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Evaluation of Heavy Metals and Nutrients in Powdered Milk Marketed Within Kaduna Metropolis, Nigeria

*F. Abubakar[1], L. Salihu[2]
[1]*Department of Applied Science, College of Science and Technology, Kaduna Polytechnic*
[2]*Department of Chemistry, Nigerian Defence Academy, Kaduna*
Corresponding Author: F. Abubakar

Abstract: *The heavy metals (Pb and Cd) and essential elements (Cu, Fe, Ca and K) of five selected commercial brands of powdered milk produced in Nigeria and marketed within Kaduna metropolis were analyzed Atomic Absorption Spectrophotometer and Flame photometer. The protein contents were also determined using Kjeldahl titration. The representative powdered milk samples were coded as M1, M2, M3, M4 and M5. The results showed that the highest concentration of lead was recorded inM2 (0.116 mg/kg) and the lowest inM1 (0.068 mg/kg). Other values of lead obtained were 0.083 mg/kg and 0.097 mg/kg forM4 and M3 respectively. The highest concentrations of copper was recorded inM5 (0.278 mg/kg) and the lowest was recorded inM4 (0.045 mg/kg). Other values obtained were 0.2233 mg/kg, 0.2204 mg/kg, and 0.2156 mg/kg forM1, M2 and M3 respectively. The highest concentration of iron was recorded inM4 (4.970 mg/kg) and the lowest inM1 (1.119 mg/kg). Other values obtained were 1.188 mg/kg, 1.491 mg/kg and 1.790 mg/kg forM2, M3 and M5 respectively. The concentration of zinc in the milk samples ranged from 2.575 - 3.797 mg/kg. Cadmium and Mercury were however not detected in any of the samples analyzed.The amount of the protein in the samples ranged from 22.10% - 27.20%. The concentrations of heavy metals and essential elements in the various brands of powdered milk samples were statistically significant at (P<0.05) except for lead, zinc and potassium which were not significant (P<0.05). The results obtained show that the brands of milk are good sources of mineral nutrients and the highly toxic metals like mercury and cadmium were below detection limit. Furthermore, the essential minerals such as calcium, potassium and chromium did not exceed their permissible limit and the recommended dietary allowance.*

Keywords: *Powdered milk, Heavy metals, Flame photometer, atomic absorption spectrophotometer, Kaduna*

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I. Introduction

The issue of pollution is central in man's quest to develop himself. Industrial activities result in redistribution of mineral substances from their natural deposits into foods and beverages [1]. Many of these mineral elements or substances undergo chemical changes and are transformed either in solution or in finely dispersed form through many channels to the food chain. High levels of these materials in the environment facilitate their entry into the food chain thereby increasing their possibility of having toxic effects on humans and animals. The phrase 'chemical contamination' is used to indicate situations where chemicals are either present or are at higher concentrations than they would naturally have occurred [2].Chemical contaminants in milk comprise of chemical hazards that may be introduced during milk production, dairy processing or packaging. Drugs, heavy metals, radionuclides, mycotoxins and pesticides are chemical contaminants that can be found in animal feed and on consumption as residues in milk [3]. Heavy metals are persistent as contaminants in the environment and are at the fore front of dangerous substances causing health hazards in human. Industrial and agricultural activities have resulted in an increased concentration of heavy metals in air, water and soil. They are subsequently taken up by plants or animals and they eventually find their ways into the food chain [4, 5]. Although the amount of heavy metals in uncontaminated milk is admittedly low, their concentration may be significantly altered and magnified through manufacturing and packaging processes [5].

Heavy metals are non bio-degradable substances and they accumulate in the environment up to a considerable extent. They are bio-transferred, bio-accumulated and bio-magnified in food chains and food webs. Animals like cows, sheep, and buffalos feed on grasses and plants which may contain pollutants like heavy metals which may either accumulate in their tissues causing various health hazards or transferred to their consumers. Although, toxic metals by and large remain in ground water and soil, they tend to accumulate to maximum and toxic levels in human and animal tissues feeding from water and soil sources [6]. Living organisms normally need some of these heavy metals as essential metals up to certain limits and in case of increased accumulation it will lead to severe fatal effects [6]. Toxic metals are generally not removed even after

the treatment of waste water at sewage treatment plants.This results in the risk of toxic metal pollution of the soil and subsequently the food chain. Intake of toxic heavy metals through the food chains or food webs by human populations has been widely reported around the globe [7].

