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RESEARCH ARTICLE

DETERMINATION CADMIUM, LEAD AND ZINC IN HUMAN HAIR BY USING FLAME ATOMIC ABSORPTION SPECTROMETRY (FAAS)

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ABSTRACT

The heavy metals mean serious hazard in environmental pollution. Some of them are vital for many organisms in a low concentration, however the others ought to be poisonous at low concentrations, too. This paper gives an example for the correlation of the attention in human hair and in the environment of different heavy metals. Human hair (n=50) Volunteers (35 males and 15 females) of different age groups between 1 to 57 years samples were collected in Al - Ajailat, Libya. Hair samples were analyzed for heavy metals (Cd, Pb and Zn) by Flame Atomic Absorption Spectrophotometric technique (FAAS). The results showed that the samples concentrations ranged between 0.0001 and 0.3840 mg.kg^{-1} for cadmium, followed by zinc between 68.99 mg kg^{-1} and 225mg. kg^{-1}while lead was between 0.632 mg kg^{-1} and 7.708mg. Kg^{-1}. The results indicated that metal concentrations in male samples varied based on age, such that age group 33-43 years had the highest zinc concentration (206.2±11.6 mg/kg), and age group 1-10 years had the highest Cd (0.384±0.01 mg/kg) and Pb (1.929±0.05 mg/kg) concentrations. while, the cadmium and lead contents in children's hair samples of both sexes was higher than compared to the values available in some countries. The difference between male and female concentration could be due to individual differences in exposure to heavy metal load as a result of habitual or environmental factors.

KEYWORDS

Heavy Metals, Human Hair, Spectrometry

1. INTRODUCTION

In the last few decades, the analytical study of concentrations of the minor and trace elements in biological and human samples have become very important. Occupational diseases, poisoning, and environmental diseases are accurately diagnosed by using trace elemental analysis of human biological samples and the state of health can be characterized with the analytical results (Bialy et al., 2014). The heavy metals are contacted thru the meals chain with residing organisms. The human biological samples for trace element analysis of reliably detected many cases of occupational disease, poisoning, environmental hazards, and the use of the effects of analyzes of health status can be characterized (Kiss et al., 2018). Hair has been used as indicator of chemical hazard in biological and environmental investigations. Human hair has captured interest as a clinical sample due to its advantages over other clinical samples such as urine or blood samples (Skalny et al., 2015).

Human hair offers longstanding different trace element concentrations by providing better estimation of general trace element concentrations. Another advantage of hair is that samples can be gathered more easily and rapidly than other samples such as urine and blood. In addition, unique storage settings are not required. Other advantages of hair samples include inertness and homogeneity in chemical structure (Kiss et al. 2018; Atsever et al., 2020). However, a number of limitations for using hair as substrate of trace element status analysis exist. In particular, hair metal content may vary due to a number of factors like gender, age, occupation, geographical location, climate, ethnicity, and living and dietary habits (Abdulrahman et al., 2012; Brito et al., 2018). Scientists have been using scalp hair in diagnosing the chemical levels of trace elements in human body since 1920s.

This is due to the higher sensitivity of hair toward chemical accumulations in biological systems and that many trace elements accumulate in hair at concentrations higher than in blood serum or urine (Hubbart, 2012). The chemical status of hair can be related to the present conditions of nutrition, metabolism and the surrounding environment (Eneji et al., 2015). Therefore, hair can be used as a biomarker tool in supporting risk assessment in epidemiologic and laboratory studies (Luo et al., 2017). Furthermore, the keratin-rich composition of hair tissue rend the sample high stability and robustness. Hair also is easier and safer to collect, ship, and store than blood or urine and the analysis is less expensive. These multiple advantages make hair a strategic tool for screening and analysis in chemical, medical and environmental studies (Czerny et al., 2020).

