



Trace Elemental Characterization of Selected Edible Vegetable Oils

Ichu Chigozie .B and Nwakanma Henry .O
Materials and Energy Technology Department,
Projects Development Institute (PRODA),
P.M.B. 01609, Enugu, Nigeria

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ABSTRACT

Trace element content of edible vegetable oils is a basic criterion in the assessment of the quality of the oils with regard to freshness, keeping properties, storage and their influence on human nutrition and health. They

are also known to have an effect on the rate of oil oxidation. In this study, the levels of 10 elements which include such essential metals as Ca, Mg, Na and K, trace elements such as Cu, Mn, Co and Ni and such toxic metals as Cd and Pb in 8 varieties of edible vegetable oils (palm, palm kernel (P.K.O), sesame, soya bean, coconut, ground nut, olive and mustard) collected in Enugu were determined using the direct solvent method and a Buck Model 210VGP atomic absorption spectrophotometer. The concentrations of Ca, Na, K, Mg, Cu, Co, Mn, Ni, Pb and Cd were observed in the range of 0.69 - 0.23, 1.57- 0.48, 2.90 - 1.28, 1.30 - 1.05, 0.60 - 0.00, 1.12 - 0.51, 0.80 - 0.44, 0.00 - 0.00, 3.07 - 0.00, and 0.77- 0.55 mg/kg respectively. Ni was not detected in all the samples. The values for Pb and Cu were higher than the maximum values recommended by FAO/WHO and EU.

Keywords: Trace elements, vegetable oils, Nigeria, direct solvent method.

1. INTRODUCTION

Edible oils like palm oil, ground nut oil and soya beans oil are major components of the Nigerian diet. The population of Nigeria is 150 million (Ottong, 2013), but as at July 2012, this figure was estimated to be at 170,123,740 (WFB, 2013). This increase in population is also driving the increased demand for these products. It is also expected that more of these oils will be consumed as quality of life improves and the attendant dietary changes are made. These oils, possibly the most widespread cooking ingredient in the world, are extracted from many sources. These include fruits (e.g. olive, coconut, palm, etc.), nuts (e.g. palm kernel, walnut, macadamia, almond, etc.), seeds (e.g. sesame and sunflower, etc.), and plants (e.g. soya bean, canola, chili, etc.). These oils are not only used in cooking (e.g. baking, frying, soup and stew making), but in non-cooking products as well (e.g. salad dressing and dips) (Masone, J. *et al.*, 2014). The content of metals and their species (chemical forms) in edible oils depends on several factors. The metals can be incorporated into the oil from the soil or be introduced during the production process. Hydrogenation of edible seed oils and fats has been performed using nickel catalysts. The presence of copper and iron can be caused by the processing equipment as well (Sarojam, P. 2009).

The quality of edible oils with regard to freshness, storability and toxicity can be evaluated by the determination of metals. Trace levels of metals like Fe, Cu, Ca, Mg, Co, Ni and Mn are known to increase the rate of oil oxidation while As, Cd, Cr, Se and others are known for their toxicities (Sarojam, P. 2009). Acute or chronic exposure to heavy metals can lead to damaged nervous system function and have detrimental effects on vital organs (Bass, D. and Bosnak, C.P. 2011). Due to its extensive human consumption, it is essential to monitor these oils to ensure safe, non-toxic, and regulatory-compliant products. This will help to avert what may eventually be a health crisis due to an accumulation of these contaminants in the human body. The aims of this work therefore are to assess the levels of some trace (Cu, Co, Mn, Ni), essential (Ca, Mg, K, Na) and toxic (Cd and Pb) elements in selected edible vegetable oils and to determine any health effect through consumption by comparing these levels in oils with regulatory maximum limits.

2. MATERIALS AND METHODS

2.1 Sample Collection

Popular brands of eight commonly available edible oils (palm, palm kernel, sesame, soya bean, coconut, ground nut, olive and mustard) were bought from retail markets in Enugu, Nigeria. These samples were kept in polyethylene bags and taken to the chemical analysis laboratory of Projects Development Institute (PRODA) Enugu. They were stored in a cool dry place prior to further analysis.

