ChemSearch Journal 12(2): 50 – 54, December, 2021
Publication of Chemical Society of Nigeria, Kano Chapter

Received: 11/10/2021 Accepted: 28/11/2021
http://www.ajol.info/index.php/csj

Determination of some Heavy Metals and Proximate Composition of Camel, Cow, Goat and Sheep Milk

***Abba, B., Petrol, B. B., Ali, H. A., Chamba, G., Sanda, F. S. and Modu, S.**
Department of Biochemistry, University of Maiduguri, Borno State, Nigeria.
***Correspondence Email:** bintubukar@yahoo.com

ABSTRACT

The study investigated the level of Zn, Fe, Ni, Cu, Cd, and the proximate composition of camel, cow, goat and sheep milk from Kasuwan Shanu market in Maiduguri, Borno State. Samples were collected during the early morning milking. Samples were digested by the optimized microwave digestion method using HNO_3 and H_2O_2 and analyzed by Atomic Absorption Spectrophotometer AA6800 series Shimadzu Corp. The proximate composition (ash, fibre, fat, Nitrogen free extract, protein and dry matter) was determined by AOAC Methods. Data were expressed as mean ± Standard error mean (SEM) and analyzed by one-way analysis of variance (ANOVA). The results showed that the concentrations of zinc, iron, copper and cadmium in milk of Camel, cow, goat and sheep were below the permissible limit set by World Health Organization (WHO). However, the concentration of nickel in goat milk was higher (1.15 ± 0.04) mg/L than the permissible limit (0.43) mg/L. The protein of milk of Camel (4.05 ± 0.13) mg/L was higher than that of cow (3.34±0.02) mg/L., goat milk (2.58±0.01) mg/L, and sheep milk (2.02±0.01) mg/L. camel milk had a significantly higher fat content (5.66±.10) as compared to cow milk (4.06±0.11) mg/L, goat (2.92±0.01) mg/L. and sheep milk (4.61±0.03) mg/L. Therefore, camel milk was found to be superior to cow, goat and sheep milk in terms of quality.

Keywords: Heavy Metals, Microwave Digestion, Milk, Proximate Composition

INTRODUCTION

Milk and dairy products are important components of the human diet. Milk has been described as a complete food because it contains vital nutrients including proteins, essential fatty acids, lactose, vitamins and minerals in balanced proportions (Licata *et al.*, 2004). However, milk and dairy products can also contain hazards, chemicals and contaminants, which constitute a technological risk factor for dairy products, for the related commercial image and, above all, for the health of the consumer (Licata *et al.*, 2004). From the nutritional point of view, metals contents of milk and dairy products can be grouped into essential elements (iron, copper and zinc) at low doses and non-essential or toxic ones (lead and cadmium). The presence of the latter, even in low concentrations, is invaluable and leads to metabolic disorders with extremely serious consequences. Dairy animals ingest metals while grazing on the pasture and when fed on contaminated concentrate feeds. However, in the cow, transfer of minerals to milk is highly variable (Khan *et al.*, 2008).

Toxic metals such as lead and cadmium are common air pollutants and are emitted into the air as a result of various industrial activities. Various industrial environmental contamination of soil, waters, foods and plants with these metals cause their incorporation into the food chain and impose a great threat to human and animal health. Lead and cadmium residues in milk and dairy products are of particular concern since they are largely consumed by infants and children. Food is the main route of lead (Pb) and cadmium (Cd) exposure in the general population (representing 90% of the total Cd intake in non-smokers), although inhalation can play an important role in very contaminated areas. Lead and cadmium are considered potential carcinogens and are associated with etiology of a number of diseases in the cardiovascular system, kidneys, nervous system, blood and skeletal system (Zhuang *et al.*, 2009). Micronutrient elements such as iron, copper and zinc are essential for many biological functions. Deficiencies of such elements contribute significantly to the global burden of disease; however, if present at higher levels, they can have a negative effect on human health (Kazi *et al.*, 2009). Both toxicity and necessity vary from element to element. Milk and dairy products are considered very poor sources of iron and copper and can supply smaller quantities of zinc (Kazi *et al.*, 2009). The trace element contents of milk and dairy products depends on the stage of lactation, nutritional status of the animal, environmental and genetic factors, characteristic of the manufacturing practices and possible contamination from the equipment during processing (Cashman, 2011).

