



## METAL CONCENTRATION IN TWO POPULAR LOCAL DRINKS CONSUMED IN BENUE STATE, NIGERIA

Gav BL<sup>1</sup>, Tor PN<sup>1</sup>, Tsaviv NJ<sup>1</sup>

<sup>1</sup>Department of Chemistry, Federal university of Agriculture, P.M.B.2373 Makurdi, Nigeria.

### ABSTRACT

The study was carried out on assessment of metal concentration in two popular local drinks consumed in Benue State, Nigeria. Kunu and Zobo samples were collected in five local Governments and were analyzed for trace metals (Cu, Zn, Fe, Mn, Pb, Cr and Ni) (except Na, K, Ca and Mg) using Atomic Absorption Spectrophotometer. Na and K were analyzed using Flame Photometer while Mg and Ca were determined using EDTA titration. The results obtained from the local drink samples in mg/L showed that Cu ranged from below detectable level to 0.01; Zn(0.47 to 0.5); Fe(0.1 to 1.40); Mn(0.05 to 0.16); Pb(0.03 to 0.08); Cr(0.02 to 0.05); Ni(below detectable level to 0.01); Ca(25.28 to 36.64); Mg(4.77 to 4.95); Na(3.66 to 4.74) and K(5.26 to 7.66). The results showed that the concentration range for Pb (0.03 to 0.08 mg/L) were above the WHO recommended guideline of 0.01 mg/L for beverage drinks. The average concentration value for Fe in Kunu (0.98 mg/L) was higher than the WHO recommended guidelines of 0.3 mg/L for beverage drinks, while the Fe concentration for Zobo samples (0.18 mg/L) falls below the WHO permissible limit of 0.3 mg/L for beverage drinks. The concentration levels of other metals were either below detectable level or falls within the WHO standard guideline for beverage drinks. However, the presence of some heavy metals especially lead and iron in these local drinks were localized pollution influences, which is a pointer to the contamination source as few of the samples that were affected. The reason for higher lead levels was as a result of the source of water and iron levels in Kunu drink was attributed to use of rusting metal drums and vessels used in processing of the two drinks, unlike Zobo drink which does not require the same processing of method. Therefore, consumers should be careful of the environment where those drinks are prepared, as well as the vessels used.

**Keywords:** Trace metals, Kunu, Zobo, AAS.

### INTRODUCTION

The knowledge of metals in foods is essential for calculating the dietary intakes of essential metals and evaluation of human exposure to toxic elements [1]. Apart from fruits juices and concentrates, other plant materials are often used in the preparation of alcoholic and non-alcoholic beverages. The simplicity of production availability of raw materials in many rural communities has resulted to an increase in production and consumption of many local beverages at cottage levels in Nigeria. The local beverages are also reported to have various medicinal values.

Determination of trace metals is of interest because while some are essential nutrient some are toxic. Metals like Zinc, Manganese, Copper, Chromium, Iron, and Cobalt are essential trace elements for humans,

animals and plants. Heavy metals such as Lead, Cadmium, Nickel, Arsenic, and Mercury are toxic even at low level, found to have harmful effect on human physiology and other biological systems when they are above the tolerance level. Excessive intake of these toxic heavy metals can lead to several diseases such as organ failure, cancers, retardation of mental development in children in pregnant women [2]. It is important to monitor the level of such pollutants in the environments especially the foods and drinks consumed in the rural areas of developing countries like Nigeria which suffers neglect from the government.

Kunu is a popular drink consumed throughout Nigeria, mostly in the North. It is usually made from grains such as millet or sorghum, although it can be made

from maize as well. The variety of the drink made from sorghum is a milky light-brown colour, while Kunu made from millet and maize is whitish in colour [3].

