



Primary Study for Determination of some Toxic Heavy Metals in Goat Milk Samples in Sirte, Libya

Gazala Mohamed Ben-Hander^{1*}, Ibrahim Ahmed Alsaeh¹, Ashraf Ahmed Ali Abdusalam²

¹Department of Chemistry, Faculty of Sciences. Sirte University, Sirte Libya.

²Department of Pharmaceutical Sciences, Faculty of Health Sciences. Sirte University, Sirte Libya.

ABSTRACT

This research was planned to determine the level of heavy metal residues in milk samples collected from goats grazed around Sirte City, Libya during March 2018. Sixteen milk samples were collected from different farms at Sirte Zone, Libya and then the samples were transferred directly to laboratory and preserved in refrigerator for future analyses. The concentration of lead (Pb), cadmium (Cd) and nickel (Ni) in the samples were investigated using Flame Atomic Absorption Spectrometer (FAAS). The results indicated that Cd was detected in eight samples out of sixteen, but this level was below the recommended limit, while Ni was not detected in all samples under the study. The Pb was detected in all samples and found to be above the permissible limit recommended in the health criteria by the World Health Organization (WHO), that was might due to the city affected twice by the wars in 2011 and 2016.

KEYWORDS: Heavy metals, Fresh goat's milk, Flame atomic absorption spectroscopy.

1. INTRODUCTION

Nowadays, one of the critical issues is the entry of potential pollutants such as heavy metals to the milk and dairy products. Heavy metals considered one of dangerous contaminated that found in the environment; accumulate in plant and animal tissues [1]. It can release into the environment by either natural or human activities, causing environmental and health hazards that show an impact on human and animal's health. Heavy metals like (Pb and Cd) are essential but does not have any biological role, while others like (Cu and Fe) are essential to the living organisms in the process of maintaining proper metabolic activity [2]. Moreover, if the concentration of heavy metals in the environment exceed permissible values, this can be destructive to all living organisms. Intake the high level of these metals through ingestion, inhalation or any other mean can cause many health problems such as cancer, damage nervous system and ultimate death [3]. Milk is composed of a complex, bioactive substance that supports the growth as well as the development of infants and considers as a very important in the human diet and constant consumption, particularly for young children. Also, milk is rich in vitamins, proteins, sugars, mineral and fats that make it as a nearly a complete food. However, milk and it is dairy products may contain different amounts of toxic contaminants [4,5]. Monitoring and detection of milk contamination with heavy metals have become an urgent requirement in recent times [6]. Determination of the quality of milk and its validity for human consumption depends on the analysis of its content of heavy elements. To identifying the sources of milk, milk powder and cheese, the method of multi-element analysis has been used, where the accuracy reached more than 90% [7,8]. Milk contaminated with different heavy metals such as selenium, zinc, cadmium, lead, iodine, sulphur, and perhaps cyanide and arsenic, which are more dangerous [9]. Because of the increase in environmental pollution, it became necessary to monitor and determine the levels of heavy metal in milk, due to the significant influence on human health [10-12]. Many studies report the presence of heavy metals in milk as well as other food products [13,14]. Due to the low concentration levels of the heavy metal ions and complex emulsions like matrices in the milk determines the trace element challenging task. In the literature digestion procedures to oxidise organic matrices found in different milk samples to have been reported [15,16]. The acid digestion procedures are well known and most popular techniques for sample pre-treatment for elemental analysis in environmental and biological samples and also well-established method acid digestion induced by microwave energy [17,18]. Several instrumental techniques have been reported for determination of heavy metals, such as infra-red spectroscopy [19], Atomic absorption spectroscopy, flame atomic absorption spectrometry, ion chromatography including indirect photometric chromatography [20-22], also, furnace atomic absorption spectrometry [23], potentiometric stripping [24], Flame Atomic Absorption Spectrophotometer also was used [25,26].

* **Corresponding Author:** Gazala Mohammed Ben-Hander, Department of Chemistry, Faculty of Sciences. Sirte University, Sirte Libya.

The present study aimed to determine the presence of some heavy metals such as cadmium, zinc and lead in the goat milk samples using atomic absorption spectrophotometer and compare the obtained results with a standard allowable limit.

2. MATERIAL AND METHODS

2.1 Sample collection

A total of sixteen goat milk samples were collected from different areas around Sirte city in spring season 2018. Before sampling, all the glassware were kept in 10% HNO₃ for 24 hours, then washed with distilled water for 48 hours and dried. The samples were collected in plastic bottles of each farm and placed in an icebox. Then the samples were placed in refrigerator within an hour until analysis to avoid from fermentation.