2.2 Sample Pre-treatment

The direct determination of trace metals in the oils was done by the direct solvent method (The Perkin Elmer Inc, 2006) by solubilizing the samples in an organic solvent 10g of each oil sample was carefully diluted with 30 g of acetone in polypropylene vials. These diluted solutions were directly aspirated into the atomic absorption spectrophotometer (AAS) Model 210VGP, Buck Scientific Incorporated USA. The results were determined in triplicates.

2.3 AAS Analysis

Analytical grade reagents and distilled water were used in preparing all solutions. Stock solutions containing 1000 mg/kg of the analytes were prepared from nitrate salts of Cd, Cu, Mn and Pb and chloride salts of Co, Ni, Ca, Mg, K and Na. Working standard solutions were prepared by appropriate dilutions of the stock solutions. Blank determinations were run by using the same reagents in equal quantities as described in the analysis procedure. The concentrations of the metals in each solubilized sample were determined with the Buck Model 210VGPAAS with an air-acetylene flame. Metal contents were calculated by comparison with the standard curves of the respective metals. Hollow cathode lamps having resonance lines at 228.9, 327.4, 279.5, 283.3 and 352.7 nm, were used as radiation sources for the determination of Cd, Cu, Mn, Pb and Co respectively. Others are 341.5, 422.7, 202.6, 703.0, and 589.0 nm, for Ni, Ca, Mg, K and Na respectively. Lamp intensity and band pass were used according to the manufacturer's recommendations. Acetylene and air flow rates were 5 and 20 L min⁻¹, respectively, for all the elements.

2.4 Statistical Analysis

Statistical analysis of data was treated using IBM-SPSS 20.0 statistical package program. Standard deviations for the oils were calculated and are based on measurements in triplicate. Tests for significance in variations were conducted using one-way analysis of variance (ANOVA) and One-Sample T test. Also, two-tailed correlation analyses of relationships among the metals were also conducted. All the variations were considered significant at $p < 0.05$.

3. RESULTS AND DISCUSSION

3.1. Elemental concentrations of the vegetable oils

The results obtained for all the samples were classified in the following tables for better comparison with each other. The data obtained from each determination are presented as mean \pm SD (standard deviation). The concentrations of the trace elements in eight groups of vegetable oils bought from retail markets are given in Tables 3.1, 3.2 and 3.3.

Table 3.1: Essential Metals (mg/kg)

S/N	Sample	Ca	Mg	Na	K
1	Groundnut Oil	0.57 \pm 0.32	1.27 \pm 1.10	1.57 \pm 0.30	2.90 \pm 0.51
2	Mustard Oil	0.69 \pm 0.30	1.30 \pm 1.13	0.98 \pm 0.19	2.82 \pm 0.93
3	Soya Oil	0.53 \pm 0.34	1.13 \pm 0.98	1.20 \pm 0.52	2.35 \pm 0.31
4	Coconut Oil	0.35 \pm 0.29	1.10 \pm 0.95	0.76 \pm 0.48	1.93 \pm 1.10
5	Palm Kernel Oil	0.41 \pm 0.28	1.19 \pm 1.03	1.19 \pm 0.65	2.32 \pm 0.56
6	Olive Oil	0.37 \pm 0.32	1.09 \pm 0.94	0.81 \pm 0.63	1.99 \pm 1.23
7	Sesame Oil	0.40 \pm 0.33	1.15 \pm 0.99	0.90 \pm 0.41	2.16 \pm 1.05
8	Palm Oil	0.23 \pm 0.20	1.05 \pm 0.91	0.48 \pm 0.42	1.28 \pm 1.11

The concentrations of Ca, Na, K, Mg, Cu, Co, Mn and Ni (mg/kg) were observed in the range of 0.69 - 0.23, 1.57- 0.48, 2.90 - 1.28, 1.30 - 1.05, 0.60 - 0.00, 1.12 - 0.51, 0.80 - 0.44, 0.00 - 0.00 respectively. Pb and Cd were observed in the range of 3.07 - 0.00, and 0.77- 0.55. In this study, the highest metal concentrations were found in mustard oil for Pb (3.07 mg/kg), groundnut oil for K (2.90 mg/kg) and Na (1.57 mg/kg), mustard oil for Mg (1.57 mg/kg), groundnut oil for Co (1.12 mg/kg), mustard oil for Mn (0.80 mg/kg), mustard for Cd (0.77 mg/kg) and Cu (0.77 mg/kg).

