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Identification and quantification of heavy metals in local drinks in Northern Zone of Nigeria

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Nine heavy metals were studied in locally prepared drinks, namely, "Zobo" and "Kunnu Zaki". The samples were prepared from the outer covering (calyx) of the fruits of roselle *Hibiscus sabdariffa* and cereals (millet or guinea corn), respectively. Twenty samples of "Zobo" coded Zb_1-Zb_{20} and twenty samples of "Kunnu Zaki" coded Kz_1-Kz_{20} were bought from different parts of Samaru-Zaria, Nigeria. The qualitative analysis of the samples was by official methods and were quantitatively analyzed using Atomic Absorption Spectrophotometer (AAS). Iron (Fe), Copper (Cu), Zinc (Zn) and Lead (Pb) were detected in most Zb and Kz samples, while Chromium (Cr), Manganese (Mn), Silver (Ag), Mercury (Hg) and Bismuth (Bi) were absent in all the samples. The Fe values ranged from 3.13 to 5.48 mg/L; Cu ranged from 0.12 to 0.62 mg/L, Zn ranged from 0.02 to 0.22 mg/L and Pb ranged from 0.54 to 1.28 mg/L in Zb samples. The Fe values for Kz samples ranged from 18.63 to 31.25 mg/L, Cu ranged from 0.03 to 0.11 mg/L, Zn ranged from 0.08 to 0.39 mg/L and Pb ranged from 0.80 to 1.55 mg/L. The higher values detected in Fe, Zn and Pb for Kz samples compared with Zb samples could be due to the different materials used in their preparation. The implication of the results in public health is discussed.

Key words: Cereals, drinks, heavy metals, samples, *Hibiscus sabdariffa*.

INTRODUCTION

Metals are elements that cannot be decomposed to simpler units by chemical means. They are shinny, ductile, malleable and usually good conductor of heat, and electricity. Metals have high densities, high melting points, high molar heat of fusion and evaporation (Graham and John, 1978).

Local drinks are non-alcoholic drinks produced and consumed within a locality. Usually, they contain sweetening, flavouring and other naturally occurring or locally obtained ingredients. In Nigeria, the common local drinks are "Zobo" (Zb), "Kunnu Zaki" (Kz). Zb is a brick red non-alcoholic drink prepared by boiling the dried calyx of *Hibiscus sabdariffa* in water. The extract is filtered and more water can be added. The extract can

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then be sweetened with sugar after adding the flavouring agent.*H. sabdariffa* (*Roselle*) is an annual herb native to tropical Africa reaching up to 2 m. The dried calyces contain the flavonoids gossypetine, hibiscetine and sabdaretine. Small amount of delphinidin 3-monoglucoside, cyanidin 3-monoglucoside (chrysanthenin), and delphinidin are also present (Bernd and Franz, 1990). Juice made by cooking a quantity of calyces with water is used as a cold drink in the West Indies, tropical America, Jamaica, Mexico, Egypt and Nigeria as "Zobo" (Kolawole and Maduenyi, 2004). Kz is prepared from cereals (millet or guinea corn). Other ingredients used in its preparation are ginger, black pepper and sweet potatoes or sugar. It can be prepared by soaking the cereal in water for about twelve hours to get soft. The ginger and the black pepper together with the sweet potatoes are ground together, while the soaked cereal is ground separately using a grinding machine. Hot boiling water would be used to make a thick paste with the ground cereals. The ground ginger, pepper and potatoes mixture would be diluted very well with cold water and mixed with the thick paste with vigorous stirring. The mixture would be allowed for about six hours in which the chaffs from the cereals and the ground ingredient would have settled down. The mixture is filtered with fine sieve. The resulting mixture is colloidal in nature, made up of fine starch granules suspended in a sugar solution that settles on standing. The sweet potatoes can serve as a sweetening agent, but granulated sugar can be added to the desired taste. The ginger and black pepper can be used as flavouring agents.

The massive consumption of these drinks could be due to the poor economic state of the country, the nutritive and medicinal values. The production of these drinks in most cases goes through non-hygienic conditions. It lacks uniformity, specificity of source of water, purification of the ingredient and there is no specification of packaging materials and place of production; these are the sources of impurities in the finished product resulting in hazardous effect on the health and total well being of the consumers.

