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Assessment of Heavy Metals in Women's Dyed Hair Samples in the South of Libya

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Abstract:

Heavy metals apparent toxicity to humans is a result of long term or extreme level exposure to pollutants like cosmetics and hair dyes. In this study, the concentrations of some toxic metals have been measured in different hair samples dyed by products sold at local markets in Taraghun, Libya. Five different brands used by eight ladies. Hair samples were prepared by acid digesting using Microwave oven. The heavy metals (As, Ba, Cd, Cr, Cu, Pb, and Zn) concentrations in hair samples were evaluated by inductively coupled plasma mass spectrometry ICP- MS. The sample's concentration of heavy metals ranged from (1.18- 4.18 ppm) for Arsenic, (15.22- 3729ppm) for barium, (0.002 -1.91 ppm) for cadmium, (2.08- 5.80ppm) for chromium, (13.0-34.9ppm) for copper, (4.19-52.8ppm) for lead, and (109.6-258.6 ppm) for zinc. High levels of toxic metals could put-up potential health hazard to consumers such as skin problems or cancer.

Keywords: Heavy Metals, Hair, Dyes. Acid Digesting, Microwave.

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Introduction

Hair dyeing is the practice of changing the color of hair, is achieved through the use of hair dye cosmetic products. These products are classified into two categories based on their duration in the hair, temporary and permanent. This classification is based on the type of active ingredients used in the dyeing process as well as the dyeing process itself, which is commonly referred to as non-oxidative and oxidative hair dye products. Because of the various side effects described for these active cosmetic ingredients, some have been prohibited in recent years, while others have been restricted under the different legislations. [1]

The hair colorant industry is currently under intense pressure to develop economical, natural hair dyes. Although it has not yet been commercialized, there may be some potential for using DOPA (3,4 dihydroxyphenylalanine), which when oxidized yields a natural brown dye. Natural red pigments (pheomelanins) can be formed from DOPA in the presence of cysteine, and the presence of sulfur-containing nucelophile (rather than cysteine) can expand the range of hair color shades even further. Although basic atmospheric oxygen can be used, hydrogen peroxide is a better oxidizer in this case. If potassium ferricyanide is added, brown colors can be deepened to intense blacks.

In developed countries, 70% of women dye their hair at least once, and many do so frequently.[2] Some hair colors contain heavy metal impurities, including lead, arsenic and others causing their adverse effects including allergic contact dermatitis, cancer and other systemic diseases.[3]

Modern hair dyes are classified as permanent (or oxidative), semi-permanent, and temporary. Permanent hair dyes, which make up about 80% of currently marketed products, consist of colorless dye “intermediates” (chemicals called aromatic amines) and dye “couplers.” In the presence of hydrogen peroxide, the intermediates and couplers react with one another to form pigment molecules. Darker colors are formed by using higher concentrations of intermediates. Semi-permanent and temporary hair dyes are non-oxidative and include colored compounds that stain hair directly. Over 5,000 different chemicals are used in hair dye products, some of which are reported to be carcinogenic in animals [4–6]. Because so many people use hair dyes, scientists have tried to determine whether exposure to the chemicals in hair coloring products is associated with an increased risk of cancer in people.

Heavy metals have been reported to affect cellular organelles and components such as cell membrane, mitochondrial, lysosome, endoplasmic reticulum, nuclei, and some enzymes involved in metabolism, detoxification, and damage repair. Moreover, metal ions interact with cell components such as DNA and nuclear proteins, causing DNA damage and conformational changes that may lead to cell cycle modulation, carcinogenesis or apoptosis. Numerous studies have demonstrated that reactive oxygen species (ROS) production and oxidative stress play a key role in the toxicity and carcinogenicity of metals such as arsenic, cadmium, chromium, lead and mercury. Due to their high degree of toxicity, these five elements rank among the priority metals that are of great public health significance. According to the United States Environmental Protection Agency (U.S. EPA), and the International Agency for Research on Cancer (IARC), these metals are also classified as either “known” or “probable” human carcinogens based on epidemiological and experimental studies showing an association between exposure and cancer incidence in humans and animals.[7]