Table 3.2: Trace Metals (mg/kg)

S/N	Sample	Cu	Mn	Ni	Co
1	Groundnut Oil	0.60 \pm 0.53	0.71 \pm 0.62	0.00 \pm 0.00	1.12 \pm 0.97

2	Mustard Oil	0.77±0.68	0.80±0.69	0.00±0.00	0.94±0.81
3	Soya Oil	0.27±0.25	0.58±0.46	0.00±0.00	0.82±0.71
4	Coconut Oil	0.00±0.00	0.44±0.38	0.00±0.00	0.80±0.69
5	Palm Kernel Oil	0.53±0.46	0.68±0.50	0.00±0.00	0.99±0.86
6	Olive Oil	0.23±0.21	0.50±0.43	0.00±0.00	0.79±0.69
7	Sesame Oil	0.17±0.15	0.50±0.38	0.00±0.00	0.84±0.73
8	Palm Oil	0.00±0.00	0.45±0.39	0.00±0.00	0.51±0.44

Palm oil contains lower amounts of Cu (0.00 mg/kg), Co (0.51 mg/kg), Mg (1.05 mg/kg), K (1.28 mg/kg), Na (0.48 mg/kg) and Ca (0.23 mg/kg) compared to the other vegetable oils. Among all the determined metals, K was found to be the dominant elemental ion followed by Pb and Mg. It is important to note that no trace of Ni was found in the oils.

Table 3.3: Toxic Metals (mg/kg)

S/N	Sample	Cd	Pb
1	Groundnut Oil	0.61±0.53	2.73±1.31
2	Mustard Oil	0.77±0.67	3.07±0.80
3	Soya Oil	0.63±0.55	1.50±2.60
4	Coconut Oil	0.70±0.31	0.37±0.64
5	Palm Kernel Oil	0.55±0.48	1.67±2.12
6	Olive Oil	0.65±0.28	0.00±0.00
7	Sesame Oil	0.60±0.50	0.00±0.00
8	Palm Oil	0.75±0.16	0.57±0.98

3.2. Discussions and Relationship between metals

a) Mg

The highest value of this macro-element at (1.30±1.13) mg/kg, in mustard oil is not significantly ($p>0.05$) higher than its value in groundnut oil (1.27±1.10) mg/kg. There was also no significant variation ($p>0.05$) in its levels across the oil types. Its lowest value was detected in palm oil (1.05±0.91) mg/kg. This metal shows a high positive correlation with the other metals except Na and Cd.