Zobo is a healthy Nigeria drink from the dried red calyces and sepals of the Roselle plant (*Hibiscus Sabdariffa*) known as Zobo leaves in Nigeria. Zobo is usually served as a chilled refreshing drink but can also be enjoyed as a relaxing hot tea and leaves used in production of jam/jelly, food colouring, syrups and soup/sauces. According to several scientific investigations, weather in form of tea, jams or sauces is said to help reduce high blood pressure, aid digestion, promote the health of the urinary tract and also great for overall health. According to several scientific investigations, millet and other grains use in the production of these local drinks contains a poly-nutrient called ligman, which has cancer fighting properties and is beneficial in the treatment of heart disease. It is also known to reduce the risks associated with diabetes. Burukutu, Kunu and Zobo are good for woman that have reached the stages of menopause as to helps them relax their muscles. These drinks are recommended for nursing mothers as they help increase the flow of their milk. These drinks contain fibre thus helping to promote a healthy digestive system and also help in the prevention of chronic inflammatory diseases such as rheumatoid arthritis. Water is the main component of these drinks, the concentrations of metals of these popular local drinks may be related to the purity of the water used in the production processes. The processing of these local drinks is carried out in a small scale enterprise involving the possible use of low water quality, there is a distinct possibility of contamination of these products with understand able elements [4].The availability of metals in our local drinks may be as result of the bioaccumulated metals in the plants which are used for the production processes.

## MATERIALS AND METHODS

### Study area

Benue State is one of 36 states in the Federal Republic of Nigeria. It is located North-Central of Nigeria. The state is made of twenty three Local Government Areas. Benue State lies within the lower river Benue trough in the middle belt region of Nigeria. Its geographic coordinates are longitude  $7^{\circ} 47'$  and  $10^{\circ} 0'$  East. Latitude  $6^{\circ} 25'$  and  $8^{\circ} 8'$  North and shares boundaries with five other States namely: Nasarawa State to the North, Taraba State to the east, Cross-River State to the south, Enugu State to the south-west and Kogi State to the west. The state also shares a common boundary with the Republic of Cameroon on the south-east. Benue occupies a landmass of 34,059 square kilometers (Fig1). According to 2006 census, the state has a population of about 4,253,641. It is inhabited predominately by Tiv and Idoma peoples, who speak the Tiv language and Idoma language respectively. There are other ethnic groups,

including the Igede, Etulo and Abakwa, Jukun, Hausa, Akweya and Nyifon. With its capital at Makurdi, Benue is a rich agricultural region; some of the crops grown there are potatoes, cassava, soyabean, guinea corn, sorghum, flax, yams, sesame, rice and grand nuts [5].

The physical features of the area are generally low lying (averaging 100m-250m) and gently undulating with occasional in selbergs, knoll, laterite etc. It has a typical climate of the tropical zone because of its location. Its climate is quite pleasant with average maximum and minimum temperatures of  $35^{\circ}\text{c}$  and  $21^{\circ}\text{c}$  in summer and  $37^{\circ}\text{c}$  and  $16^{\circ}\text{c}$  in winter respectively. The climate is characterized by two distinct seasons, wet and dry. The dry season spans from October to March while the wet season is from April to September. The month of December, January and February are cold due to harmattan wind blowing across the Local Government areas from the North-East of Nigeria. The sediments are generally sandy-loam shelf basement complex and alluvial plain. The vegetation of the state consists of rain forests which have tall trees, tall grasses and oil palm trees. More than 80 percent of the inhabitants are predominately farmers [5].

### Sample Collection

A total of ten freshly prepared samples of Kunu, and Zobo drinks were randomly bought from five different producers each in Makurdi, Gboko, Otukpo, Oju and Katsina-Ala towns of Benue State, Nigeria. All the samples were collected in a clean plastic bottles on the 16<sup>th</sup> and 17<sup>th</sup> October, 2015 and were kept in deep freezer prior to analysis.

### Sample treatment

Prior to analysis, the samples were degassed using ultrasonic bath for 5 minutes and the samples were digested according to the Aqua Regia method. In this method  $30\text{cm}^3$  of Aqua solution (mixture of  $\text{HNO}_3$  and  $\text{HCl}$  in the ratio 3:1) was added to  $3\text{cm}^3$  of the sampes and the mixture was heated on a hot plate in a fume cupboard until complete clarification were observed. The samples were allowed to cool at room temperature, filtered and made up to  $100\text{cm}^3$  with deionized water which were forwarded for metal analysis.

### Mineral Analysis

All the digested samples were subjected to elemental analysis (except Na,K,Ca, and Mg) using Atomic Absorption Spectrophotomer (AAS) for trace metals in triplicate. Sodium and Potassium were analyzed using flame phometer while Ca and Mg were analyzed using EDTA titration. The instrument setting and operational conditions were done in accordance with the manufacture's specification.

### Statistical Analysis

All the data generated were analyzed statistically [6]. Parameters evaluated were means, standard deviation and coefficient of variation percentage. All the data were determined in triplicate.

