

**DETERMINATION OF TYPICAL HEAVY METALS IN HAIR DYES BRANDS
SELECTED FROM LIBYAN MARKETS**¹Wafa Khalleefah Amhimmid, ²Salha Ali Fatah and ¹Sarra Sharef Altabeeb¹Chemistry Department, Azzaytuna University, Tarhuna, Libya.²Chemistry Department, Sebha University, Taraghun, Libya.***Corresponding Author: Wafa Khalleefah Amhimmid**

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ABSTRACT

Heavy metals exist in our environment, making it difficult to avoid their presence and impact on the human body. Heavy metal toxicity in humans is caused by long-term or high-level exposure to pollutants found in the environment, including the air, water, food, and many consumer products such as cosmetics, one of which is hair dyes. We measured the levels of toxic metals in different hair dye products sold at local shops in Tripoli, Libya, for this study. Five hair dyes were selected as popular brands in Libyan markets. Wet digestion was used to prepare the samples. And the analysis of heavy metals was done by the ICP-MS. Heavy metals such as Cd, Pb, Cu, Cr, Ba, As, and Zn were detected in all of the hair dye samples tested. The concentrations of heavy metals in the analyzed hair dyes varied. Also, low concentrations of toxic heavy metals Pb and Cd were detected in all samples. However, these heavy metals are strictly prohibited from being used as a material (EU Directive No. 1223/2009) in the production of cosmetic products, including hair dyes. The majority of the concentrations were above acceptable cosmetic levels. Heavy metals have been shown to cause toxicity in the human body, even at low levels, highlighting the need to strengthen control over cosmetic products by the competent authorities in Libya.

Index Terms - Heavy metals, Hair Dye, Toxic Levels, ICP-MS.**1. INTRODUCTION**

Heavy metals are the most serious threat to human health. These metals have been extensively researched, and their effects on human health are regularly reviewed by international bodies such as the World Health Organization (WHO). Heavy metal exposure continues to occur despite the fact that several adverse health effects of heavy metals have been known for a long time. Toxic elements, even at a low concentration, can be extremely harmful if consumed for an extended period of time.^[1] Heavy metals are widely available in our environment, making it difficult to avoid their presence and impact on the human body. Some heavy metals are necessary for the human body, but only in small amounts.^[2]

Heavy metals are known to be present in many cosmetic products, including hair dyes, which can enter the body through the skin and root of the hair. As a result, if they are present in high concentrations in the body, they can cause a variety of health problems.^[3] It is thus more important to determine the content of heavy metals in hair dyes by using different types made by different manufacturers. The complexity of commercial hair dye formulas, with dozens of components and formulas that differ between manufacturers, In general, hair dyes

contain dyes, antioxidants, modifiers, alkalizes, ammonia, soaps, fragrance, wetting agents, and a variety of other chemical materials that are used in small amounts to transfer special qualities to hair (such as softening the tissue) or to give the dye a desired process (such as making it more or less durable). Typically, dye chemical materials contain amino compounds and appear on hair dye component lists with names like 4-amino-2-hydroxytoluene and m-Aminophenol. Metal oxides, such as titanium dioxide and iron oxide, are frequently used as pigments.^[4,5]

Cosmetics and hair dye have been identified as heavy metal pollution resources. The dyeing of hair can change the content of heavy metals in hair, but the degree of effect varies by element.^[6]

For many years, scientists suspected that hair dye could cause cancer, particularly in women who used darker colors. In fact, some studies have found that using hair dye on a regular basis may increase the risk of non-Hodgkin's lymphoma and multiple myeloma. Despite scores of studies, the findings linking hair dye to cancer were frequently contradictory and inconclusive until now.^[7]

According to new research published in the American Journal of Epidemiology, women who have spent years coloring their hair are at a higher risk of developing non-Hodgkin's lymphoma, a cancer of the lymph system that kills roughly half of all victims. The dye's main ingredients are paraphenylenediamine, resorcinol, propylene glycol, sodium ethylene diamine tetraacetic acid (EDTA), preservatives, and perfumes. Paraphenylenediamine (PPD) is the main toxin responsible for the toxicity.^[8]