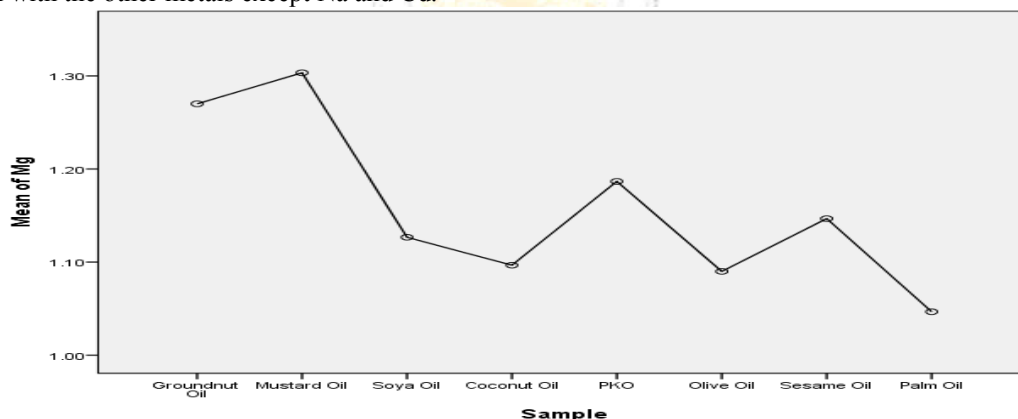


Figure 3.1: Mg in edible oils

The importance of Mg has been revealed in its function in the skeleton as well as in muscles and soft tissues, such as a co-factor of many enzymes involved in energy metabolism, protein synthesis, RNA and DNA synthesis, and maintenance of the electrical potential of nerve tissues and cell membranes (Mir-Marqués, *et al.*, 2012). However, dietary deficiency of Mg which is sufficient to induce pathologic changes is rare (FAO/WHO, 2002). This range of values is lower than those obtained by other studies: (Farzin, *et al.*, 2014) (Nnorom, *et al.*, 2014). It is however the same with the range of values obtained by Umar (2004). The plot of Mg in the oils is shown in figure 3.1.

b) Ca

The variation of this metal content in mustard oil (0.69±0.30) mg/kg was more significant ($p<0.05$) than other metals. However, no significant difference ($p>0.05$) exist in its value in the other metals. Palm oil at (0.23±0.20) mg/kg is its lowest value. In groundnut oil, its value was (0.57±0.32) mg/kg, soya oil (0.53±0.34) mg/kg, coconut oil (0.35±0.29) mg/kg, palm kernel oil (0.41±0.28) mg/kg, olive oil and sesame oil (0.37±0.32) mg/kg and (0.40±0.33) mg/kg respectively. This metal shows a positive correlation with all the metals except Na and Cd. Ca plays essential role in neuromuscular function, many enzyme-mediated processes, blood clotting, and providing rigidity to the skeleton via phosphate salts (Mir-Marqués, *et al.*, 2012). These values are however far lower than those obtained by Nnorom, *et al.*, (2014), Farzin, *et al.*, (2014) and (Umar, 2004). The plot of Ca in the oils is shown in Figure 2.