A heavy metal is a member of loosely defined subset of elements that exhibit metallic

properties. It mainly includes the transition metals, some metalloids lanthanides and actinides. Many different definitions have been proposed some are based on densities, some on atomic number or atomic weight and some on chemical properties or toxicities (Cashman, 2011). The term heavy metals have been called a "misinterpretation" in the International Union of Pure and Applied Chemistry (IUPAC) technical report due to the contradictory definitions and it lack of a "coherent scientific bases). There is an alternative term toxic metal, for which no consensus of exact definition exists either. As discussed below, depending on context, heavy metals can include element lighter than carbon and can exclude some of the heaviest metals (Aslam *et al*., 2011). Heavy metals occur naturally in the ecosystem with large variation in concentration. In modern terms anthropogenic source of heavy metals, i.e. pollution have been introduced to the ecosystem (Zhuang *et al.*, 2009).

Cow, goat, sheep and camel's milk composition can vary widely between different breeds and during different stages of lactation. In the first few days after birth, a special type of milk called colostrum is excreted which is rich in fats and protein. Colostrum also contains important infection-fighting antibodies which strengthen the immune system of the young mammal. The transition from colostrum to true milk occurs within a few days following birth. All milk produced by animals contains carbohydrate, protein, fat, minerals and vitamins but the major component is water (Ahmed *et al.*, 2014). Water dilutes the milk allowing its secretion from the body; without water it would be impossible to express milk. Additionally, the water in milk is essential to the newborn for hydration. In this paper, the level of zinc, iron, nickel, copper and cadmium and the proximate composition of camel, cow, goat and sheep milk were investigated.

MATERIALS AND METHODS

Sample Collection

Different milk samples were collected from Kasuwan Shanu area of Maiduguri from camel, cow, goat and sheep milk during the early morning milking directly into sterile bottles labelled A, B, C, D. The samples were placed in refrigerator to avoid fermentation.

Sample Preparation

Three millimeters (3.0cm^3) of each liquid milk sample was transferred into a 60cm^3 Teflon digestion vessel and then optimized volumes of 6cm^3 of 70% nitric acid and 1ml of 30% hydrogen peroxide were added and the mixture was shaken carefully and kept for 10minutes before closing the vessel. The samples were subjected to microwave digestion at the optimized microwave digestion program in the sequence of 50W, 165^{0}C (10minutes): 80W, 190 ^{0} C (20minutes); and OW, 50^{0}C (10minutes). After heating, the samples were cooled to room temperature to avoid foaming. The digestedsamples were diluted to 25ml with deionized water and used for analysis. Blanks and reference material were run with the samples. Finally, the digest was analyzed for the concentrations of Zn, Fe, Ni, Cu and Cd using a graphite furnace atomic absorption spectrometer AA 6800 series Shimadzu corp.

Proximate Composition (AOAC 2000)

Proximate analysis was carried out according to standard method described by AOAC, (2000) to determine the ash content, crude protein, crude fibre, fat content, dry matter as well as carbohydrate (nitrogen free extract) composition of the blends. The respective methodology for each of the stated parameters is given below:

Determination of Dry Matter Content

A clean flat dish made of silica was dried in an oven and cooled in desiccators. The cooled dish was then weighed (W_1). Sample (5 grams) was introduced and spread into the dish and weighed accurately (W_2). The dish and its content were transferred into an air oven at 105 ºC to dry for 3 hours using a pair of tongs. The dish was then transferred into a desiccator and allowed to cool before weighing. The dish was returned to the oven for half an hour and again cooled in the desiccators and weighed. This process was repeated till a constant weight was attained (W_3).

$$Dry\ Matter\ Content = \frac{W_2 - W_3}{W_2 - W_1}\ x\ 100$$

Determination of Ash Content

A silica dish was cleaned, ignited, cooled (in a desiccator) and weighed (W_1). Test substance (5 grams) labeled W_2 was weighed accurately directly into the silica dish. Using a pair of tongs, the weighed sample was placed in a muffle furnace and the temperature was set 500ºC until fully ashed (grey colour of ash). Upon ashing, the dish with the ash was removed from the furnance and kept in a desiccator to cool before weighing (W_3).

$$\%\ Ash = \frac{W_3 - W_1}{W_2 - W_1}\ x\ 100$$

Determination of Fiber Contents

Two grams (2g) of the sample was weighed and transferred into 250ml quick conical flask,100ml of the digestion mixture was added and refluxed with occasional shaking for 45 min. The mixture was filtered through ashless filter paper using gentle suction. This was then washed with 100ml of boiling water and 50 ml of alcohol followed by 50ml of petroleum ether, the filter paper with the sample was dried at 100^{o}C to

constant weight. The filter paper was weight to obtain the weight of the residue. The residue was then put in a crucible and ashed at 600^{o}C in a muffle furnace for 4 hours. The crucible was then be removed and placed in a desiccator to cool after which it was weighed again.