## RESULTS AND DISCUSSION

The level of trace metals in Kunu drinks consumed in Makurdi, Gboko, Otukpo, Oju and Katsina-Ala towns of Benue State is shown in table 2. Copper and Nickel were not at detectable range of Atomic Absorption Spectrophotometer in all the five towns where Kunu samples were collected. Lead was not detected in Kunu samples of Gboko and Katsina-Ala town. Also Nickel was not at detectable range for samples collected Makurdi, Oju, Otukpo and Katsina-Ala towns. Among the detectable trace metals in Kunu samples collected, Calcium had the highest metal concentration in Makurdi sample was 34.29 mgL<sup>-1</sup>, 35.12 mgL<sup>-1</sup> in Gboko sample, 27.56 mgL<sup>-1</sup> in Otukpo sample, 36.57 mgL<sup>-1</sup> in Oju sample and 36.52 mgL<sup>-1</sup> in Katsina-Ala sample, followed by magnesium with metal concentration of 4.11 mgL<sup>-1</sup> in Makurdi, 4.80 mgL<sup>-1</sup> in Gboko, 5.47 mgL<sup>-1</sup> in Otukpo, 4.11 mgL<sup>-1</sup> in Oju and 5.36mgL<sup>-1</sup> in Katsina-Ala towns. The least concentrated trace metal was manganese for all the Kunu samples collected in the five sampling sites of the State. The highest variability was found in Chromium (170 %) and the least varied was Calcium(9.82 %). The order of abundance was found to be as: Ca>K>Mg>Na>Fe>Zn>Mn>Pb>Cr>Ni.

The levels of trace metals in Zobo drinks collected in Makurdi, Gboko, Otukpo, Oju and Katsina-Ala towns of Benue State is shown in Table 3. Copper was not at detectable range of AAS in Zobo drinks collected in Makurdi, Gboko, Otukpo, Oju and Katsina-Ala respectively. Manganese was not detected in Makurdi sample of Zobo drinks. Lead was not at detectable range in Zobo samples collected in Makurdi, Gboko, Otukpo, Oju and Katsina-Ala towns of the State. Chromium was also not at detectable range in Otukpo, Oju and Katsina-Ala towns respectively. Also Nickel was not detected in Makurdi, Gboko and Otukpo towns. Among the detectable trace metals in the Zobo samples, Calcium had the highest concentration followed by Magnesium. The concentration of Calcium in Makurdi Zobo drinks was 29.25 mg L<sup>-1</sup>, Oju 39.50 mgL<sup>-1</sup>, and Katsina-Ala 40.00 mgL<sup>-1</sup>, followed by magnesium with metal concentration of zobo in Makurdi, Gboko, Otukpo, and katsina-Ala was 4.36 mgL<sup>-1</sup>, 5.11 mgL<sup>-1</sup> 4.61 mgL<sup>-1</sup> and 5.42mgL<sup>-1</sup> respectively. The least concentrated trace metal was Chromium (0.08 mgL<sup>-1</sup>) for the Zobo samples collected in the five sampling sites of the State. The highest variability was found in Lead(170 %) while the least was manganese (7.61%). The order of abundance was as follow: Ca>K>Mg>Na>Fe>Zn>Mn>Pb>Cr>Ni.

Comparison of the average levels of trace metals in Burukutu, Kunu and Zobo collected in the sampling