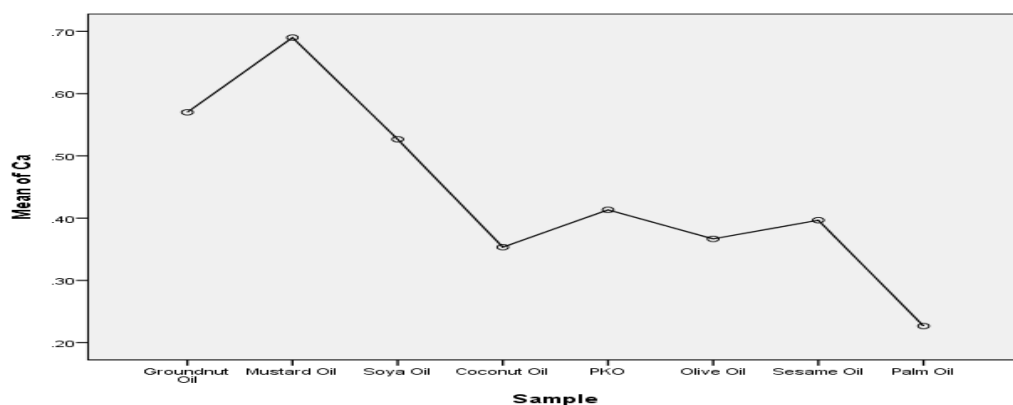


Figure 2: Ca in edible oils

c) K

Traces of this useful essential mineral were detected in all the edible oils assessed. The highest value of (2.90±0.51) mg/kg was detected in groundnut oil while the lowest value of (1.28±1.11 mg/kg) was detected in palm oil. The variations observed in groundnut oil (2.90±0.51) mg/kg, mustard oil (2.82±0.93) mg/kg, soya oil (2.35±0.31) mg/kg, and palm kernel oil (2.32±0.56) mg/kg are significant ($p < 0.05$). These variations are however not significant ($p > 0.05$) in coconut oil (1.93±1.10) mg/kg, olive oil (1.99±1.23) mg/kg, sesame oil (2.16±1.05) mg/kg and palm oil (1.28±1.11) mg/kg. This range of values are lower than those obtained by (Nnorom *et al.*, 2014), but are similar to those obtained by (Cindric, *et al.*, 2007; Mendil, *et al.*, 2009; Zeiner, *et al.*, 2005). K has been described as being vital for disease prevention and control; it is an essential electrolyte for maintaining normal fluid balance in cells and a delicate balance of this element is reported to prevent an increase in blood pressure and maintain normal cardiac rhythm (Desideri, *et al.* 2012). This metal showed positive correlations with other metals except Cd. The plot is shown in figure 3.

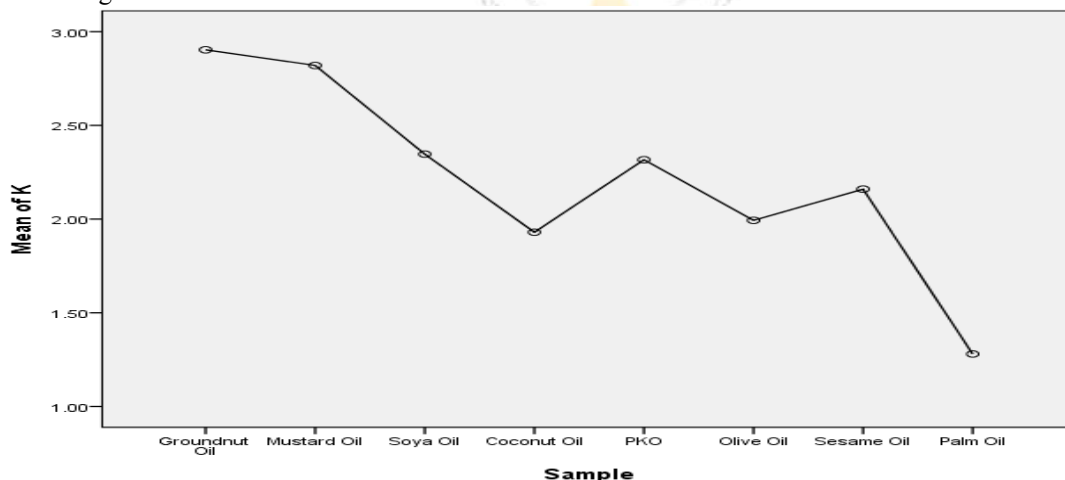


Figure 3: K in edible oils

Na

The range of this metal is (1.57±0.30) mg/kg in groundnut oil and (0.48±0.42) mg/kg in palm oil. The variations observed its concentration in groundnut oil (1.57±0.30) mg/kg and mustard oil (0.98±0.19) significant ($p < 0.05$). The variations however are not significant ($p > 0.05$) in soya oil (1.20±0.52) mg/kg, coconut oil (0.76±0.48) mg/kg, palm kernel oil (1.19±0.65) mg/kg, olive oil (0.81±0.63) mg/kg, sesame oil (0.90±0.41) mg/kg, and palm oil (0.48±0.42) mg/kg. These values are lower than those obtained by Umar, (2004); Cindric, *et al.*, (2007); Mendil, *et al.*, (2009); Zeiner, *et al.*, (2005) and Nnorom, *et al.*, (2014). Na is necessary to maintain balance in physical fluid systems and is also required for the operation of nerves and muscles, but high-sodium diets are linked to a number of health problems including damage of the kidneys and increase in the possibilities of hypertension (Mir-Marqués, *et al.*, 2012). No correlations exist between this metal and other metals except for positive correlations with K and Co. The plot is shown in figure 4.