Hair and nails are biomaterials primarily composed of fibrous protein structure, notably keratin. The changes in their appearance and composition are visible signs of deficiency or presence of stored substances in the body. Therefore, they have been recognized as valuable tissues for monitoring human environmental exposure. The amount of elements in human hair and nails is a good alternative indicator of public and occupational exposure to natural radionuclides and other metals that can reflect the actual exposure over a long period of months, or even years.[8] Therefore, nail tissue is more attractive diagnostic tool in assessing heavy metals, as it is an economical method and not susceptible to infections and contamination.[9] Also, Hair analysis is inexpensive and fast; it also detects and measures the content of heavy metals and minerals of the hair. The Global Environmental Monitoring System (GEMS) of the United Nations Environment Program selected human hair as one of the important monitoring materials for worldwide biological monitoring of pollution. [10]

Hair has the potential of being an excellent bio-monitor due to its historical representation of intake over prior weeks to years and can be utilized for investigating the exposure of individuals or populations to toxins and pollutants, such as heavy metals. The analysis of hair for metal content reveals environmental exposure [11, 12] and is informative of the environmental contamination since it was shown in many cases a positive relationship between soil/water and air content and the internal content of many metals in the hair of exposed populations. [13-15]

For most metals, their accumulation in hair reflects the accumulation in the whole body [15-17]. There are exceptions like Cu and Zn, whose accumulation in hair may be regulated by the organism and are not therefore indicators of environmental exposure. [15] Many studies have shown a correlation between heavy metals concentration in hair and blood [18]. Most trace elements (Cd, Cr, Ni and Pb) have higher concentration in hair than other body compartment, which helps in the analytic process. [14] Hair sampling is a not invasive procedure and allows collecting high number of samples that can be stored easily. The multi-elemental analysis by ICP/MS, in appropriate methodological conditions, allows for the determination of internal metal content in the hair. [19, 20]

The main goal of the present work is to assess hair as bio-indicator of heavy metals contamination by hair dye exposure and estimate the levels of heavy metals (arsenic, cadmium and lead) in different dyed hair samples.

Material and methods

Chemicals and instrumentation

Glass wares, a Microwave oven used for experiments, some storage bottles of 5,10 and 50 ml, wash bottles, 2 ml serological pipettes and pipette pump determined by inductively coupled plasma mass spectrometry ICP- MS Made-in-china were used for measurements and digestion performed under inert atmosphere. Analytical balance, distilled water, and tools commonly used in laboratories. Analytical grade nitric acid (65 %, density 1.512 g/mL) from Merck (Germany), hydrogen peroxide H2O2of 30% from Merck (Germany).

Sample Preparation

Eight dyed hair samples were taken for women aged from 25 to 45years, in the areas around Murzuq (southeast Libya). The sampling of hair was done on the nape of the neck including the nearest 2-3 cm from the skin, and considering an average growth rate of the hair between 0.6 and 3.6 cm/month, we measured the amount of metals incorporated during the previous 3 maximum 4 months, thus from middle August to middle December 2021, date of the sampling.

Analytical Method

A (0.5 g) of the prepared sample was accurately weighed by using analytical balance, Wash hair samples first with acetone, and then several times with distilled water, then drying in oven for 24 hours, at a temperature of 70°C. (0.23g) of hair, samples were taking after drying in an empty crucible.

A mixture of 4 mL nitric acid (65%) and 2 mL of 30% hydrogen peroxide was added and the samples placed in the microwave for 15 minutes at 110°C. allowed to cool to room temperature for 30 minutes, and then add (24ml) of diluted nitric acid (1m) to each sample, then add acid until the size reaches (30 ml). The digest was diluted to 50 mL and ready for ICP-MS analysis. For analysis of As, Ba, Cd, Cr, Zn, and Pb.

Results and discussion

The data presented in **Table 1** revealed that the measured heavy metals (As, Ba, Cd, Cr, Cu, Pb, and Zn) levels were significantly high in almost all hair samples.