sites of the state is displayed in Tab 4. Calcium has the highest concentration in all the popular local drinks ranging from 25.28mgL<sup>-1</sup> in 34.01mgL<sup>-1</sup> in Kunu and 36.64mgL<sup>-1</sup> in Zobo followed by Magnesium ranging from 4.77mgL<sup>-1</sup> and 4.86 mgL<sup>-1</sup> in Kunu and Zobo drinks respectively. It is a well known fact that mineral elements are necessary for life [7]. Calcium leads to be a kind of coordination among inorganic element, if excessive amount of potassium, Magnesium or Sodium are present in the body. Calcium is capable of assuming a corrective role [8]. Calcium plays an important role in blood clotting, in muscles contraction and in certain enzymes in metabolic processes. Magnesium functions as an essential constituent for bone structure of reproduction and for normal functioning of the nervous system. It is also a part of the enzymes system [9]. The Calcium and Magnesium content of the local drinks fall within the WHO recommended range and could be said to be desirable for drinking without adverse effect. Potassium concentrated values ranged from 6.82 mgL<sup>-1</sup> in Kunu and 66 mgL<sup>-1</sup> in Zobodrinks. While the Sodium varied from 3.66mgL<sup>-1</sup> and 4.74 mgL<sup>-1</sup> in Kunu and Zobo respectively. Potassium is primarily an intracellular cation found mostly bound to protein in the body along with Sodium where they influence osmotic pressure and contribute to normal pH equilibrium [8]. The sodium content in water is important for health reasons, except when combined with excessively high concentrations of sulphate such combination can lead to gastro-intestinal initiation for persons placed on low sodium diet as a result of heart, kidney or circulatory ailment or complications pregnancy. The usual Na diet allowed in local drinks is 20 mgL<sup>-1</sup> [10]. The values recorded for both K and Na in the present study fall within the WHO limits. The average concentration of Nickel was 0.01 mg L<sup>-1</sup> in all the three local drinks in the sampling sites of the State. These values fall within the WHO limit. From these results prolonged intake of these drinks can cause decreased body weight, heart and liver damage and skin irritation. Even though a small amounts of Nickel are needed by human body to produce red blood cells [11].

The average concentration of Chromium was below the WHO standard of 0.05mgL<sup>-1</sup> in the local beverage drinks under study. Chromium toxicity is very dependent on the species and oxidation states present. It is normally found in the considerably less toxic trivalent state in foods and is poorly absorbed in the gastrointestinal tract. Chromium has been reported to have beneficial effects on type 11 diabetes [2]. However, the hexavalent form is carcinogenic. It has been estimated that human requires nearly 1 ugcr/day.

The average concentration of Lead in this study was above the WHO recommended standard of 0.01 mgL<sup>-1</sup> in the three local beverage drinks. The high content of Lead in the three samples could be the water source or the production materials. Lead is a well known toxicant that

has several deleterious effects even at minute concentration and has no known function in biochemical processes [12]. An onset of lead pollution of surface water has been reported [13, 14]. The source, being the use of Lead gasoline [15]. Lead is commonly known to inhibit active transport mechanism involving ATP to depress the activity of the enzyme cholinesterase, to suppress cellular oxidation-reduction reaction and to inhibit protein synthesis [16]. Prolonged consumption of Lead may also increase red cell fragility and kidney tubular cells and may become necrotic, while chronic exposure may lead to intestinal nephritis. Prolong consumption of Lead may result to impairment of the hearing process.

The average concentration of Mn in the local beverage drinks were below the WHO permissible limits of 0.4 mgL<sup>-1</sup>. Mn is an essential element and one of moderate toxicities. Mn has been implicated in neurological problems, especially when inhaled [17].

The average concentration of Fe in the present study is above the WHO recommended limit of 0.3 mgL<sup>-1</sup>

in Kunu drink. The high metal content of Fe in Kunu could be from cooking utensil where high temperature was applied during the production process. This is not acceptable to the consumers, as it could give rise to iron dependent bacteria which in turn cause further deterioration in the quality of local drinks by prohibition of slimes, or objectionable colour [18]. The results obtained may be due to run-offs and geological formations of the water samples and metal instrument used in the preparation processes while in Zobo drinks, the mean concentration of metal was below the WHO permissible limit of 0.3 mgL<sup>-1</sup> for beverage drinks. The mean concentration of Zn was found to be below the WHO limit for local drinks standard of 3.0mgL<sup>-1</sup> in all the three popular local drinks in this study. Copper was not detected in Kunu but the mean concentration of Cu in Zobo was below or fall within WHO recommended range of 2.0 mgL<sup>-1</sup> for local beverage drinks without adverse effect.