Milk powder is one of the most popular dairy products due to its long shelf life and its employment in the manufacture of many dairy products such as ice cream, cheese, evaporated milk, condensed milk and infant milk formula and also as an ingredient in many bakery products, processed meats and soups. Usually, essential elements are added to milk powder during processing, in order to meet nutritional requirement [8]. Hence, it is necessary to control the level of the added elements because if in excess may play a role as a potential source of exposure to heavy metals. Therefore this study was aimed at evaluating the concentration of cadmium, lead, copper, iron, calcium and potassium as well as the protein content in some selected powdered milk marketed within Kaduna metropolis.

II. Materials And Methods

2.1 Sampling

Five (5) different brands of instant powdered sachet milk coded M1, M2, M3, M4 and M5 were purchased from markets within Kaduna metropolis before their expiry dates and stored in air tight containers at ambient temperature until needed.

2.2 Determination of Metals

Dry ashing was carried out by weighing 5g of each dried milk sample into a crucible, placing it in a muffle furnace, heating at 550^{o}C for 4 hours and cooling in a desiccator [9]. 0.5 g of the ash obtained was weighed and transferred into a beaker and 10 cm^3 of aqua regia was added to the sample. The content was placed on a heating mantle and heated in a fume cupboard until the solution reduced to about 5 $cm^3$with a characteristic colour which indicated complete digestion. Each sample was allowed to cool and 20 cm^3 of distilled water was added and stirred. Each solution was filtered into a 100 cm^3 volumetric flask, made up to its mark with distilled water and transferred into a labeled sample bottle. The metals of interest: cadmium, lead, copper, iron and calcium were determined with an atomic absorption spectrophotometer while potassium was determined with a flame photometer [10].

2.3 Determination of Protein:

1 g of the dried milk sample was weighed into a Kjeldahl digestion flask. 25 cm^3 of concentrated H_2SO_4 and 1 g each of $CuSO_4$ and K_2SO_4 were added into the flask as catalysts. The flask was heated gently until the mixture became colourless. The mixture was allowed to cool, and then 200 cm^3 of distilled water was added. The flask was then connected to the Kjeldahl distillation apparatus and 85 cm^3 of 50% sodium hydroxide solution was added to the mixture and then heated to boiling. Ammonia gas was condensed into the receiving flask containing 50 cm^3 of 2% boric acid. 3 drops of methyl red indicator was added to the mixture drop wise. The alkaline distillate was titrated against 0.05 M sulfuric acid till the colour changes from blue to pink [9]. The percentage nitrogen and hence, the percentage protein were calculated using equations 1 and 2 respectively.

$$\%N = \frac{\text{Titre value x } 0.0014 \text{ x } 100}{\text{Mass of sample}} \quad (1)$$

%Protein = %N x 6.38 (SON, 2013)

III. Results And Discussions

Table 1 shows the results of heavy metal concentration in different brands of powdered milk.The concentrations of lead range from 0.083-0.116 mg/kg as shown in Table 1. The highest concentration of lead was recorded in M2 (0.116 mg/kg) and the lowest in M1 (0.068 mg/kg). Other values obtained were 0.097, 0.083 and 0.083 mg/kg forM3, M4 and M5 respectively. The concentrations of lead in the powdered milk samples were not statistically significant at ($P<0.05$).

