Determination of Trace and Major Elements in Palm wine from Industrial and Non-industrial Areas of Enugu State Nigeria

Ape David I.[1], John Nnenna S.[2], Nwafor Emmanuel C.[3], and Ekpe Ikedichi O.[4]

[1-4]Materials and Energy Technology Department, Projects Development Institute (PRODA), Emene, Enugu State, Nigeria

[1]apedavid4u@yahoo.com

Abstract– **The objective of this research is to investigate the degree of contamination of toxic elements in industrial areas comparatively to non-industrial areas with special interest to lead (Pb) and cadmium (Cd) which are hazardous to human health. The concentration of some heavy metals (K, Mg, Ca, Na, Fe, Zn, Mn, Cu, Cr, Co, Cd, Ni, and Pb) in palm wines obtained from two non- industrial sites (NIDS) and two industrial sites (IDS) in Enugu state Nigeria was determined using Atomic Absorption Spectrophotometer (AAS). The result showed the concentration of the metals from NIDS and IDS as follows: NIDS 1 and 2; Cr (0.01ppm, 0.03ppm), Cu (0.13ppm, 0.15ppm), Cd (ND), Fe (1.99ppm, 2.95ppm), Mn (0.21ppm, 0.17ppm), Ni (0.02ppm, ND), Pb (ND), Zn (0.89ppm, 0.24ppm), K (1.25ppm, 1.45ppm), Co (0.02ppm, 0.03ppm) Mg (0.97ppm, 0.79ppm), Ca (0.42ppm, 0.35ppm), Na (1.02ppm, 0.87ppm), while that of IDS 1 and 2; Cr (0.24ppm, 0.26ppm), Cu (0.45ppm, 0.36ppm) Cd (ND) Fe (2.98ppm, 2.75ppm), Mn (0.5ppm, 0.6ppm), Ni (0.02ppm, 0.01ppm), Pb (0.002ppm, ND), Zn (0.3ppm, 0.41ppm), K (2.05ppm, 1.99ppm), Co (0.04ppm, 0.02ppm), Mg (1.05ppm, 0.96ppm) Ca (0.93ppm) Na (1.62ppm, 1.53ppm). Comparison of the concentration of these heavy metals in the palm wine with those of the international/national standards of heavy metals for food, vegetables, cereals and drinking water shows that all metal were within allowable limit. Though Zn showed a little variation as it was higher in concentration in the NIDS 2 as compare to the IDS 1&2 even in NIDS 1, this variation however did not affect the standards for consumption since it is still within the permissible limit. This shows that the palm wine obtained from both non-industrial sites and industrial sites from oil palm trees is suitable for consumption.**

Keywords– **Palm Wine, Heavy Metals, Industrial and Trace Elements**

I. INTRODUCTION

The term wine describes an alcoholic beverage that contains product of fermentation of the juice either from sap or grape [1]. Wines naturally contains about 85-89% water, 10-14% alcohol. Wine character its taste and smell is derived from many factors including the sap or grape it's made from and the geographical areas they are grown.

Wine is one of the common alcoholic beverages consumed in all over the world [2]. In West Africa palm wine is a popular traditional beverage consumed by more than ten million people [3]. It is a sweet effervescent drink obtain from the sap of an oil palm tree, Elaeis guineense and raphia hookeri. The drink is a rich nutrient medium containing sugar, protein, amino acids, alcohol and minerals [4], it also contain dense population of yeast [5] though when it is allowed to stand for a long time, fermentation converts the sugar to alcohol and subsequently acetic acid leading to loss of sweetness, shortage of shelf life and decreased acceptability [6].

In Nigeria the eastern states have a dense oil palm tree plantation and are known for tapping palm wine in large amount or quantity of palm wine which they use for commercial purposes and consumption of this natural nutritive alcoholic beverage which Enugu state the research area is not left out.