Heavy metals present in the body are of great danger particularly when present at a concentration above the tolerance limit (Nriagn, 1988). Most heavy metals are regarded as toxic to living organisms, because of their tendency to accumulate in selected tissues. More over their presence is a causative agent of various sorts of disorder including neuro-, nepro-, carcino, terato- and immunological (Zukowska and Biziuk, 2005). Accumulation of non essential investigated heavy metals (e.g. Pb, Cd, and Cr) in the environment could be useful indicators of the possible toxic effect for the consumers (Liu, 2003; Tasi, 2005).

Acute toxicity was observed in patient with renal failure following hemodialysis with water stored in Zinc galvanized tank. The patient suffered nausea, vomiting, fever and severe anemia (Galley et al., 1972). Lead is toxic to such as the nervous, gastrointestinal and genital system (Abou-Arab, 2001) and also a possible human carcinogen (Yakasai et al., 2004) and the accumulation of Mn may cause hepatic encephalopathy (Layrangues et al., 1998). Outbreak of "Minamata" disease caused by Mercury poisoning has been reported in Iraq and Canada. In Iraq, 7.2% of 6,350 people hospitalized died (Masazum and Smith, 1975). Péter et al. (2012) reported the accumulation of some heavy metals in milk of grazing sheep in North-East Hungary. Due to the health hazards caused by these toxic metals which might be present in the raw materials or water used in the preparation of drinks. The present study was carried out to investigate the presence of metallic impurities and to determine the quantity in these local drinks.

MATERIALS AND METHODS

Measurement were made with a Buck Model 210 Variant Giant Pulses Correction (VGP) system Atomic Absorption Spectrophotometer (AAS) equipped with the corresponding hollow cathode lamp (Lead, Copper, Iron and Zinc) at the time of analysis. Lamp current 10 mA, wavelength 217.0 nm, band pass 0.5 nm with flame type consisting of air/acetylene and stoichiometric fuel flow at 0.9 to 1.21 min^{-1}.

Samples

The samples were bought from Samaru-Zaria, Nigeria and were coded Zb_1-Zb_{20}, (Zobo), Kz_1-Kz_{20} (Kunnu Zaki); they were refrigerated until the time of use.

Reagent

All the reagents were analytical grade from British Drug House (BDH).

Official methods were used for the identification of the metals (USPXX, 1990). Stock solution of each metal was prepared as follows: Iron (Fe), 1.00 g of iron powder was dissolved in 40 ml of 2 M hydrochloric acid and 10 ml of 2 M nitric acid; this was made up to 1 L in volumetric flask with deionized water to give 1000 mg/L Fe solution; Lead (Pb), 1.598 g lead nitrate was dissolved in 50 ml nitric acid and the solution was made to volume in 1 L volumetric flask with deionized water to make 1000 mg/L Pb solution; copper (Cu), 1.00 g of copper metal was dissolved in 50 ml nitric acid and was diluted to mark in 1 L volumetric flask with deionized water to 1000 mg/L Cu solution; Zinc (Zn), 1.245 g of zinc oxide was dissolved in 50 ml of 2 M hydrochloric acid. This was diluted to mark in 1 L volumetric flask with deionized water to 1000 mg/L Zn solution.

Preparation of calibration curve

Standard solutions were prepared from each metal stock solution of 1000 mg/L by further dilution using deionized water. Working standard solutions of Fe ranged from 2.00 to 10.00 mg/L for Zb samples and from 10.00 to 50.00 mg/L for Kz samples. Cu ranged from 0.05 to 0.80 mg/L for Zb samples and from 0.02 to 0.10 for Kz samples. Zn ranged from 0.02 to 0.40 mg/L for both samples. Pb ranged from 0.50 to 2.00 mg/L for both samples. 100 ml of the

Table 1. Qualitative analysis of heavy metals impurities in twenty "Zobo" (Zb1-Zb20) samples.