Table 1: Concentration of Heavy Metals in Powdered Milk Samples

Sample ID	Pb (mg/kg)	Cd (mg/kg)
M1	0.068 ± 0.039^a	ND
M2	0.116 ± 0.001^a	ND
M3	0.097 ± 0.003^a	ND
M4	0.083 ± 0.018^a	ND
M5	0.083 ± 0.011^a	ND

values with different superscripts along the column are significantly ($P<0.05$) different

The values obtained were below the maximum residue limit (2.0 mg/kg) set by the Standard Organisation of Nigeria and NAFDAC [11] but above the maximum residue limit of 0.02 mg/kg set by the

European Union and CODEX [12, 13]. Similar results were reported by Moges, where values ranging from 0.038-0.1688 mg/kg were obtained for milk samples in Harar, Ethopia [14]. However, Tona *et al*., reported much lower values (0.0025 - 0.0061 mg/kg) in different milk products sold in Ogbomosho, South-Western, Nigeria [15].The presence of lead in these brands of powdered milk could be attributed to the exposure of lactating cows from which powdered milk was made to contaminated fodder, climatic factors, use of agro-chemicals and very importantly drinking water [14]. Cadmiumwas not detected in the brands of powdered milk investigated (Table 1) This could be due to the fact that there is low pollution with respect to cadmium in the area of study. However, Moges reported a concentration of 0.068 ppm in powdered milk samples obtained in Harar, Ethopia [14]. The tolerable cadmium intake established by WHO is 0.06 mg/day for adult women and 0.070 mg/day for adult men while the CE Regulation, set the permissible limit for cadmium in food to be 0.075 mg/g [16, 17].

Table 2 shows the results of essential metals concentration in different brands of powdered milk.

Table 2: Essential Metals in Powdered Milk Samples

Sample ID	Cu (mg/kg)	Fe (mg/kg)	Ca (mg/kg)	K (mg/kg)
M1	0.2233 ± 0.00^{b}	1.119 ± 3.26^{b}	1301.97 ± 140.8^{b}	2283.33 ± 202.07^{a}
M2	0.2204 ± 0.00^{c}	1.188 ± 0.71^{b}	1255.47 ± 14.86^{b}	2383.33 ± 256.58^{a}
M3	0.2156 ± 0.00^{d}	1.491 ± 3.53^{b}	1278.16 ± 60.23^{b}	2016.67 ± 700.60^{ab}
M4	0.0045 ± 0.00^{e}	4.976 ± 4.86^{a}	2162.19 ± 79.5^{a}	1900.0 ± 229.13^{ab}
M5	0.278 ± 0.00^{a}	1.790 ± 7.72^{b}	1306.35 ± 39.63^{b}	1466.67 ± 76.38^{b}

values with different superscripts along the column are significantly (P<0.05) different

The concentrations of copper in the brands of milk ranged from 0.0045-0.278 mg/kg as shown in Table 2. The highest concentrations of copper was recorded in M5 (0.278 mg/kg) and the lowest in M4 (0.0045 mg/kg). Other values obtained were 0.2233 mg/kg, 0.2204 mg/kg, and 0.2156 mg/kg forM1, M2 and M3 respectively. The concentrations of copper in the milk samples were statistically significant at (P<0.05). Values obtained in this study are within the tolerable limit set by the Standard Organisation of Nigeria which is 2.0 mg/kg and recommended dietary allowance (0.7-3.0 mg/kg) [11, 18]. It has been reported that deficiency in copper cause many hematological diseases such as anemia, leukopenia and neutrophils [19]. Akpanyung reported 0.60 - 1.51 mg/100 g of copper in various powdered milk [10]. While, Lutfullah *et al*., and Lawal *et al*., reported values ranging from 0.10 - 1.40 mg/kg and 5.30 - 7.10 mg/kg respectively [20, 21]. Burch and Hahn had earlier observed that milk and dairy products are poor sources of copper, which concurs with this finding [22].

The concentration of iron in the milk samples ranged from 1.119-4.970 mg/kg as shown in Table 2. The highest concentration of iron was recorded in M4 (4.970 mg/kg) and the lowest in M1 (1.119 mg/kg). Other values obtained were 1.188 mg/kg, 1.491 mg/kg and 1.790 mg/kg for M2, M3 and M5 respectively. The concentrations of iron in the various brands of powdered milk samples were statistically significant at (P<0.05). Similar results were reported by Lutfullah *et al*.,where values ranging from 1.30 - 4.30 mg/kgwere obtained in various powdered milk samples[20]. Akpanyung reported values ranging from 9.02-11.82 mg of iron per 100 g in different powdered milk samples [10]. The values obtained in this study were below the recommended dietary allowance (10-15 mg/day) set by Food and Nutrition Board [18].