Heavy metals can seriously poison enzyme systems, increase free radical production, and displace or mix them with necessary elements that make up metallo-enzyme mixtures, as well as combine them with nutritional mineral imbibitions, as lead acetate is used as a color additive in "gradualist" hair dye products. These products are applied over a specific period to achieve a gradual coloring effect.^[9]

Lead levels in the body will either rise in tissues, particularly bone tissues, as well as in the kidneys, liver, pancreas, and lung tissues^[10], Pregnant women and young children are specifically vulnerable because lead can easily cross the placenta and enter the fetal brain.^[11] It can also be easily transmitted to infants through breastfeeding (Agency of Toxic Substances and Disease Registry.^[12] Lead stored in bone also serves as a source of fetal lead exposure.^[13]

Cadmium is used in cosmetics products due to its color property, as it has been used as a color pigment in many industries^[14], cadmium is absorbed into the body, accumulating in the kidney and liver. In Practice, it can be found in almost all adult tissues.^[15]

If the body is exposed to long-term copper exposure, whether it is carcinogenic or not, it causes vexation of the nose, mouth, and eyes, as well as headaches, stomachaches, dizziness, vomiting, and diarrhea. Copper poisoning, both intentionally and unintentionally, can cause liver and kidney damage, and even death. Several scientific articles have been published that suggest a link between long-term exposure to high concentrations of copper and a decrease in intelligence in young teenagers. Wilson's disease caused by chronic copper poisoning includes hepatic cirrhosis, brain damage, demyelization, and renal disease.^[16]

The European Commission adopted Directive 2012/21/EU, which limits the use of about 45 chemicals

in hair dyes, as well as EU Directive 76/768/EC for make-up and Regulation (EC) No. 1233/2009, to ensure that hair dyes contain only safe substances.^[17,18] Most commercial hair dyes have complicated formulas containing dozens of ingredients, and formulas differ greatly between manufacturers. In general, hair dyes contain dyestaff, modifiers, antioxidants, alkalizers, soaps, ammonia, wetting agents, scents, and a variety of other chemicals used in small amounts to impart special qualities to the hair (such as softening texture), the majority of which contain heavy metals.

Many analytical atomic spectrometry methods are available for element determination, including flame atomic absorption spectrometry (FAAS), glow discharge atomic absorption spectrometry (GD-AAS), graphite furnace atomic absorption spectrometry (GF-AAS), flame atomic emission spectrometry (FAES), glow discharge atomic emission spectrometry (GD-AES), inductively coupled plasma atomic emission spectrometry (ICP-AES), glow discharge atomic fluorescence spectrometry (GD-AFS), inductively coupled plasma atomic fluorescence spectrometry (ICP-AFS), glow discharge mass spectrometry (GD-MS), and inductively coupled plasma mass spectrometry (ICP-MS) have been used for many years for the determination of elements since they meet the needs required in analytical applications.^[19,20]

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was used in this study for the analysis of seven heavy metals (As, Ba, Cd, Cr, Cu, Pb, and Zn) in hair dyes due to its high sensitivity, low detection limit, and minimal analyte loss of interest during digestion processes in the conventional method of (ASS) to evaluate the risks that such cosmetics may pose to consumers.^[21]

2. MATERIALS AND METHODES

2.1 Sample Collection

Five sample of hair dyes brands were bought from different local markets in Tripoli, Libya. To determine the concentration of heavy metals. Samples were numbered from C1 to C5 according to Table 1.

Table 1.2: Samples of hair Dyes from different manufacturers.

Sample	Brand	Color	Manufacturer	Origin
C1	vatika	Dark brown	Dabur Vatika	India
C2	Beauty M18	Black	SOLVEX Cosmetic	Bulgaria
C3	Soyss	Black	Schwarzkopf &Henkel	Germany
C4	Garnier Color Naturals	Dark blond	Loreal group	Turkey
C5	Beauty Colour SENSE S03	Light brown	SOLVEX Cosmetic	Bulgaria

2.2 Chemicals and Reagents

Analytical grade Hydrochloric acid (72%, Sigma Aldrich) and nitric acid (65%, Sigma Aldrich) were used to prepare the samples. All of the solutions were prepared in double distilled water.