Determination of Fat content (Soxhlet Extraction Method)

Five grams (5g) of the sample was accurately weighed using a weighing dish. The flat bottom flask was weighed (W_1) before the extractor was mounted on it. The thimble was held half way into the extractor and the weighed sample was then be carefully transferred into the thimble. The weighing dish was rinsed with petroleum ether and poured into the thimble. The thimble was then be plugged with cotton wool and dropped fully into the extractor. The solvent was thereafter added to reach about two thirds of the volumes of the flask and extraction was continued for five hours. When extraction is complete, the solvent was evaporated on water bath at 60^{o}C followed by drying of the residue. The flask and residue were then be cooled and weighed (W_2).

$$\% \, Fat = \frac{W_2 - W_1}{W_1} \, x \, 100$$

Determination of Protein Content (Kjeldahl method)

Digestion of sample

Two grams (2g) of sample was weighed into a digesting tube (Kjedahl digestion tubes) and twenty milliliters (20ml) of sulphuric acid was added. The digester was connected and allowed to run for 3 hours. Fifty milliliters of 40 % NaOH was added, and the volume was made up to 100ml using distilled water.

Distillation

Five milliliters (5mls) of Borate (2%) was pipetted into a cornical flask and 3 drops of bromocresol and methylene indicator was added into the cornical flask. Five milliliters of digested sample were introduced into the distillation flask through the funnel and twenty (20mls) of 40 % NaOH was then be added into the distillation flask. All the inlets were closed. The conical flask containing the borate and mixed indicators was placed at the extended tube (outlet) of the distillate unit and seventy-five (75 mls) of the distillation was collected into the conical flask. This was titrated with the standard 1M HCl.

Standardization of HCl

Five milliliters (5mls) of ammonium solution was pippeted and distilled with about fifteen milliliters (15mls) of 40% NaOH solution. The liberated ammonia was collected in a conical flask containing five milliliters (5mls) of 2% boric acid and 4 drops of mixed indicator. The ammonia solution was titrated with the standard 0.1M HCl. The amount of HCl required for the titration was the acid factor that will be used in the calculations of crude protein content.

The percentage protein will be calculated using the formula:

$$\% \, Protein = \frac{A \, x \, N \, x \, F \, x \, 14.007}{Weight \, of \, Sample \, x \, Aliquot \, taken}$$

Where; A = Volume of the acid used
N = Molarity of the acid
F = Factor 6.25

Determination of Carbohydrate (Nitrogen-free extract)

The carbohydrate (Nitrogen-free extract) content was determined by the difference obtained after the subtraction of total crude protein, fat, ash and crude fibre from the total dry matter.

Percentage of carbohydrate (Nitrogen-free extract) = 100 - (% moisture + % protein + % ash + % fat + % crude fibre).

Statistical Analysis

Data were expressed as Mean ± Standard error mean (SEM) and statistically analyzed by one-way analysis of variance (ANOVA).

RESULTS AND DISCUSSIONS

The concentrations of heavy metals in camel, cow, goat and sheep milk is presented in Table 1.The highest concentration of zinc was found in milk of camel (6.25±0.03)mg/L. and lowest zinc concentration was found in cow milk (2.71±0.02)mg/L. Camel milk had the highest concentration followed by sheep, goat and then cow milk. The zinc concentration in all the samples were below the permissible limit of 121mg/L. The concentration of zinc in this study is consistent with earlier reports by (Ijaz *et al*., 2017)mg/L. The concentration of iron in camel milk (0.85±0.03)mg/L. followed by goat milk (0.74±0.01) mg/l., sheep milk (0.48±0.02)mg/l. and then cow milk (0.17±0.01)mg/L. The concentration of iron in this study were less than those reported by Garba *et al*.(2018), while Meshraft *et al.*(2014) reported higher concentrations as compared to this study. The concentration of Nickel was higher in goat milk (1.15±0.01)mg/L. as compared to cow milk (0.33±0.01)mg/L., camel milk (0.22±0.01)mg/L. and sheep milk (0.42±0.01)mg/L. The concentration of Ni in cow, sheep and camel milk were within the permissible limit(0.43)mg/L., however the concentration Ni in goat was higher than the limit set by WHO, Cadar *et al*.(2016) reported highest concentration of Ni in milk of cow, goat and sheep. The highest concentration of cupper in this study was observed in milk of goat (4.21±0.10)mg/L, camel milk had