Enugu state covers a landmark of 7,660.2 square kilometres with latitude $6^0$30' north and longitude $7^0$30' east. With respect to 2006 census figure, Enugu state population is 3,267,837 with density of 262 people per kilometre and Enugu state account for 2.3% of Nigerian population. Of this population 80% of the populace consume palm wine [7].This beverage drink is presented as a cultural rite as it is served at every important occasion held at every location of the research state, In events like wedding ceremonies, birthday celebrations, child dedications, village meetings just but to mention a few.

The content of metals in palm wine can be attributed to the natural sources, the atmospheric deposition of airborne particulate matter on palm trees and transfer of metals from the soil through roots to the palm trees and finally to the palm wine [8]. Metals of primary natural origin comes from soil on which the oil palm tree is grown and reach the sap (wine) through roots and stems.

The concentration of primary metals is characteristic and comprises of the largest part of the total content in wine, it is connected with the maturity of oil palm tree, their variety, the type of soil in the plantation and the climatic conditions during growth. The contribution of metals of secondary origin is associated with external impurities that reach sap (wine) during growth of oil palm trees. During the growth of oil palm trees in a plantation, contaminations can be classified as geogenic (originating in the soil) from protection and growing practices, or from environmental pollution [9]. Differences in Cu, K, Ca, content can be due to fertilizers used for cultivation [11]. Application of fertilizers, rodenticides, fungicides, and pesticides containing Cd, Cu, Mn, Pd and Zn compounds during growing season of plantation leads to increase in the amount of these metals in wine [12]. Wine from plantations that are found close to the road traffic or located in industrial areas might contains higher levels of Cd and Pb because vehicles exhaust fumes or other emissions to air, water and soil [12].

Taking of palm wine in a moderate quantity daily contribute significantly to the requirements of the human organism for essential element such as K, Ca, Mg, Cr, Co, Fe, F, I, Cu, Mn, N, Se, and Zn. More so several metals such as Pb, Cd and As are known to be potentially toxic at the same time the analyses for certain elements in palm wine is of special interest due to their toxicity in case of excessive intake and also the effect they seems to have on organoleptic properties of wine [9,11]. A typical example is Cu, which is both an essential and a potential toxic for humans. When in excess, several elements including Cu, Fe, Al, and Zn contribute to haze formation and sometimes taste effects. Determination of other elements such as Pb, As, and Cd is of considerable importance due to their potential toxic effect. Furthermore the content of some metals can be used to identify geographical region in which the oil palm trees are grown due to direct relationship with soil composition [4].

Metallic composition of palm wine depend on many factors which might include specific production area, soil and climate due to their influence of all these factors, a great variability in the metal content in palm wines from different areas, regions, and countries is observed. Determination of typical levels of metals in palm wines is a very useful tool to differentiate palm wines from different geographical regions as well as to detect falsification and adulteration of palm wines [13].

The study investigates the levels of major and trace elements (K, Mg, Ca, Na, Fe, Zn, Mn, Cu, Cr, Co, Cd, Ni, and Pb) in palm wines from industrial (IDS) and non-industrial regions (NIDS) of Enugu state, Nigeria. It also compares the level of elements among the regions (industrial and non-industrial).

II. MATERIALS AND METHODS

A) Reagents and Chemicals

Nitric acid (HNO_3) 69-72% and hydrogen peroxide H_2O_2 30% were used for the digestion of the wine samples. Lanthanum nitrate hydrate 99% was used for molecule suppressor (to release calcium and magnesium from their common phosphates). A stock standard solution containing 1000mg/l in 2% HNO_3 of the metal (K, Mg, Ca, Na, Fe, Zn, Mn, Cu, Cr, Co, Cd, Ni, and Pb). Buck scientific puro-Graphic was used for the preparation of calibration standards.

B) Sampling

In this study four litres of palm wine were collected from two non-industrial areas and two industrial sites. Non-industrial site 1 (NIDS 1) Akegbe-ugwu village in Nkanu west local government, non-industrial site 2 (NIDS 2) Nkpologwu village in Enugu east local government. Industrial site 1 (IDS 1) Ngwo nineth mile in Udi local government, Industrial site 2 (IDS 2) Emene industrial area in Enugu east local government area(s) of Enugu state, Nigeria. One liter each from different oil palm trees at random at the study sites. The samples were refrigerated until the time of the analyses.