Table1 Concentration of selected elements in mg/kg (ppm) for dyed hair samples

sample	As	Ba	Cd	Cr	Cu	Pb	Zn
	Concentration (ppm)						
F1	2.31	1852	0.69	2.76	13.77	5.58	138.0
F2	2.04	839.8	<0.002	2.12	22.1	4.19	240.6
F3	4.18	974.4	3.73	5.80	16.34	16.7	133.5
F4	3.03	3729	0.27	3.25	25.8	11.8	109.6
F5	3.67	34.09	1.91	3.69	21.6	52.8	220.1
F6	1.61	24.24	<0.002	3.14	20.6	13.4	258.6
F7	1.18	27.28	<0.002	2.08	34.9	9.36	147.8
F8	2.14	15.22	<0.002	2.10	13.0	5.26	129.7

As showing in **Figure 1** Arsenic in all hair samples was detected in concentrations ranging from (4.18 to 1.18 ppm). Witch significantly much higher than that found by (Amira et al. 2016) [21] witch was (1.6ppm), and similar to (Samanta et al., 2003), [23] at (3.43ppm).

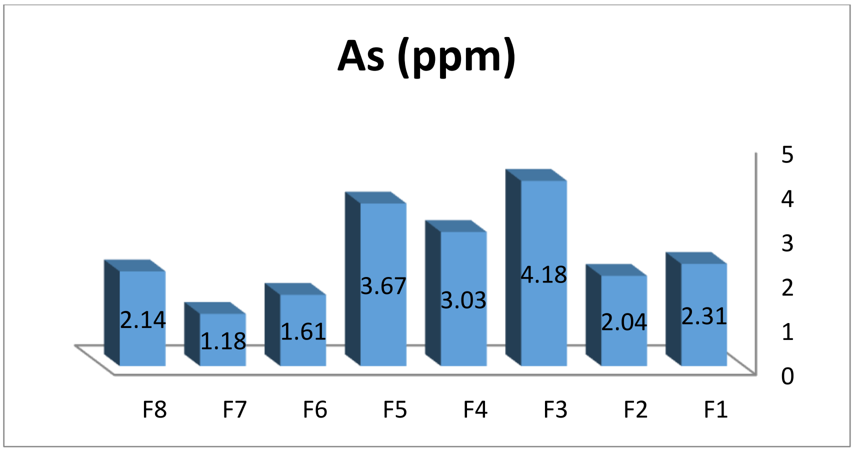

Figure 1: Level of Arsenic in Dyed Hair samples

Figure 2 below showed that the Barium was found in all hair samples, the highest level of Ba was in sample (F6 = 258.6ppm), and the lowest (F4 = 109.6 ppm).

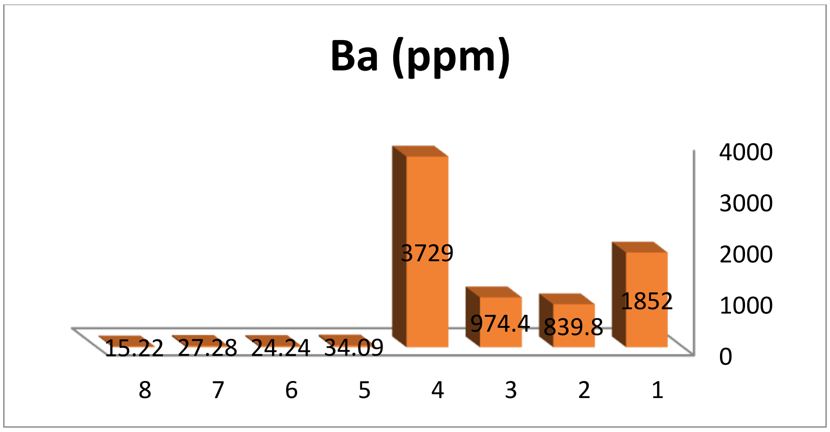

Figure 2: Level of Barium in Dyed Hair samples

Barium (Ba) is found in chlorides, in nitrates and sulfides, and can be toxic. Persistent elevated levels of hair Ba are often a result of diagnostic medical tests. Ba side effects are similar to those caused by chlorine exposure. Elevated Ba causes the following health symptoms: tingling in the arms and legs, skin irritation, difficulty breathing, muscle twitches, increased heart rate. [22]