Trace elements, such as lead, mercury, cadmium and arsenic are essential to human body and its functions. However, when concentration levels of

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these metals exceed the safe limit, potential health problems may develop. For example, toxic concentrations of cadmium (Cd) can be carcinogenic to human reported that toxic lead potentially imposes mental and behavioral disorders in children pointed to the development of serious illness symptoms in human health due to excessive intake or absence of Zinc (Sherief et al., 2015; Eneji et al., 2015; Ndiritu et al., 2012). The Global Environmental Monitoring System (GEMS) of the United Nations' Environment Program considered hair as one of the important monitoring materials for worldwide biological monitoring of pollution (Atsever et al. 2020). Therefore analyses of heavy metals in human hair serves as an assessment for environmental contamination and can be used to sensitize individuals towards maintaining a healthier life style in their environments (Peter et al., 2012).

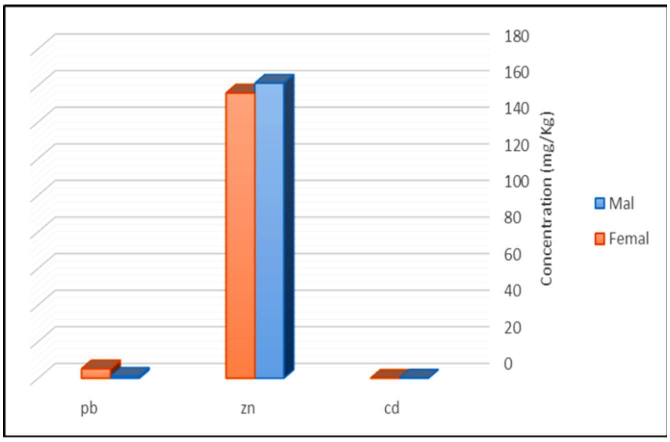

Figure 1: Average concentration of heavy metals in population sample.

The accurate determination of trace elements in real samples is an important and challenging task in environmental analytical chemistry. Inductively coupled plasma-mass spectrometry, inductively coupled plasma-optic emission spectrometry and atomic absorption spectrometry, etc. are common modern instrumental detection techniques for the determination of elements at trace levels in the environmental and biological samples (Habila et al., 2017). Lastly, Exposure biomarkers play an important role in estimating the internal dose of a person exposed to an environmental contaminant, and they are often essential in determining exposure–health effect relationships in epidemiological studies, For example, lead (Pb) levels in blood and bone are accepted as well-validated Pb exposure biomarkers, and they helped establish the association between Pb exposure and health risk in children and adults. Similarly, blood cadmium (Cd) levels have been shown to reflect Cd exposure from environmental sources (Children, 2018).

2. The Aim of This Study

The present study aims at assessing the potential chemical risk of three trace elements Cd, Pb and Zn in human hair samples collected from the inhabitants of Ajailat City, West Libya. The findings are analyzed and compared with reference studies to support the decision-making and projecting some remedial measures to mitigate the risk.

3. Materials and Methods

The concentration levels of the target elements were detected by Flame Atomic Absorption Spectrophotometry (FAAS) method. The laboratory materials consisted of oven, hot plate (model: SV3, voltage: 220V, current: 2A, power rating: 450W and a maximum temperature of 425°C), atomic absorption spectrometer. The reagents consisted of ethanol, deionized water,65%HNO_3, 30% w/w H_2O_2. All reagents 65%HNO_3, 30% (w/w) H_2O_2 and 99% CH3CH2OH) were of high purity procured from Sigma Chemical Company St Loius.

3.1 Sample Collection

Fresh scalp hair samples were collected from 50 people (35 males and 15 females) living in the study area. Their ages varied between 1 to 57 years. The samples were quickly transferred to coded polythene bags. During sampling, a questionnaire survey was conducted on the target population for formulating a basic knowledge on gender, age, occupation, population density and water source of the study area. The hair samples of women were obtained from those individuals who did not have colored or treated hair.