2.3 Sample Digesting

Samples were wet digested with a 4:1 mixture of nitric acid (65%) and hydrochloric acid (70–72%) on a hot plate in fuming hood near to dryness by slowly increasing the temperature for 2–3 h because oily compounds are exothermic and burns with flame. If brown or black color appeared the same procedure was repeated by slowly and continuously heating the mixture

of concentrated acid until the evolution of white fumes) indicating the end of the digestion process) and close to dryness. The solutions were allowed to cool before being filtered into a calibrated flask (100mL) by whatman no. 42, and were diluted up to the mark with distilled water and ready for ICP-MS (NexIon™, China) analysis.^[22]

3. RESULTS AND DISCUSSIONS

Table 2. gives the analysis of the concentrations of heavy metals in 7 hair dyes samples from various origins and markets in Tripoli.

Table 2.3: Heavy metals concentration in hair dyes samples.

Sample	Concentration (ppm)						
	Pb	Ba	Cd	Cr	Cu	As	Zn
C1	1.97	8.58	0.06	42.9	7.19	5.14	17.2
C2	5.85	4.39	0.25	1.48	1.24	2.23	5.83
C3	2.23	1.54	<0.002	1.18	1.77	1.77	5.60
C4	2.14	1.73	<0.002	1.23	0.99	2.79	7.61
C5	73.1	1.00	<0.002	0.70	0.79	1.27	5.36

The concentrations of seven metals (Arsenic, Barium, cadmium, Chromium, copper, lead, and Zinc) were measured in five hair dye samples. All of the products contained lead in concentrations ranging from (1.97 to 73.1) ppm, with highest concentration obtained in Beauty Colour SENSE S03. and the lowest concentration obtained in Vatika. The Centers for Disease Control and Prevention (CDC) and many other experts agree that lead exposure is not safe at any level [23-25], The FDA has set limits for lead as an impurity in color additives as part of the requirements for their safe use. Typically, the allowed levels range from 10 to 20 (ppm).

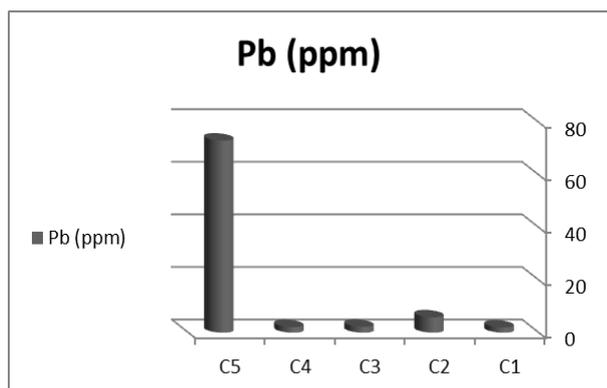


Figure 1: Levels of Lead in different brands of hair dyes.

Second dangerous ingredient present is heavy metal Barium in the form of Barium Peroxide is used in henna based hair dye (such as poor quality Black Henna) preparations as an oxidizing agent. Barium is a known poisonous ingredient that is also an irritant to the eyes and skin. This action severely weakens and damages the hair cuticle. In muscular systems, this metal causes

vasoconstriction, hypertension, and toxicity.^[26,27] We found that the range of this element in samples studied was between 1- 8.58ppm.

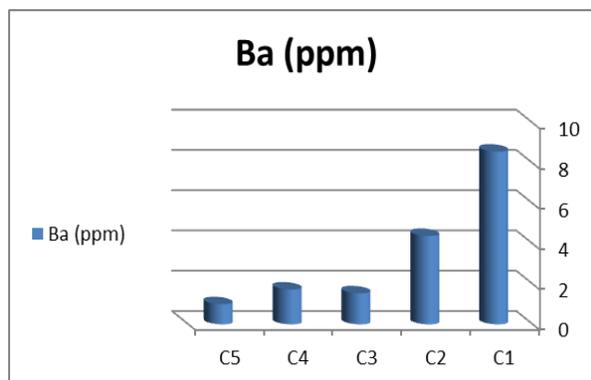


Figure 2: Levels of Barium in different brands of hair dyes.

