 2002) as 0.0017  $\mu\text{g}/\text{mL}$  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 (Bundesamt für Verbraucherschutz and Lebensmittelsicherheit, 1995-2002).

From Table 1, cadmium concentrations in canned beers sampled ranged between 0.003 - 0.008  $\mu\text{g}/\text{ml}$ , with brand beer 'A' having the highest value of concentration of 0.008  $\mu\text{g}/\text{ml}$ , and the lowest brand being 'E' with the value of 0.003  $\mu\text{g}/\text{ml}$  (World Health Organization (WHO), 1989). In 2007, the average content of Cd in beers from the Italian market was reported as 0.16 - 0.15  $\mu\text{g}/\text{L}$ . Similarly, World Health Organization (WHO) (2001) reported a Cd content varying from 12.9 - 14.3  $\mu\text{g}/\text{L}$  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 (World Health Organization (WHO), 2001, 2010). The JECFA limit for Cd is 1  $\mu\text{g}/\text{kg}$  bw/day (Standard Organization of Nigeria (SON), 2003). The estimated provisional tolerable daily intake of Cd in this study ranged from 0.0 to 0.005  $\mu\text{g}/\text{kg}$  bw/day.

Results in Table 1 indicate that the mean concentration of Nickel (Ni) in sampled beers ranged between 0.004 and 0.10 ( $\mu\text{g}/\text{ml}$ ), with brand 'D' having the highest mean concentration of 0.10 ( $\mu\text{g}/\text{ml}$ ), and brand 'I' having the lowest mean value. The WHO maximum permissible limit of Ni in drinking water is 0.02  $\mu\text{g}/\text{mL}$  (World Health Organization (WHO), 2010). 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  $\mu\text{g}/\text{kg}$  bw/day (Expert Group on Vitamins and Minerals (EVM), 2003; Biurum et al., 1991). The estimated provisional tolerable daily intake of Ni in this study ranged from 0.02 to 0.05  $\mu\text{g}/\text{kg}$  bw/day.

The Copper (Cu) content of the sampled canned beers varied between 0.05 and 0.08 ( $\mu\text{g}/\text{ml}$ ), with brand 'B' having the highest concentration value of 0.08 ( $\mu\text{g}/\text{ml}$ ), and the lowest being brand 'D' with the mean value of 0.05 ( $\mu\text{g}/\text{ml}$ ). The permissible limit for Cu in the drinking water in Nigeria is 1.0 mg/L (Standard Organization of Nigeria (SON), 2003; World Health Organization (WHO), 1993). The Cu content of the beer samples was below the permissible limit (Amelia and Mariana, 2011). The JECFA provisional maximal tolerable daily intake of Cu

was 500  $\mu\text{g}/\text{kg}$  bw/day and a safe upper limit of 160  $\mu\text{g}/\text{kg}$  bw/day was 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  $\mu\text{g}/\text{kg}$  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 and 0.34 ( $\mu\text{g}/\text{ml}$ ), with brand 'B' having the highest mean value of 0.34 ( $\mu\text{g}/\text{ml}$ ), and brand 'I' having the lowest value of 0.17 ( $\mu\text{g}/\text{ml}$ ). The average daily intake of chromium in this study ranged from 2.74 to 10.96  $\mu\text{g}$  per day, which is below the recommended dietary allowance of 130  $\mu\text{g}/\text{day}/\text{person}$ . The permissible limit of chromium in drinking water is 0.05 mg/L (Biurum et al., 1991). All the samples examined had chromium concentrations above the permissible limit in drinking water. However, the EVM guidance level for chromium is 150  $\mu\text{g}/\text{kg}$  bw/day for total dietary intake of trivalent chromium (World Health Organization (WHO), 1993). The estimated provisional tolerable daily intake of chromium in this study ranged between 0.05 and 0.18 WHO  $\mu\text{g}/\text{kg}$  bw/day.

The Iron (Fe) content in the sampled canned beers varied between 0.23 and 0.56 ( $\mu\text{g}/\text{ml}$ ), with the highest concentration of Fe in sampled canned beers being 0.56 ( $\mu\text{g}/\text{ml}$ ) in brand 'A', and the lowest concentration with the value of 0.23 ( $\mu\text{g}/\text{ml}$ ) in brand 'H'. The National Agency for Food, Drug Administration and Control (NAFDAC)'s maximum allowed limit of Fe in drinking water is 0.30 mg/L (Amelia and Mariana, 2011). 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  $\mu\text{g}/\text{kg}$  bw/day. The estimated daily intake of Fe is below the recommended dietary allowance of 35 - 700  $\mu\text{g}/\text{gd}$  (1 person).

From the results in Table 1, Lead (Pb) concentration in the sampled canned beers ranged between 0.021 and 0.045 ( $\mu\text{g}/\text{ml}$ ), with brand 'B' having the highest concentration of Pb in sampled canned beers of 0.045  $\mu\text{g}/\text{ml}$ , and brand 'A' having the lowest value of 0.021  $\mu\text{g}/\text{ml}$ . 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 (Biurum et al., 1991). 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 (Bamforth, 1999b). Soliman and Zikovsky (1999) reported Pb content varying from 13 to 52 mg/L in Brazilian beer samples. In 2003, World Health Organization (WHO) (2001) reported Pb levels ranging from not detected to 290 mg/L. Similarly, (Chukwujindu et al., 2012) 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 (Chukwujindu, 2012). World Health Organization (WHO) (1989), in a 2007 survey, reported that the average

content of Pb in beers from the Italian market was 1.83 - 3.24  $\mu\text{g/L}$ . The concentrations of Pb in the present study are comparable to the levels reported in beers from other parts of the world (World Health Organization (WHO), 1989, 2001; Soliman and Zikovsky, 1999; Chukwujindu et al., 2012; Chukwujindu, 2012; Iwegbue et al., 2009). The estimated dietary intake of Pb from Table 1 shows the metal content ( $\mu\text{g/mL}$ ) in a mix of canned beers available in the Nigerian market.

Zinc (Zn) concentration in sampled canned beer ranged from 0.07 - 0.15  $\mu\text{g/ml}$ , with brand 'G' having the highest concentration of 0.15  $\mu\text{g/ml}$ , and brand 'D' having the lowest value of 0.07  $\mu\text{g/ml}$  in the sampled canned beers respectively. The estimated provisional tolerable daily intake of Zn in this study ranged from 0.005 - 0.07  $\mu\text{g/kg bw/day}$ . The Joint FAO/WHO Expert Committee on Food Additives' (JECFA) provisional maximal tolerable daily intake of Zn is 1,000  $\mu\text{g/kg bw/day}$  (Iwegbue et al., 2009), and the EVM safe upper limit (SUL) for Zn is 4.2 mg/day (equivalent to 700  $\mu\text{g/kg bw/day}$  in a 60 kg adult) for total dietary intake (World Health Organization (WHO), 1993). The estimated intake of Zn from canned beers constituted less than 1% of the safe upper limit for Zn.

## 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 (World Health Organization (WHO), 1982). 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 that 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 12(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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