3.2 Sample Preparation

The sample preparation phase in the present study followed the recommendations of the International Atomic Energy Agency (IAEA) and the laboratory procedure of (Eneji et al., 2015; Peter et al., 2012). The procedure consisted of two processes: cleaning and digestion. In the cleaning process, the collected samples were cut to about 200 - 250 mg by using stainless steel scissors rinsed in ethanol, then coded and stored. The stored samples were further cut into approximately 0.3 cm pieces and mixed to allow a representative sub sampling. These were washed first in ethanol once, then three times in distilled water, once again in ethanol and followed finally in distilled water, accordingly. They were placed in crucibles and dried in the oven at 75°C±5°C for 15-25 minutes. About 0.1065 g of pre-treated hair sample was weighed using analytical balance.

In the digestion process, the 0.1065g-sub-sample was weighed using analytical balance (AB 54-S METTLER TOLEDO) and doped into a 50 ml crucible for digestion. Precisely 8.0 ml of conc. HNO3 was added, covered with the lid, placed on a hotplate and heated to a gentle boil. Hair was digested at 85°C for about 30 min until the solution becomes clear (yellowish). The crucible was not allowed to go dry as exactly 1.0 mL of 30% H_2O_2 was added to each sub sample and heating resumed at the lowest setting until bubbling stopped. The solution was allowed to cool; the crucible was rinsed twice with about 3cm^3deionized water and was then transferred into a 100 ml sample bottle.

4. Results and Discussion

Mineral absorption or depletion in human tissues (hair) may occur due to environmental and/or occupational exposure, poor diet, disease, and intake of certain medications or treatments. Although the relationship between the concentration of trace elements in scalp hair and environmental exposure to metals is quite complex, it has been reported that changes of trace elements in hair may reflect the exposure of the general community in dust, household and soil. Despite the problems caused by external pollution and the lack of a standardized methodology in hair analysis, the World Health Organization (WHO) has recommended the use of hair testing to monitor heavy metals in some cases (Fakayode et al., 2013).

Table 1: Mean Concentration (mg/kg±SD) of Heavy Metal in Male Samples by Age

Age (years)	Number of Male Samples	Heavy metals		
		Cd	Pb	Zn
1-10	10	0.384±0.01	1.929±0.05	85. 16±1.3
11-21	7	0.002±0.0003	0.660±0.02	182±3.8
22-32	6	0.247±0.01	0.632±0.02	191.1±5.5
33-43	8	<0.00006	0.751±0.03	206.2±11.6
44 - 75	4	0.006±0.0001	1.4568±0.03	142.1±5.4

Table 2: Descriptive Statistical Analysis of Estimated Values of cd Contaminant Level (mg/kg) in Male Samples

Variable	Mean	St. Dev	Minimum	Maximum
cd	0.1278	0.1781	0.0001	0.3840
zn	161.3	48.7	85.2	206.2
pb	1.086	0.581	0.632	1.929

Table 1 and Table 2 summarize the results of FAAS analysis for male individuals of the population sample. The concentrations of target heavy metals (mg/kg) were as the following: Cd (<0.00006-0.384); Pb (0.632-1.929); and Zn (85.16-206.2). The results also indicated that metal concentrations in male samples varied based on age, such that age group 33-43 years had the highest zinc concentration (206.2±11.6 mg/kg), and age group 1-10 years had the highest Cd (0.384±0.01 mg/kg) and Pb (1.929±0.05 mg/kg) concentrations.

Table 3 and Table 4 summarize the results of FAAS analysis for female individuals of the population sample. The results showed that metal concentrations in female samples varied based on age, such that age group 11-21 years had the highest zinc concentration (225.9 ± 10.4 mg/kg), and age group 1-10 years had the highest Cd (0.071±0.008mg/kg) and Pb (7.708±0.09mg/kg) concentrations.