2.2 Sample digestion

A volume of 20 ml of each goat milk sample was transferred into the beaker, and 20 ml of aqua regia was also added. The digestion was carried out by heating the content in the beaker to near dryness. After evaporation and cooling the sample, 20ml of distilled water was added and stirred to make a clear solution of the samples. Finally, the sample was filtered into 50 ml volumetric flask and filled to the mark with distilled water. It was then transferred into a sample bottle, and heavy metals were further analysed using Atomic Absorption Spectrophotometer.

3. RESULTS AND DISCUSSION

The major problems with heavy metals are their ability to bio-accumulate, and their residues found in the milk, and therefore became a particular concern due to consumption of the milk mainly by infants children and adults [27].

The concentrations of lead, cadmium and nickel in goats milk samples obtained from the east of the city are presented in Table 1. As showing in the Table, all of the samples contaminated with a high concentration level of Pb ranged between 0.394-2.467 mg L⁻¹, which is above the recommended authorized limit by WHO (Pb: 0.02 mg L⁻¹) [28]. In the case of cadmium, the concentration was found in the range of (0.008-0.011 mg L⁻¹) which is less than permissible limit by WHO standard (Cd: 0.05 mg L⁻¹) [28] in all east of the city samples, this is may due to low pollution to this metal in these areas. Among the seven areas analysed in the east of the city side, nickel was not detected.

Table 1: The concentration of heavy metal in goat milk samples collected from east of the city

S.No.	Study area	Concentrations of heavy metals (mg L ⁻¹)		
		Pb	Cd	Ni
1	E ₁	0.394	ND	ND
2	E ₂	1.315	0.011	ND
3	E ₃	1.464	0.002	ND
4	E ₄	0.881	ND	ND
5	E ₅	1.530	ND	ND
6	E ₆	2.143	0.001	ND
7	E ₇	2.467	0.008	ND

E East of the city

In the west side of the city, six samples were analyzed from six different places. The concentration of Pb, Cd and Ni in all of goats milk samples are summarized in Table 2. The results showed that the level of Pb ranged from 0.213-1.787 mg L⁻¹. Since the permissible limit for Pb is 0.02 mg L⁻¹, all the samples were above this limit. As we can see in the table, the cadmium was detected in two samples out of six at concentration 0.013 mg L⁻¹ but, this level was also below the recommended limit. Ni was not detected in any of the six goat's milk samples.

Table 2: The concentration of heavy metal in goat milk samples collected from west of the city

S.No.	Study area	Concentrations of heavy metals (mg L ⁻¹)		
		Pb	Cd	Ni
1	W ₁	0.942	0.013	ND
2	W ₂	1.068	0.013	ND
3	W ₃	1.787	ND	ND
4	W ₄	0.694	ND	ND
5	W ₅	0.552	ND	ND
6	W ₆	0.213	ND	ND

W west of the city

In the case of the south of the city area, three samples were analysed from different locations. Table 3.0 present the concentration of heavy metals (Pb, Cd and Ni) in goat milk samples collected from the area. All samples contained a high level of Pb in the range of 1.980-2.125 mg L⁻¹, which exceeded the permissible limit. Moreover, decreasing in Pb concentration was observed as we go far from the centre of the city toward the south, that probably due to the war experienced inside the city. The cadmium element in this side was also detected in two samples, but still less than the permissible limit by WHO standard. Finally, Nickel as the other areas of the study was not detected in all analysed samples.

Table 3: The concentration of heavy metal in goat milk samples collected from south of the city

S.No.	Study area	Concentrations of heavy metals (mg L ⁻¹)		
		Pb	Cd	Ni
1	S ₁	2.125	ND	ND
2	S ₂	1.980	0.004	ND
3	S ₃	1.151	0.019	ND

S South of the city

According to the results of this study, it is clear that lead is detected in all the samples collected from three different sides around the city and the concentrations varied from 0.213 to 2.467 mg L⁻¹. The results show that the goat's milk in the study area is rich in lead. That could be ascribed to the pollution of agricultural land in the city because of the two wars that the country experience. Although no beneficial biological function for the lead and it is well known that the lead accumulates in the human body and will affect human health and biological system. Many adverse health effects can cause when exposure to lead even at low concentrations, especially in pregnant women as well as young children. The lead is known as a neurotoxin that permanently interrupts normal brain development [29, 30]. Moreover, it has been associated with different diseases, such as cardiovascular, neurological and cancer diseases.