**Table 1. Metal Concentrations(mgL<sup>-1</sup>) in Kunu Drink Samples from Benue State, Nigeria**

Metal	MKK	GBK	OTK	OJK	KAK	Mean	SD	CV %
Cu	BDL	BDL	BDL	BDL	BDL	NA	NA	NA
Zn	0.53	0.45	0.68	0.55	0.57	0.56	0.08	13.57
Fe	0.78	3.05	0.43	0.35	0.28	0.98	1.05	107.14
Mn	0.05	0.06	0.02	0.06	0.07	0.05	0.02	32.00
Pb	0.13	BDL	0.13	0.13	ND	0.08	0.06	77.50
Cr	BDL	BDL	BDL	BDL	0.08	0.02	0.03	170
Ni	BDL	0.03	BDL	BDL	BDL	0.01	0.01	110
Ca	34.29	35.12	27.06	36.57	36.52	34.01	3.34	9.82
Mg	4.11	4.00	5.47	4.11	5.36	4.77	0.59	12.37
Na	3.70	3.20	5.10	3.40	3.20	3.66	0.75	20.49
K	4.30	7.80	6.10	7.80	8.10	6.82	1.44	21.11

MKK=MakurdiKunu; GBK= GbokoKunu ;OTK= OtukpoKunu;OJK= OjuKunu;KAK= Katsina –AlaKunu; BDL= Below Detection Level ; NA= Not Applicable; SD= Standard Deviation; CV % =Coefficient of Variation Percent

**Table 2. Metal concentrations(mgL<sup>-1</sup>) in Zobo Drink Samples from Benue State, Nigeria**

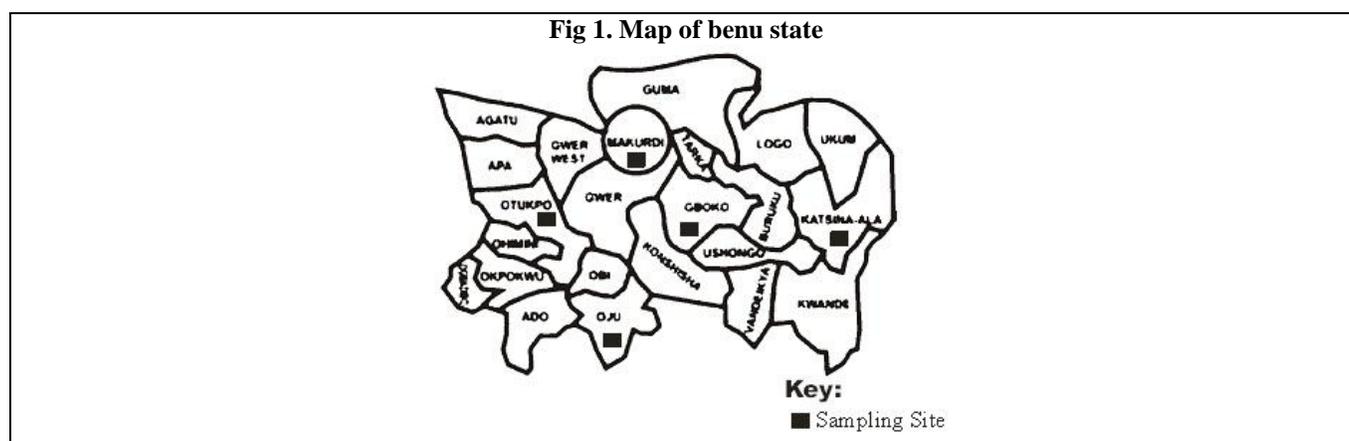
Metal	MKZ	GBZ	OTZ	OJZ	KAZ	Mean	SD	CV %
Cu	0.03	BDL	BDL	BDL	BDL	0.01	0.01	110
Zn	0.62	0.45	0.45	0.33	0.46	0.47	0.09	20
Fe	0.28	0.07	0.07	0.28	0.21	0.18	0.18	52.78
Mn	ND	0.13	0.06	0.14	0.47	0.16	0.16	101.25
Pb	BDL	0.13	BDL	BDL	BDL	0.03	0.05	170
Cr	0.17	0.08	BDL	BDL	BDL	0.05	0.07	136
Ni	BDL	BDL	BDL	0.03	0.03	0.01	0.01	120
Ca	29.25	39.15	35.30	39.50	40.00	36.64	4.05	11.05
Mg	4.36	5.11	4.61	5.42	4.80	4.86	0.37	7.61
Na	4.50	4.30	4.20	5.90	4.80	4.74	0.62	13.10
K	5.90	7.20	7.80	3.90	13.50	7.66	3.21	41.91

MKZ=MakurdiZobo; GBZ= GbokoZobo;OTZ= OtukpoZobo;OJZ= OjuZobo;KAZ= Katsina –AlaZobo ; BDL= Below Detection Level ; NA= Not Applicable; SD= Standard Deviation; CV % =Coefficient of Variation Percent