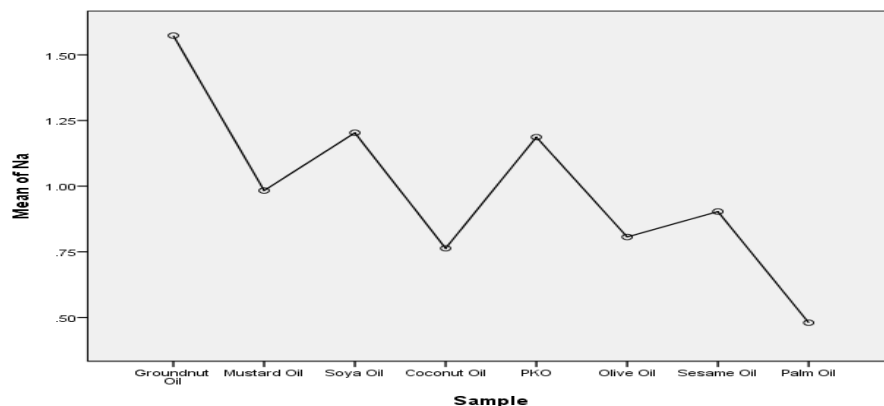


Figure4: Na in edible oils

Mn

The highest value of (0.80±0.69) mg/kg was detected in mustard oil while the lowest value of (0.44±0.38) was detected in coconut oil. There exists no significant difference ($p>0.05$) in the variation of its concentration in these edible oils. These values however are in agreement with the values obtained by Pehlivan, *et al.*, (2008); Lorent-Martinez, *et al.*, (2011) and Umar (2004). A study identified that the deficiency of Mn can result in severe skeletal and reproductive abnormalities in mammals while high doses of manganese produce adverse effects primarily on the lungs and on the brain (Zhu, *et al* 2011) . Mn has positive correlations with all the metals except Na and Cd. Its plot in the oils is represented in figure 5.

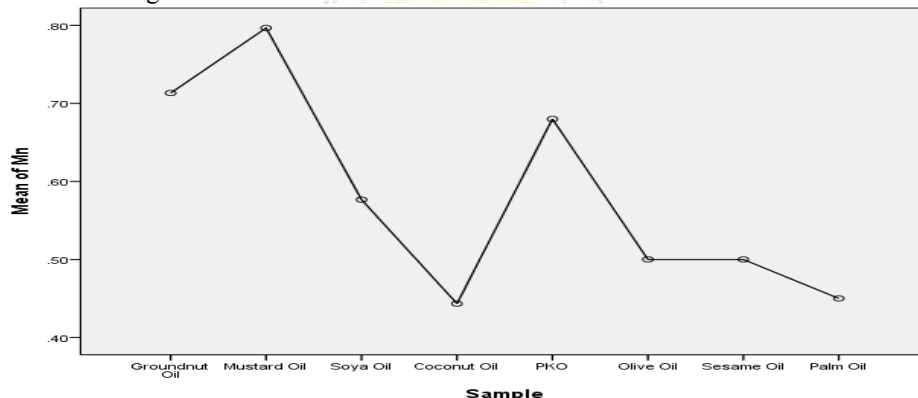


Figure 5: Mn in edible oils

Cu

The level of this trace metal is highest in mustard oil (0.77±0.68) mg/kg and lowest in both coconut and palm oils at (0.00±0.00) respectively. There exists no significant difference ($p>0.05$) in these observed variations which further shows that the oil type does not affect the change in the metal concentration.