4. CONCLUSION

In conclusion, from the obtained results of this primary study, it could be concluded that all examined goat milk samples contained high concentrations of lead exceeded the authorized limit by WHO standard. Cd detected only in eight samples out of sixteen samples, but the concentrations did not exceed the permissible limit, while Ni has not been detected in all samples. However, the number of analysed heavy metals and sample were limited in this study. Therefore, further studies are strongly recommended to evaluate "toxic" heavy metals on a greater number of fresh milk samples from different areas of Sirte City.

Acknowledgements

Financial support of the work by the Chemistry Department, Faculty of Science, Sirte University and Scientific research lab, Sebha University are gratefully acknowledged.

REFERENCES

- [1] Ziarati, P., Moghimi, S., Arbabi-Bidgoli, S. and Qomi, M., 2012. Risk assessment of heavy metal contents (lead and cadmium) in lipsticks in Iran. *International Journal of Chemical Engineering and Applications*, 3(6), p.450.
- [2] Ayar, A., Sert, D. and Akin, N., 2009. The trace metal levels in milk and dairy products consumed in middle Anatolia—Turkey. *Environmental monitoring and assessment*, 152(1-4), pp.1-12.
- [3] Onundi, Y.B., Mamun, A.A., Al Khatib, M.F. and Ahmed, Y.M., 2010. Adsorption of copper, nickel and lead ions from synthetic semiconductor industrial wastewater by palm shell activated carbon. *International Journal of Environmental Science & Technology*, 7(4), pp.751-758.
- [4] Ataro, A., McCrindle, R.I., Botha, B.M., McCrindle, C.M.E. and Ndibewu, P.P., 2008. Quantification of trace elements in raw cow's milk by inductively coupled plasma mass spectrometry (ICP-MS). *Food chemistry*, 111(1), pp.243-248.
- [5] Basnet, S., Schneider, M., Gazit, A., Mander, G. and Doctor, A., 2010. Fresh goat's milk for infants: myths and realities—A review. *Pediatrics*, 125(4), pp.e973-e977.
- [6] Ping, J., Wu, J. and Ying, Y., 2012. Determination of trace heavy metals in milk using an ionic liquid and bismuth oxide nanoparticles modified carbon paste electrode. *Chinese science bulletin*, 57(15), pp.1781-1787.
- [7] Bontempo, L.U.A.N.A., Larcher, R.O.B.E.R.T.O., Camin, F.E.D.E.R.I.C.A., Hölzl, S., Rossmann, A., Horn, P. and Nicolini, G., 2011. Elemental and isotopic characterisation of typical Italian alpine cheeses. *International dairy journal*, 21(6), pp.441-446.
- [8] Tan, K.Y., Liang, X.L. and Liao, L., 2015. Determination of milk powder geographical origin based on multi-element analysis. *Science and Technology of Food Industry*, 2, pp.52-56.
- [9] Nasr, I.N., Sallam, A.A.A. and Abd El-Khair, A.A., 2007. Monitoring of certain pesticide residues and some heavy metals in fresh cow's milk at Gharbia Governorate, *Egyptian journal of applied science*.7(20), pp.3038-3044.
- [10] Steijns, J.M., 2001. Milk ingredients as nutraceuticals. *International Journal of Dairy Technology*, 54(3), pp.81-88
- [11] Licata, P., Trombetta, D., Cristani, M., Giofre, F., Martino, D., Calo, M. and Naccari, F., 2004. Levels of “toxic” and “essential” metals in samples of bovine milk from various dairy farms in Calabria, Italy. *Environment International*, 30(1), pp.1-6.
- [12] Singh, A., Sharma, R.K., Agrawal, M. and Marshall, F.M., 2010. Health risk assessment of heavy metals via dietary intake of foodstuffs from the wastewater irrigated site of a dry tropical area of India. *Food and Chemical Toxicology*, 48(2), pp.611-619.
- [13] Soylak, M., Saraçoğlu, S., Tüzen, M. and Mendil, D., 2005. Determination of trace metals in mushroom samples from Kayseri, Turkey. *Food Chemistry*, 92(4), pp.649-652.
- [14] Tuzen, M., Saracoglu, S. and Soylak, M., 2008. Evaluation of trace element contents of powdered beverages from Turkey. *Journal of Food & Nutrition Research*, 47(3).
- [15] Arain, M.B., Kazi, T.G., Jamali, M.K., Afridi, H.I., Jalbani, N. and Memon, A.R., 2007. Ultrasound-assisted pseudodigestion for toxic metals determination in fish muscles followed by electrothermal atomic absorption spectrophotometry: Multivariate strategy. *Journal of AOAC International*, 90(4), pp.1118-1127.
- [16] Mingorance, M., 2002. Focused microwave-assisted digestion of vegetal materials for the determination of essential mineral nutrients. *Analytical and bioanalytical chemistry*, 373(3), pp.153-158.
- [17] Demirel, S., Tuzen, M., Saracoglu, S. and Soylak, M., 2008. Evaluation of various digestion procedures for trace element contents of some food materials. *Journal of hazardous materials*, 152(3), pp.1020-1026.
- [18] Jalbani, N., Kazi, T.G., Jamali, M.K., Arain, B.M., Afridi, H.I. and Baloch, A., 2007. Evaluation of aluminum contents in different bakery foods by electrothermal atomic absorption spectrometer. *Journal of Food Composition and Analysis*, 20(3-4), pp.226-231.