Sample code	Zinc (Zn)	Copper (Cu)	Iron (Fe)	Lead (Pb)
Zb1	A	A	P	P
Zb2	P	P	P	P
Zb3	P	P	P	P
Zb4	P	P	P	P
Zb5	P	P	P	P
Zb6	P	P	P	P
Zb7	P	P	P	P
Zb8	P	P	P	P
Zb9	P	P	P	P
Zb10	P	P	P	P
Zb11	A	A	P	P
Zb12	P	P	A	P
Zb13	P	P	A	P
Zb14	P	P	P	A
Zb15	P	P	P	P
Zb16	P	P	P	P
Zb17	P	P	A	P
Zb18	P	P	P	P
Zb19	A	P	A	P
Zb20	P	A	A	P

P: Present; A: Absent.

standard solution of each metal was adjusted to pH of 2.5 by adding 1 M trioxonitrate (v) acid. Each standard solution and blank was transferred into an individual 250 ml separating funnel. One milliliter ammonium pyrrolidine dithriocarbamate was added followed by the addition of 10 ml methyl isobutyl ketone and the solution was shaken vigorously for 2 min and allowed to settle. The aqueous layer was drained off and discarded, while the organic layer was then aspirated directly into the flame (zeroing the instrument on methyl isobutyl ketone) and the absorbance was recorded. The nebulizer, atomizer and burner were flushed each time with distilled water after each sample solution was aspirated before the next. The stability of the instrument was checked at intervals by introducing the highest working standard solution and the blank.

Pre-treatment of the samples

100 ml of each of the samples were measured into series of weighed platinum crucibles and labeled accordingly. The platinum crucibles were then placed on series of hot plates for about three hours to evaporate to dryness with low heat. The dried crucibles were then cooled in a desiccator and the weight recorded. The differences in the weight were recorded and the residue removed from the crucible. Method digestion in mixture acids was employed using nitric acid, perchloric acid and hydrofluoric acid mixture. 0.2 g of each pre-treated sample was treated with 5 ml of deionized water to dampen the sample; 6 ml of concentrated nitric acid were then added, followed by 1 ml of perchloric acid and heated on a water bath to the appearance of white fumes. 5 ml of hydrofluoric acid was added after cooling and the resulting mixture boiled for 10 min. This was filtered and made up to mark with deionized water in a 100 ml volumetric flask. The sample solutions were then analyzed as described under preparation for calibration curve. The concentration of each metal from sample was determined from the calibration curve.

RESULTS AND DISCUSSION

The result of qualitative tests using official methods showed that Iron (Fe), Copper (Cu) and Zinc (Zn) and Lead (Pb) were present in most Zb and Kz (Tables 1 and 2), respectively. Chromium (Cr), Manganese (Mn), Silver (Ag), Mercury (Hg) and Bismuth (Bi) were absent in all the samples.

The result of the quantitative tests for Zb and KZ in Tables 3 and 4 show that higher values of Fe, Zn and Pb were detected in Kz compared with Zb. However, the value of Cu detected in Zb was more than that of Kz. This could be due to the different material used in their pre-paration. The values of Fe and Pb were both high and not within the tolerance limits of metals set by World Health Organization (WHO, 1996) (Table 5). Although, Iron performs important roles in the body but when in excess, especially the ferric salt, produces irritation of the gastro-intestinal tract which is characterized by abdominal pain and diarrhea most especially when on empty stomach. Lead can be described as an element that is purely toxic. Some elements, although toxic at high levels, are actually required nutrients at lower levels. This is clearly not the case for lead. No nutritional value or positive biological effect has been shown to result from lead exposure. Also,

Table 2. Qualitative analysis of heavy metals impurities in twenty "Kunnu Zaki" (KZ1-KZ20) samples.

Sample code	Zinc (Zn)	Copper (Cu)	Iron (Fe)	Lead (Pb)
KZ1	P	P	P	P
KZ2	A	P	P	P
KZ3	P	A	P	P
KZ4	P	P	P	P
KZ5	P	P	P	P
KZ6	P	P	P	P
KZ7	P	P	P	P
KZ8	P	P	P	P
KZ9	P	P	P	P
KZ10	A	A	P	P
KZ11	A	P	P	P
KZ12	P	P	A	P
KZ13	P	P	A	P
KZ14	P	P	P	A
KZ15	P	A	P	P
KZ16	P	A	P	P
KZ17	A	P	A	P
KZ18	P	A	P	P
KZ19	P	P	A	P
KZ20	P	A	A	P

P: Present; A: Absent.