Cadmium is very toxic, its long-term exposure to lower levels leads to a buildup in the kidneys and possible kidney disease, lung damage, and fragile bones. Hypertension, arthritis, diabetes, anemia, cancer, cardiovascular disease, cirrhosis, reduced fertility; hypoglycemia, headaches, kidney disease, and strokes are its some odd long-term results (Wadhwa et al., 2015; Sherief et al., 2015). In this study, the levels of cadmium in some the hair samples for male and female Especially in the 1-10 age group were above the reference values of various countries Italy is 0.03 mg/kg, England 0.11 mg/kg, Japan 0.05 mg/kg (Influence of Gender and Smoking Habit on the Trace Elements Levels of Washed Scalp Hair of a Control Population from Karbala ,.... Influence of Gender and Smoking Habit on the Trace Elements Levels of Washed Scalp Hair of a Control Population from Karbala 2018).

Table 3: Concentration (mg/kg±SD) of Heavy Metal in Female Samples by Age.

Age (years)	Number of Female Samples	Heavy metals		
		Cd	Pb	Zn
1-10	6	0.071±0.008	7.708±0.09	68.99±3.3
11-21	7	0.061±0.006	4.698±0.1	225.9±10.4
22-32	-	-		-
33-43	-	-	-	-
44 - 75	2	0.008±0.0001	3.196±0.1	173.2±4.1

Table 4: Descriptive Statistical Analysis of Estimated Values of Cd Contaminant Level (mg kg) in Female Samples

Variable	Mean	St. Dev	Minimum	Maximum
Cd	0.0467	0.0339	0.0080	0.0710
Zn	155.9	80.0	68.7	225.9
Pb	5.20	2.30	3.20	7.71

Table 5: Distribution and Mean Concentration (mg/kg) of Heavy Metal in The Population Sample

Variable	Mean		International Limits (NHA)
	Mal	Female	
Cd	0.1278	0.0467	0.02 - 0.79
Zn	161.3	155.9	113 – 207
Pb	1.086	5.20	0.04 – 10.8

Table 6: Comparison of Hair Metal Levels in Different Countries (mg/kg)

Country	Cd	Pb	Zn	Reference
China	0.02–0.96	0.17–6.65		[12]
Italy	0.23	7.11	150	[18]
India	0.13	4.65		[17]
USA	0.0039–0.463	0.0415–7.73		[9]
Norway	0.093	9.3	219	[6]
Poland	2.33	37.8	258	[20]
Nigeria	1.34 - 4.54	19.45 -55.67	17.98 -70.00	[1]
Iraq	.0.37m, 0.36f		232m,330f	[3]
Libya	**0.0001 - 0.3840**	**0.632 -7.708**	**68.99 -225**	**In this study**

The lead levels in hair samples analyzed in the 1-10 age group for both genders measured the upper limits of different countries. Italy 0.03 mg / kg; Japan 1.4 mg / kg (Abdulrahman et al., 2012). While the lead level in hair samples in the age groups studied was within the limits allowed by the (Liang et al., 2017). The concentration of zinc in the studied samples was the highest in hair samples for females, especially in the age group of 11 - 21, which is higher than the permissible limits by the, probably due to use of cosmetics formulations and hair treatment among them (Brito et al., 2018; Czerny et al., 2020). Thus, the current study mainly reflected these age groups for the distribution of minerals in the hair of both sexes. The concentration of minerals in scalp hair is distributed by sex and male and female hair are completely different in terms of the content of trace elements, resulting from different metabolic pathways (Accuracy et al., 2001).

5. Conclusion

In this study, heavy metals (Cd, Pb and Zn) were analyzed in hair samples for 50 samples of females and males during different age groups using the flame absorption spectrometer. The cadmium and lead contents in children's hair samples of both sexes was higher than compared to the values available in some countries. This would lead to long-term health problems due to accumulation of toxic and dangerous elements in the human body. While the highest zinc content in In both sexes in the age group 11-21 may be the cause of excessive use of hair cosmetics.

Recommendations

The authors of this paper recommend interested parties to investigate other types of cosmetic products in Libya for further analysis and conformability with WHO standards. Cosmetic manufacturers are strongly advised to test their products on regular basis, even before marketing them, by certified laboratories. They are also required to publish their information about the chemical components of their products for public awareness and evaluation especially baby cleaning products.

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