C) Digestion of palm wine samples

From the bulk samples collected, 10ml samples of wine were wet ash (digested) to decompose the organic substances and make clear solution in triplicate according to HNO_3 /H_2O_2 procedure described by Lazos and Alexakis [14] and Sanllorente et al. [15]. The digestion was achieved with the following put into cognizance.

- The digestion time
- The maximum temperature required
- The amount of HNO_3 and H_2O_2 added to the sample
- The clearness and colour of the digested sample

A 10ml aliquot of the bulk sample was taken and quantitatively transferred to a 250ml digestion flask. To the flask a freshly prepared 7ml HNO_3/H_2O_2 mixture in the ratio of 2:5 was added. The flask was shaken slightly to mix the mixture, the flask with the acid-sample mixture was then placed on a heating mantle, the temperature was first set at 60^0C and slightly increased to 180^oC, the heating continued for one hour (1hr) until the solution became clear and colourless. The flask with the digest was removed from the heating mantle and was left to cool in a desiccators for ten minutes (10min). The cool digest was transferred quantitatively to a 50ml volumetric flask and diluted to the volume with distilled deionized water; the digest was kept in a refrigerator until the time of analyses by atomic absorption spectrophotometer (AAS).

D) Instrumentation

A refrigerator (DEBO Superluxe, Italy) was used to keep the palm wine sample cool until the analysis. 250ml round bottomed flask fitted with reflux condenser were used. A heating mantle 1000ml (Techmel and Techmel, USA), a desiccator (24/29 Pyrex, England) size 150 was used to cool the sample after digestion. Bulk scientific model 210 VGP [East Norwalk, USA] atomic absorption spectrophotometer was used to analyze the analyte metals [K, Mg, Ca, Na, Fe, Zn, Mn, Cu, Cr, Co, Cd, Ni, and Pb].

Table 1: Heavy metal concentration in the palm wines

Heavy metals	**Concentration (ppm)**			
	NIDS-1	**NIDS-2**	**IDS-1**	**IDS-2**
Na	0.87	1.02	1.62	1.53
Fe	2.95	1.99	2.98	2.75
K	1.45	1.25	2.05	1.99
Ca	0.35	0.42	0.93	0.90
Mg	0.79	0.97	1.05	0.96
Cu	0.15	0.13	0.45	0.36
Mn	0.17	0.21	0.5	0.60
Zn	0.24	0.89	0.3	0.41
Co	0.03	0.02	0.04	0.02
Pb	Nil	Nil	0.002	Nil
Ni	Nil	0.02	0.02	0.01
Cr	0.12	0.03	0.24	0.26

III. RESULTS AND DISCUSSION

The increasing global pollution of the environment requires a systematic monitoring of all kinds of food including wines. Daily consumption of wine in a moderate quantity contributes significantly to the requirement of human for essential elements. The results of the analyses are summarized in Table 1.

From Figure 1, the metal concentrations of Na, Fe, and K obtain from the analyses of palm wine from oil palm trees from industrial areas(IDS) is slightly higher than the concentrations of those obtained from oil palm trees in the non- industrial areas(NIDS) with the ranges of Na, 0.87-1.53ppm, Fe, 0.99-2.98ppm, K, 1.25-205ppm. The analyses show that the concentration of both non-industrial and industrial palm wines falls within permissible limits by World Health Organization (WHO) [16].