- [19] Soyeyurt, H., Bruwier, D., Romnee, J.M., Gengler, N., Bertozzi, C., Veselko, D. and Dardenne, P., 2009. Potential estimation of major mineral contents in cow milk using mid-infrared spectrometry. *Journal of Dairy Science*, 92(6), pp.2444-2454
- [20] Ogabiela, E.E., Udiba, U.U., Adesina, O.B., Hammuel, C., Ade-Ajayi, F.A., Yebpella, G.G., Mmereole, U.J. and Abdullahi, M., 2011. Assessment of metal levels in fresh milk from cows grazed around Challawa Industrial Estate of Kano, Nigeria. *Journal of Basic and Applied Scientific Research*, 1(7), pp.533-538.
- [21] Abd-El Aal, S.F.A., Awad, E.I. and Kamal, R.M.K.M., 2012. Prevalence of some trace and toxic elements in raw and sterilized cow's milk. *Journal of American Sciences*, 8(9), pp.753-761.
- [22] Starska, K., Wojciechowska-Mazurek, M., Mania, M., Brulińska-Ostrowska, E., Biernat, U. and Karłowski, K., 2011. Noxious Elements in Milk and Milk Products in Poland. *Polish Journal of Environmental Studies*, 20(4).
- [23] Derakhshesh, S.M. and Rahimi, E., 2012. Determination of lead residue in raw cow milk from different regions of Iran by Flameless Atomic Absorption Spectrometry. *American-Eurasian Journal of Toxicological Sciences*, 4(1), pp.16-19.
- [24] Muñoz, E. and Palmero, S., 2004. Determination of heavy metals in milk by potentiometric stripping analysis using a home-made flow cell. *Food Control*, 15(8), pp.635-641
- [25] Sikirić, M., Brajenović, N., Pavlović, I., Havranek, J.L. and Plavljančić, N., 2003. Determination of metals in cow's milk by flame atomic absorption spectrophotometry. *Czech Journal of Animal Science*, 48(11), pp.481-486
- [26] Tajkarimi, M., Faghieh, M.A., Poursoltani, H., Nejad, A.S., Motallebi, A.A. and Mahdavi, H., 2008. Lead residue levels in raw milk from different regions of Iran. *Food Control*, 19(5), pp.495-498.
- [27] Tripathi, R.M., Raghunath, R., Sastry, V.N. and Krishnamoorthy, T.M., 1999. Daily intake of heavy metals by infants through milk and milk products. *Science of the total environment*, 227(2-3), pp.229-235.
- [28] Libyan National Center for Standardization and Metrology, Libyan Standard No. 357 /2016.
- [29] World Health Organization/SDE/WSH/03.04/104/Rev/1., 2004, Manganese in drinking water. Background document for development of WHO Guidelines for Drinking-water Quality
- [30] Abadin, H., Ashizawa, A., Stevens, Y.W., Lladós, F., Diamond, G., Sage, G., Citra, M., Quinones, A., Bosch, S.J. and Swarts, S.G., 2007. Toxicological Profile for Lead; Agency for Toxic Substances and Disease Registry: Atlanta, GA, USA.