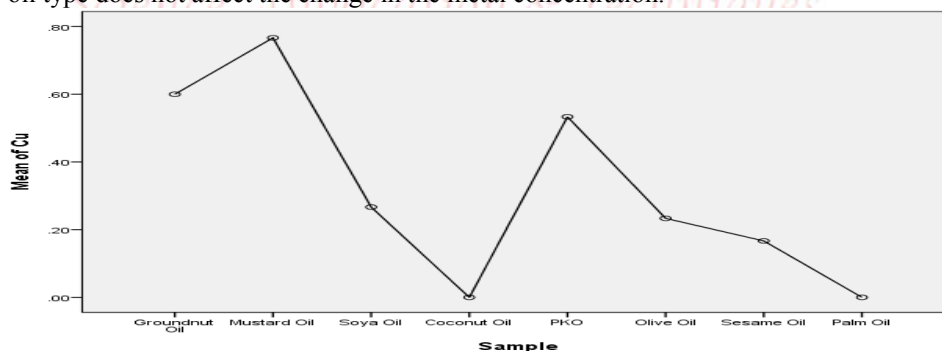


Figure 6: Cu in edible oils

Its levels in other oils include (0.60±0.53) mg/kg in groundnut oil, (0.53±0.46) mg/kg in palm kernel oil, (0.27±0.25) mg/kg in soya oil, (0.23±0.21) mg/kg and (0.17±0.15) mg/kg for olive and sesame oils respectively. This result compares well with those reported in literature (Farzin *et al.*, 2014; Olabanji *et al.*, 2013 and Zhu *et al.*, 2011). They are however lower than those reported by Nnorom *et al.*, (2014). The Cu levels in these oils are higher than the maximum value of 0.1 mg/kg recommended by FAO/WHO (Codex). Cu shows no correlations with Na and Cd but has positive a correlation with the rest of the metals. The plot of this metal in the oils is shown in figure 6.

Ni

No trace of this trace element was found in any of the edible oils.

Co

The range of this trace mineral is (1.12±0.97) mg/kg in groundnut oil to (0.51±0.44) mg/kg in palm oil. No significant difference ($p>0.05$) exists in variations in its levels in the other oils: palm kernel oil (0.99±0.86) mg/kg, mustard oil (0.94±0.81) mg/kg, sesame oil (0.84±0.73) mg/kg, soya oil (0.82±0.71) mg/kg, coconut oil (0.80±0.69) mg/kg, olive oil (0.79±0.69) mg/kg, and palm oil (0.51±0.44) mg/kg. These values are higher than those in Turkish edible oils according to Pehlivan, *et al.*, 2008) Co does not have any correlations with Pb and Cd unlike the rest of the metals where it has positive correlations. Its variations in the oils are shown in a plot in figure 7.

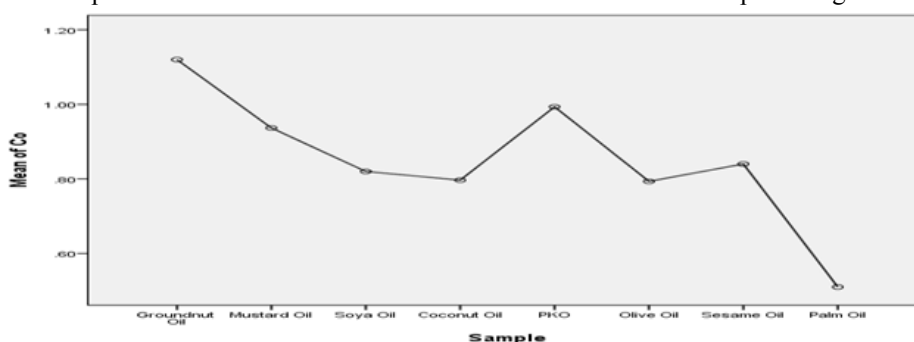


Figure 7: Co in edible oils

Pb

The range of this metal is (3.07±0.80) mg/kg in mustard oil to (0.00) mg/kg in olive and sesame oils respectively. There is a significant difference ($p<0.05$) in the variation in metal content in mustard oil unlike the rest of the oils:

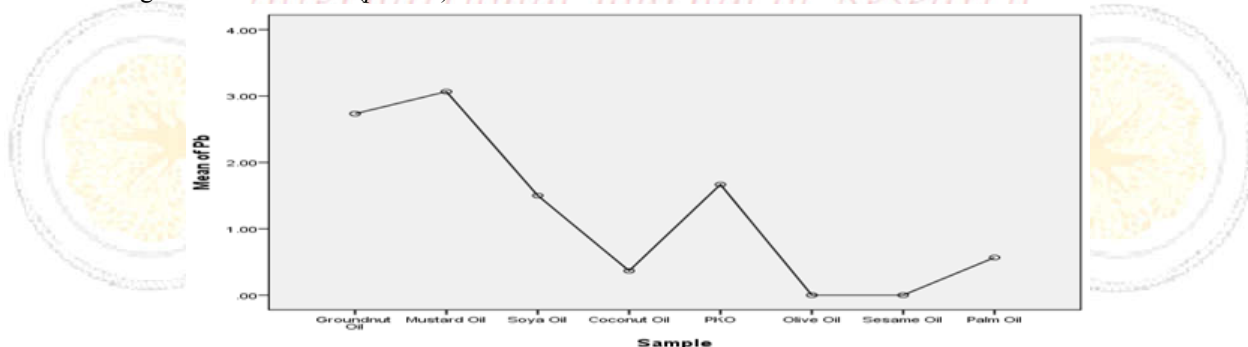


Figure 8: Pb in edible oils

groundnut oil (2.73±1.31) mg/kg, palm kernel oil (1.67±2.12) mg/kg, soya oil (1.50±2.60) mg/kg, palm oil (0.57±0.98) mg/kg and coconut oil (0.37±0.64) mg/kg. Apart from the oils where Pb was not detected, these values are higher than those in literature (Llorent-Martinez, *et al.*; 2011 and Mendil, *et al.*, 2009). These values are also higher than 0.1 mg/kg, the regulation limit of this metal in oils (EU and Codex). This is a serious health threat since Pb is a cumulative poison (Farzin, *et al.*, 2014). It has no correlations with Na, Cd and Co but enjoys positive correlations with the rest of the metals in the oils. Its variations in the oils are shown in figure 8.

Cd

The highest value of this toxic metal was detected in mustard oil (0.77±0.67) mg/kg and the lowest in palm kernel oil (0.55±0.48) mg/kg. In the test for significance, the variation that is significant is ($p<0.05$) in palm oil (0.75±0.16) mg/kg. These values are lower than that obtained from Iranian oils (Farzin, *et al.*, 2014) but compare favourably with those obtained by Mendil, *et al.*, (2009). This element is concentrated particularly in the kidneys, the liver,

blood-forming organs and the lungs. It most frequently results in kidney damage (necrotic protein precipitation) and metabolic anomalies caused by enzyme inhibitions (Farzin, *et al.*, 2014). We found that Cd does not have any correlations with all the metals. Its values for the rest of the metals are as shown in Table 3 and its plot is in figure 9.

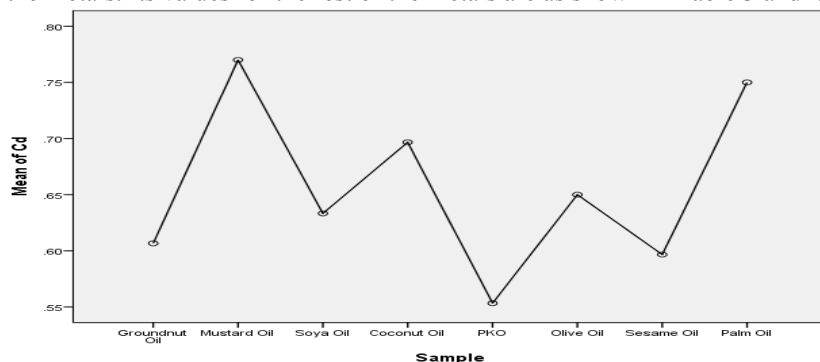


Figure 9: Cd in edible oils

The results of one-way ANOVA (Analysis of variance) of the trace elements in the analyzed eight vegetable oils showed that there is no statistically significant difference between the metal levels and oil types since $p > 0.05$. This means that the variations in the metal concentrations are not influenced greatly by the oil types.

4. CONCLUSION AND RECOMMENDATIONS

The results of this study show that these edible oils contribute significantly to the dietary intake of these important trace elements. However, Pb levels in all the oils exceeded levels reported in literature and that set by regulatory authorities. Since Pb is a cumulative poison the unchecked long term consumption of these oils may pose a toxicological risk to consumers. The National Agency for Food and Drug Administration Control (NAFDAC) and Standards Organization of Nigeria (SON) are expected to routinely monitor trace metal contamination in these oils, thereby safeguarding the health of the populace.

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