Figure 2 shows the concentrations of Ca, Mg, and Cu, analysed from palm wine obtained from palm oil trees from four areas, two from non- industrial areas (NIDS) and two from industrial areas (IDS) of Enugu state Nigeria.Human beings need 1-3mg of copper (Cu) each day for normal body functioning. From Table 1, it can be seen that Cu concentration in both NIDS and IDS falls in the range of 0.13-0.45ppm. This is in accordance with the expert group on vitamins and minerals in green vegetables, poultry and cereals which is 0.84ppm, 0.73ppm, and 1.8ppm respectively. This shows that the concentration of Cu in both NIDS and IDS is within the permissive limits [17].In as much as the concentration of Cu is slightly higher in the IDS it could be because of industrial activities in the area. For Mg, the daily recommended allowance for Mg are 320 - 420mg per day [18], it has been studied that Mg deficiency directly reduce the cell formation, another study have it that it reduces osteoblast formation in bones [19]. The concentration of Mg in the analyses of palm wines gotten from oil palm trees from non- industrial sites (NIDS) and industrial sites (IDS) in Enugu state Nigeria gave the range of Mg to be 0.79 - 1.05ppm respectively, though the concentration is higher in the IDS it falls within the acceptable limit [17]. Calcium concentration in palm wine from NIDS1, NDIS2 and IDS1, IDS2 as shown in Figure 2 revealed the range of Ca to be 0.35- 0.93ppm with Ca concentration in the IDS higher than those in the NIDS. Calcium is known in the human nutrition for the development and growth of skeletion, for example bones, teeth and coenzymes in metabolic regulations of biomolecules. Most of the Ca is stored in the bones the remaining is utilized in the multiple functioning as in nerves excitation and muscle contraction (18). Though the concentration of Ca is higher in IDS it still falls within the permissible limit [17].

Figure 3 contain the concentrations of Mn, Zn, and Co analyzed from palm wine gotten from oil palm trees from two non- industrial areas (NIDS) and industrial areas (IDS) of Enugu state Nigeria. Manganese is one of the important essential elements requires in carbohydrate metabolism as well as an antioxidant in super oxide dismutase enzymes, it is required in little quantity and deficiency rarely occur. Mn toxicity is reported in liver diseases [21]. The reported daily intake limit of Mn is 2-5mg per day. From the Figure 3 the