the lowest (2.06±0.01)mg/L. Sheep and cow milk had concentrations of (3.51±0.06)mg/L. and (2.44±0.11)mg/L (WHO,2007) respectively. The Cu concentration found in all the milk samples were within the permissible limit (24.2)mg/L. Some metals in lower concentrations are essential to maintain proper metabolic activity in living organisms. Cu is vital for the formation of proteins. It also has anti- oxidant properties and involved in the regulation of gene expression. However, excess copper leads to toxicity which consequently results into leads to conditions associated with deficiency of ceruloplasmin (Garba *et al.,* 2018). The concentrations of cu found in this study tallies within the findings of (Abdou *et al.*, 2017). Cadmium concentration was recorded high in cow milk(0.76±0.01)mg/L. and lowest in camel milk (0.12±0.01)mg/L while goat and sheep milk had concentrations of (0.74±0.01)mg/L. and (0.30±0.01)mg/L. respectively. High concentration of cadmium may be due to consumption of contaminated feeding stuff and water (Dwivedi *et al*., 1997). Cadmium is one of the toxic metals, also implicated in high blood pressure, prostate cancer, mutations and fetal deaths (Valiukenaite *et al*., 2006). Values obtained were higher than the findings reported by Konuspayeva *et al*., 2011.

The proximate composition of camel, cow, goat and sheep milk is presented in Table 2. The values of fat present in cow milk was (4.06±0.11) %, sheep milk (4.61±0.03) %, camel milk (5.66±0.10) % and goat milk had a fat content of (2.92±0.01) %. Fats are good for the body system and increases the transport of vitamins (Modu*et al*., 2011). Toxicity of vitamins especially Fat-soluble vitamins is deleterious to human health (Shiv *et al.,* 2018). The protein content of camel, cow, goat and sheep milk were (4.05±0.03) %, (3.34±0.02) %, (2.58±0.02) % and (2.02±0.01) % respectively and agrees with work of (Sabina, 2019)

Significant differences were observed in the ash and fibre contents of the milk samples. Highest dry matter was observed in goat milk (27.38±0.13) % and lowest was observed in in sheep milk (17.38±0.90) %, (Mestawet *et al.,* 2012) reported higher values.

Table1: Results of the Heavy Metals Concentrations in Camel, Cow, Goat and Sheep Milk (mg/L)

Sample	Zinc	Iron	Nickel	Copper	Cadmium
Camel Milk	6.25 ± 0.03^{a}	0.85 ± 0.05^{a}	0.22 ± 0.01^{a}	2.06 ± 0.01^{a}	0.12 ± 0.01^{a}
Cow Milk	2.71 ± 0.08^{b}	0.17 ± 0.02^{b}	0.33 ± 0.02^{b}	$2\ .44\pm0.11^{a}$	0.76 ± 0.01^{b}
Goat Milk	3.14 ± 0.03^{c}	0.74 ± 0.05^{a}	1.15 ± 0.04^{c}	4.21 ± 0.10^{b}	0.74 ± 0.01^{b}
Sheep Milk	4.32 ± 0.02^{d}	0.48 ± 0.21^{c}	0.42 ± 0.01^{d}	3.51 ± 0.06^{b}	0.30 ± 0.01^{c}

Data are expressed as ($\overline{\text{Mean}}$ ± SD) of triplicate measurements Values with different superscripts across the columns are significantly different at P<0.05.

Table2: Proximate Composition of Camel, Cow, Goat and Sheep Milk (%).

Sample	Ash	Fiber	Fat	NFE	Protein	Dry Matter
Camel	0.25 ± 0.01^{a}	0.06 ± 0.02^{a}	5.66 ± 0.10^{a}	12.2 ± 0.04^{a}	4.05 ± 0.03^{a}	19.4 ± 0.40^{a}
Cow Milk	0.38 ± 0.01^{b}	0.08 ± 0.01^{b}	4.06 ± 0.11^{b}	17.2 ± 0.16^{b}	3.34 ± 0.02^{b}	21.9 ± 0.45^{b}
Goat Milk	0.34 ± 0.01^{b}	0.11 ± 0.01^{c}	2.92±0.01c	18.8 ± 0.29^{c}	2.58 ± 0.02^{c}	27.3 ± 0.13^{c}
Sheep Milk	0.21 ± 0.01^{a}	0.05 ± 0.01^{a}	4.61±0.03b	10.3 ± 1.04^{d}	2.02 ± 0.01^{c}	17.8 ± 0.90^{d}

Data are expressed as (Mean ± SD) of triplicate measurements. Values with different superscripts across the columns are significantly different at P<0.05.

CONCLUSION

Results from this study showed that the levels of Zn, Fe, Ni, Cu and Cd were within the permissible limit set by WHO, 2007, however the concentration of Ni in goat milk was found to be higher than the permissible limit. The fat and protein content of camel milk were found to be higher as compared to cow, goat and sheep milk and therefore, there is need to determine nickel content of different goat milk.

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