Table 3. The quantitative analysis of 20 samples Zobo (Zb1 – Zb20) concentration (mg/L).

Sample code	Iron (Fe)	Lead (Pb)	Zinc (Zn)	Copper (Cu)
Zb1	5.48	0.54	N/D	N/D
Zb2	3.90	0.74	0.08	0.18
Zb3	5.48	0.80	0.06	0.22
Zb4	4.68	0.90	0.03	0.18
Zb5	5.47	0.74	0.19	0.15
Zb6	4.68	0.80	0.20	0.18
Zb7	3.90	1.06	0.22	0.25
Zb8	3.90	0.54	0.05	0.22
Zb9	5.48	0.96	0.08	0.12
Zb10	4.68	1.12	0.09	0.15
Zb11	5.48	1.20	N/D	N/D
Zb12	N/D	0.96	0.06	0.15
Zb13	N/D	1.12	0.03	0.46
Zb14	4.68	N/D	0.02	0.56
Zb15	5.48	0.80	0.06	0.62
Zb16	3.13	0.84	0.08	0.15
Zb17	N/D	N/D	0.09	0.25
Zb18	3.90	0.80	0.11	0.18
Zb19	N/D	0.74	N/D	0.22
Zb20	N/D	1.28	0.06	N/D

N/D: Not detected.

Table 4. The quantitative analysis of 20 samples Kunnu Zaki (Kz1-Kz20) concentration (mg/L).

Sample code	Iron (Fe)	Lead (Pb)	Zinc (Zn)	Copper (Cu)
Kz1	19.40	0.96	0.12	0.09
Kz2	21.75	27	N/D	0.06
Kz3	19.40	1.01	0.14	N/D
Kz4	19.40	1.12	0.11	0.03
Kz5	20.20	1.33	0.15	0.06
Kz6	23.50	0.96	0.19	0.03
Kz7	25.05	0.90	0.12	0.11
Kz8	N/D	N/D	0.14	0.09
Kz9	N/D	0.85	0.31	0.09
Kz10	24.25	0.80	N/D	N/D
Kz11	21.75	1.01	N/D	0.11
Kz12	25.83	1.07	0.39	0.11
Kz13	N/D	0.96	0.34	0.08
Kz14	18.63	N/D	0.22	0.10
Kz15	27.40	1.50	0.14	N/D
Kz16	31.25	1.55	0.09	N/D
Kz17	N/D	1.12	N/D	0.06
Kz18	N/D	N/D	0.08	N/D
Kz19	28.98	0.96	0.19	0.09
Kz20	N/D	0.90	0.39	N/D

N/D: Not detected.

Table 5. The mean ± standard deviation concentration of heavy metals in mg/L.

Sample	Fe	Pb	Zn	Cu
Zb	3.54±2.19	0.84±0.29	0.08±0.06	0.22±0.16
Kz	23.34±3.3	2.54±6.29	0. 20±0.11	0.08±0.03
WHO limits	0.100	0.01	0.01–0.075	2.00
RDA	0.01-0.06	3mg/week	0.10	7.45

WHO limit: World Health Organization Limit; RDA: Recommended Daily Allowance.

no case of lead deficiency has ever been noted in the medical literature; for lead therefore any exposure is of potential concern. The metallic impurities detected can be traced to the water used in the production, equipment, ingredients added, containers, packaging materials and environmental pollutants. Zn and Cu are within acceptable limit (WHO, 1996). The study recommends that the health authorities should think how to control the quality of these local drinks; specified amount of each ingredient should be used in the production. This might reduce the concentration of Pb in both Zobo and Kunnu Zaki. For now, the producer should reduce the ingredients and used purified water for the production of the drinks.

Conclusion

Since one means of exposure route of human to heavy metals is through ingestion of contaminated foods, drinks and beverages, efforts should be focused on the estimation of dietary intakes of potential toxic agents by consumers.

Conflicts of interest

No competing interests exist.

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