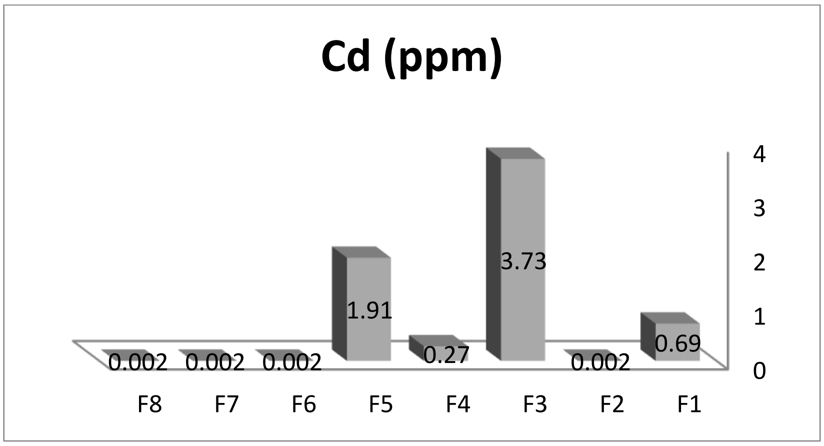

Figure 3: Level of Cadmium in Dyed Hair samples

Cadmium in hair samples F3 was the highest at 3.73 ppm, and F5 at 1.91 ppm, witch higher than (Amira et al. 2016) [21] (0.36ppm) and (Samanta et al., 2003),[23] at (0.40ppm).

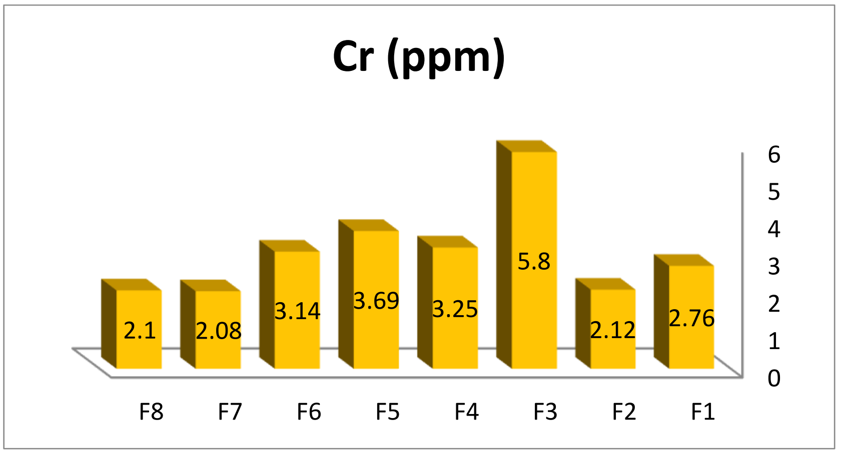

Figure 4: Level of Chromium in Dyed Hair samples

The level of Chromium was the highest in sample F3 at (3.73ppm) which is higher than (Chojnacka, K, at el, 2005)[24] at 1.04mg/kg, and (Senofonte, O, 2000) [25] 2.17 mg/kg.

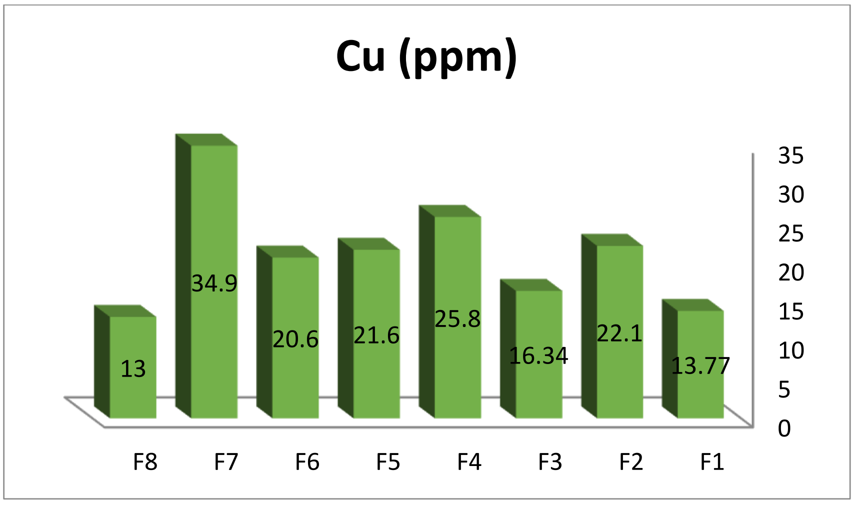

Figure 5: Level of Copper in Dyed Hair samples

Figure 5 Shown that all hair samples contain high levels of copper, the highest was in F7 at (34.9ppm), and the lowest was F8 at (13.0ppm).