Table 2 shows the concentrations of calcium in the milk samples which ranged between 1255.47 and 2162.19 mg/kg. The highest concentration of calcium was recorded inM4 (2162.19 mg/kg) and the lowest inM2 (1255.47 mg/kg). Other values obtained were 1301.97 mg/kg, 1278.16 mg/kg and 1306.35 mg/kg for M1, M3 and M5 respectively. The concentrations of calcium in the various brands of powdered milk samples were statistically significant (P<0.05). Similar results were reported by Akpanyung, with values ranging from 1080 – 1120 mg/100g in various milk samples sold within Uyo metropolis [10]. Lawal *et al*., also reported values ranging from 957.5 mg/kg to 1530.8 mg/kg in brands of powdered milk sold within Zaria metropolis [21]. Milk is known to be a very rich source for calcium. Gerrior *et al.*, reported that milk and milk products supply about 73% of the American dietary requirement [23]. The findings in this study fall within the recommended dietary allowance for calciumwhich is 700 – 1000 mg for children aged 1-8 yrs and 1000-1300mg for adults while, the tolerable upper intake level is 2000 – 3000 mg [18, 24].

The concentration of potassium in the milk samples ranged between 1466.67 and 2383.33 mg/kg as shown in Table 2. The highest concentration of potassium was recorded inM2 (2383.33 mg/kg) and the lowest inM5 (1466.67 mg/kg). Other values obtained were 2283.33 mg/kg, 2016.67 mg/kg and 1900.0 mg/kg forM1, M3 and M4 respectively. The concentrations of potassium in the various brands of powdered milk were not statistically significant (P<0.05). Akpanyung reported values ranging from 1500 – 1750 mg/100g in various powdered milk samples obtained in Uyo metropolis [10].The findings in this study is in agreement with the estimated safe and adequate daily dietary intake for potassium (550 – 4575 mg in children and 1875 – 5625 mg in adults) [18].

Table 3 shows the result of protein concentration in different brands of powdered milk.

Table 3: Percentage Protein in Powdered Milk Samples

Sample ID	Protein (%)
M1	24.27 ± 1.097^{ab}
M2	26.60 ± 0.346^{a}
M3	22.10 ± 0.34^{b}
M4	27.20 ± 3.64^{a}
M5	24.67 ± 1.361^{ab}

values with different superscripts along the column are significantly ($P<0.05$) different

The percentage of protein in the brand of milk ranged from 22.10 to 27.20%. The highest amount of protein was obtained in M4 (27.20%) and the lowest was obtained in M3 (22.10%). Other values obtained were 24.27%, 26.60% and 24.67% for M1, M2 and M5 respectively. The values obtained were statistically significant ($P<0.05$). These values fall within the standard limit of 34% set by CODEX and 23.5 - 35% set by Standard Organization of Nigeria and NAFDAC [11, 12]. Similar results were reported by Kajal *et al*., for different brands of powdered milk obtained in Mymensingh town, Bangladesh with values ranging from 25.22 – 27.02% while Khalid *et al*., reported 27.00 to 27.10% in various powdered milk samples obtained inKhartoum, Sudan [25, 26]. The findings in this study are also in conformity with the recommendation made by the American Dry Milk Institute [27].

IV. Conclusion

The results obtained showed that cadmium which is a highly toxic metal was not detected in the brands of milk analysed. Furthermore, the essential minerals such as calcium and potassiumdid not exceed their permissible limit while others such as copper and iron were found to be below the limit recommended for daily intake. The protein content in the brands of powdered milk fall within the recommended dietary allowance. These results indicate that the powdered milk analysed were safe and are therefore recommended for consumption.

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