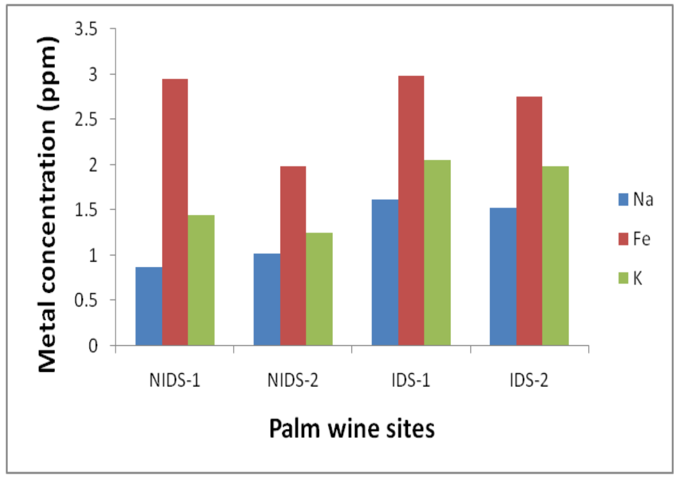

Fig. 1: concentration of sodium, iron and potassium in the palm wines

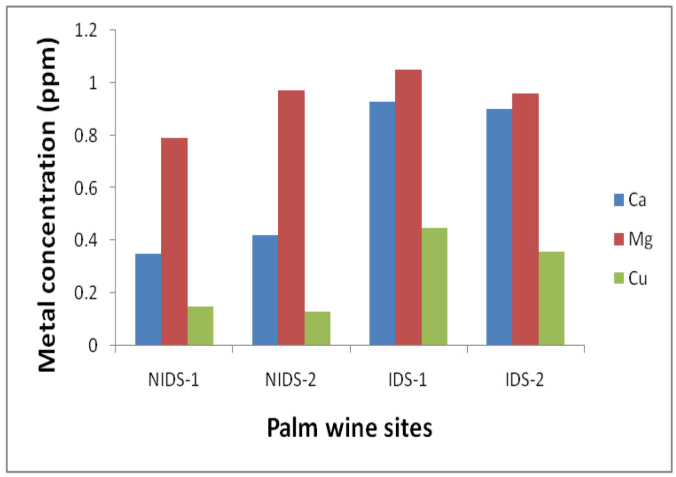

Fig. 2: concentration of calcium, magnesium and copper in the palm wines

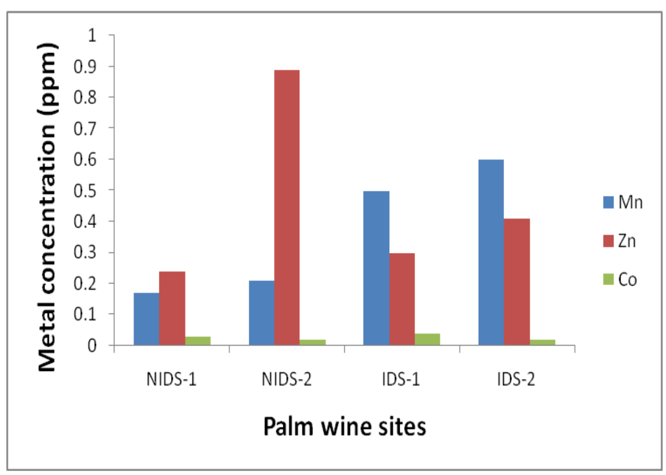

Fig. 3: concentration of manganese, zinc and cobalt in the palm wines

concentration of Mn from NIDS and IDS ranges from 0.17-0.6ppm. The concentration of Mn is higher in palm wines in IDS though still within the permissible limit of 0.6-18.33ppm

[17]. Zn is an essential trace metal involved in growth and DNA synthesis in human with normal intake of 7-16mg per day for adults. Zn is reported as a coenzyme for over 200 enzymes involved in immunity, new cell growth, acid base regulation etc. Lack of sufficient amount Zn results in reduced activity of related enzymes for example carbonic anhydrase [21], [22]. Zn is one of the less toxic metals and is essential for proper maintenance of body functioning for example, immune system, proper brain functioning and is vital for development of fatal growth, though higher uptake of Zn can lead to muscle cramps, digestive problems and kidney damage. From Figure3 it is seen that the concentration of Zn is of the range 0.24-0.89ppm. It can also be noticed that from the Figure 3, Zn appeared to be higher in NIDS2 than in all the IDS, while all the IDS appear to have higher concentration of Zn than NIDS1. Despite the conflicting result of Zn concentrations in palm wine in the study sites it still falls within the permissible limit recommended by international/national standards of heavy metals in vegetables, food and drinking water [17].

Therefore pose no threat to human health when consumed. This rise of Zn concentration in NIDS2 could be as a result of natural constituents of the soil and due to the variation of atmospheric condition, their plant uptake varies through roots to the sap [23].Cobalt is an indispensable element and is scattered in the atmosphere about 0.001%. it is found in bivalent and trivalent states. Vegetables and fruits contains 0.009mg/kg [24]. The daily recommended intake of Co in human diet is 0.005mg per day [24]. From the Figure 3 the range of Co analysed in palm wine collected from oil palm trees in the study areas NIDS 1&2 and IDS 1&2 is 0.02-0.04ppm. Co intake greater than 30mg per day (>30) can cause digestive and skin disorder in humans, the study on the dietary supplement for Co is still not clear as the insufficient data is reported [25].