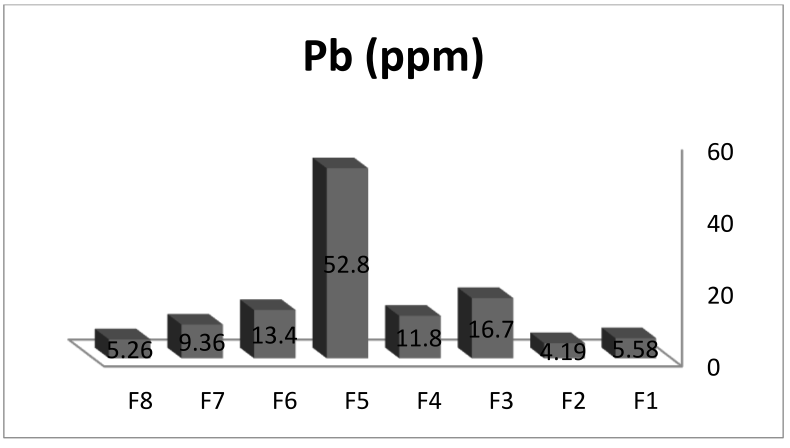

Figure 6: Level of Lead in Dyed Hair samples

Lead is one of the highest heavy metals used in hair dye products and it accumulates in hair, nails by constant usage, and creates severe damages to human body.

The level of lead was the highest in sample F5 at (52.8ppm) which higher than (Amira et al. 2016) [21] at (31.61ppm), and (Abdulrahman et al., 2012), [26] at (31.22ppm).

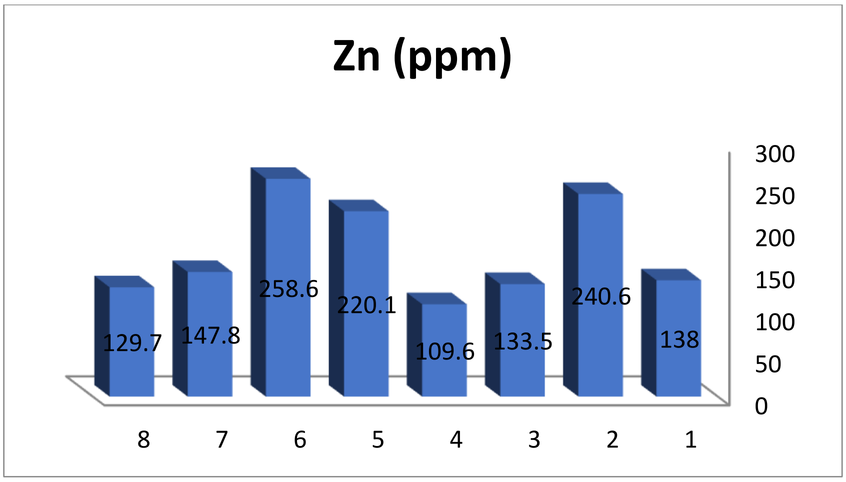

Figure 7: Level of Zinc in Dyed Hair samples

Figure 7 shown that all hair samples contain high levels of Zinc, the highest was in F6 at (258.6ppm), and the lowest was F4 at (109.6ppm).

Conclusion

Assessing hair as a bio-indicator of heavy metals is the aim of this study by hair dye exposure, and estimate the levels of heavy metals and their possible harmful effects on women's health. According to the present results, a high concentration of all metals tested was found on all dyed hair samples except cadmium that was detected in only four samples. The constant use of hair dyes and coloring products contaminated with such toxic metals could cause severe damage to health.

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