**Table 3. Levels of metals concentration(mgL<sup>-1</sup>) in Kunu and Zobo compared with WHO Standard**

Mineral	Kunu	Zobo	WHO value,2011
Cu	NA	0.01	2.0
Zn	0.56	0.47	3.0
Fe	0.98	0.18	0.3
Mn	0.05	0.16	0.4
Pb	0.08	0.03	0.01
Cr	0.02	0.05	0.05
Ni	0.01	0.01	0.02
Ca	34.01	36.64	75
Mg	4.77	4.86	50
Na	3.66	4.74	200
K	6.82	7.66	65

NA= Not Applicable; WHO- World Health Organization.



**CONCLUSION**

The study has presented metal concentration (Cu, Zn, Fe, Mn, Pb, Cr, Ni, Ca, Mg, Na and K) in Kunu and Zobo drinks popularly consumed in Benue State, Nigeria. The average concentrations level of Pb in the drink samples were above the WHO recommended guideline values for beverages drinks. Iron content was also found to be higher than WHO recommended guideline values for beverages drinks. The reason for higher lead levels is as a result of the source of water and iron levels in Kunu drinks is attributed to the use of rusting metal drums and vessels in processing of the Kunudrink, unlike Zobo

drink which does not require the same processing method. Therefore, consumers should be careful of the environments where these drinks are prepared as well as the vessels used.

**ACKNOWLEDGEMENT**

None

**CONFLICT OF INTEREST**

The authors declare that they have no conflicts of interest.

**REFERENCES**

1. Iwegbue CMA. Composition and daily intake of some trace metals from canned beer in Nigeria. *J.inst Brew*, 116, 2010, 312-315.
2. Budinoyal TK, Gergora KM, Metrov HV and Minka VN. Removal of metal ions from aqueous solution by activated carbon obtained from different raw material. *J. of chem. Tech. and Biotech*, 1994, 179-180.
3. Oluwataniwa, A. heathycase.blogspot.com.
4. Underwood EJ. Trace element toxicant occurring in foods, National Academy of Science, Washington, 1973, 43-47.
5. Ajaero C. A Brand New Image For Benue, Newswatch magazine, 2007.
6. Aremu M, Atolaiye BO, Gav BL, Opaluwa OD, Sangari DU and Madu PC. metal concentrations in sediments and water from Rivers Doma, Farinruwa and Mada in Nasarawa State, Nigeria. *Journal of Environmental Chemistry and Ecotoxicology*, 3(9), 2011, 242-249.

7. Aremu MO, Olanisakin A. Assessment of heavy metal content in some selected agricultural products planted along some roads in Nasarawa State, Nigeria. *Journal of Engineering and Applied sciences*, 1(3), 2006, 197-204.
8. Fleck H. Introduction to Nutrition 3<sup>rd</sup> Edition. Macmillan publishing Co. Inc. New York, 1976, 207-219.
9. Shills MEG and Young VR. Modern Nutrition in health and disease. Lea and Febiger, Philadelphia, USA, 1988, 276-282.
10. Ademoroti CMA. Environmental Chemistry and Toxicology. Foludex press Ltd ; Ibadan, Nigeria, 1996, 20-30.
11. [http:// www.lenntech.com/heavy-metals.htm](http://www.lenntech.com/heavy-metals.htm)
12. Crossby NT. Determination of metals in food. *A review. Analyst*, 102, 1997, 225-268.
13. Mombershora CO, Osibanjo O and Ajayi SO. Pollution studies on Nigeria Rivers; the onset of Lead pollution of surface waters in Ibadan. *Environment. International*, 9, 1983, 81-84.
14. Okoye BCO. Heavy metal and organisms in the Lagos Lagoons. *International journal of Environmental studies*, 37, 1991, 285-292.
15. Osibanjo O and Ajayi SO. Trace metal levels in the trace barks as an indication of pollution. *Environment, International*, 4, 1980, 236-244.
16. Waldren HA and Stofen D. Sub-clinical Lead poisoning, Academic press, New York, 1974, 84.
17. Fell GS. Lead toxicity problems of definition and laboratory evaluation. *Annual Clinical Biochemistry*, 21, 1984, 453-460.
18. Okedi C and Oni OO. Basic water Treatment Operation. Edited by outreach department, Published by National Water Resources Institute, Kaduna, 1997, 1-90.