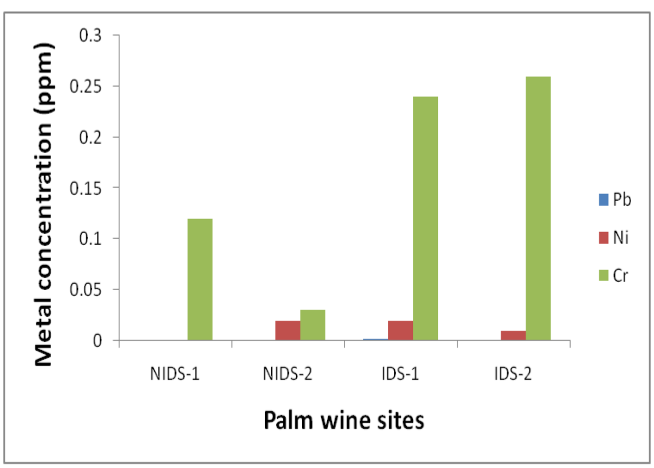

Fig. 4: concentration of lead, nickel and chromium in the palm wines

Figure 4 shows the concentrations of Pb, Ni, and Cr, analysed from palm wine obtained from oil palm trees from four areas, two from non- industrial areas (NIDS) and two from industrial areas (IDS) of Enugu state Nigeria. From the Figure, the analyses of palm wine collected from oil palm trees in NIDS 1&2 and IDS 1&2, the range of Pb is 0.00-0.002ppm. Pb is a highly toxic metal to man since it causes brain damage particularly to the young and induces aggressive behaviour [26]. The major ways of toxicity by Pb to man is caused through respiration/inhalation. From the Figure 4 it is show that the Pb concentration of palm wine is more in the palm wine obtained from oil palm trees in the IDS as compared to NIDS, of a fact the NIDS 1&2 recorded no detection limit (NDL) of Pb while IDS 1 gave Pb concentration of 0.002ppm and IDS 2 showed no detection limit. The value of Pb concentration falls within the range of international/national standards for heavy metals in all foods in solid and liquid forms which is 1-6ppm. [17], therefore it is considerate. Nickel according to Mckenzie and Symthe [27] more attention has been given to its toxicity in low concentration, this is because Ni can cause allergic reactions and Ni compounds may be carcinogenic.

The concentration in unpolluted drinks is given as 1.01-0.02ppm as recommended by international/national standards for heavy metals in vegetables, food and drinking water [17]. And therefore poses no threat in as much as is higher in the IDS. Ni plays its role as a coenzyme in different enzymes, lower contents of Ni can lead to increase in blood sugar level, hypertension and deficient growth in human but on the other hand the increase intake of Ni in drinks can reduce the blood glucose level, difficulty in breathing and nausea [28]. The acceptable intake of Ni daily is 3-7mg per day. Chromium from the analyses carried out on palm wines gotten from NIDS 1&2 and IDS 1&2 as seen in Figure 4 Cr has a range of 0.01-0.05ppm, having higher concentration in the IDS than in the NIDS, though when compared with standards of heavy metals which is 1.0ppm, it is found to be within the permissible limit for consumption [17]. Cadmium was noticed to be below detection limits for all the analyses carried out throughout the study sites with different palm wine obtained from different oil palm trees in non- industrial sites (NDIS 1&2) and industrial sites IDS (1&2). All the metals investigated in this study were within the standard permissible limit which is similar to that reported by other researchers [29], [30]. This indicates no harm in the consumption of these wines; however excessive intake must be avoided to prevent the bioaccumulation of these harmful metals in the body which might result in severe complications.

IV. CONCLUSION

The results of the analyses for the elements under investigation of trace and major elements in both non-industrial areas and industrial areas gave concentrations much lower than the international/national standards of heavy metals for food, vegetables, cereals and drinking water established permissible limits. From the analyses carried out and result obtained it is seen that cadmium (Cd) was below detection limit in all the palm wine tapped from the four oil palm trees in both non-industrial sites and industrial sites while lead (Pb) which was detected in one of the industrial sites with the concentration of 0.002ppm which is far less than the permissible limit of 1.0ppm for drinks as specified by international/national standards of heavy metals for food, vegetables, cereals and drinking water. The concentration of Pb obtained is 500 times less the permissible limit. From the analyses carried out it was found that the concentrations of major and trace metals in all palm wines fell within the permissible limits.The work therefore approve the consumption of palm wines tapped from oil palm trees of both non-industrial areas as well as industrial areas in Enugu, Nigeria.

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