Cadmium was detected in small amounts in most samples, ranging from (0.002_0.25) ppm, despite the fact that cadmium was present in trace amounts. The available data on Cd in cosmetics places the permissible limit at 3 ppm (3mg/kg) and 5 ppm (5 mg/kg) for Canada and Germany^[28] respectively, but the slow release of cadmium with low amounts may also cause harmful effects to the human body, with tests showing that minor exposure caused high blood pressure. As a result, even trace amounts are hazardous. It attacks blood vessel and heart tissue, as well as the kidneys, lungs, and brain, causing heart disease, hypertension, and liver damage.^[29]

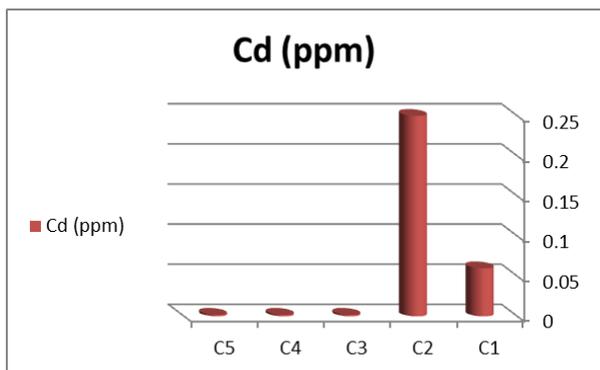


Figure 3: Levels of Cadmium in different brands of hair dyes.

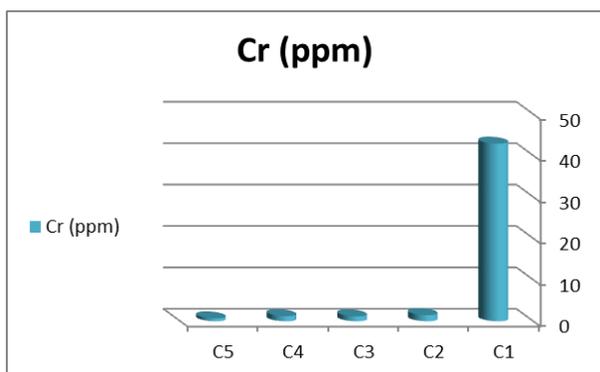


Figure 4: Levels of Chromium in different brands of hair dyes.

There is no regulation that limits the use of chromium in cosmetics, although the listing regulation for the color additive FD&C Blue No. 1 limits chromium as an impurity to 50 ppm.

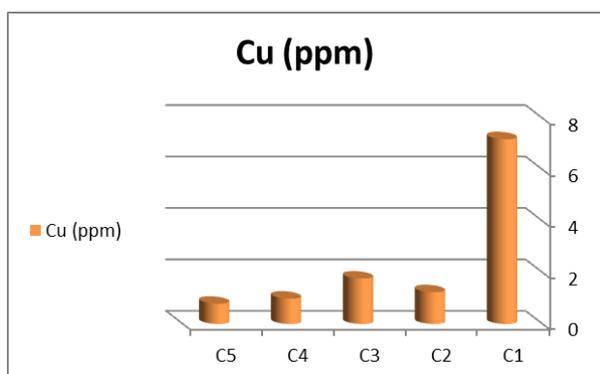


Figure 5: Levels of Copper in different brands of hair dyes.

All samples contain copper, the highest concentration obtained in Vatika-Black sample was 7.19 ppm and the lowest concentration which in Beauty Colour SENSE S03 was 0.79 ppm, Exposure to Cu could endanger the liver and cause Wilson's disease and insomnia.^[30] Furthermore, this Cd-containing metal may cause digestive disorders, diarrhea, tremor and ataxia, depression, and paralysis.^[31]

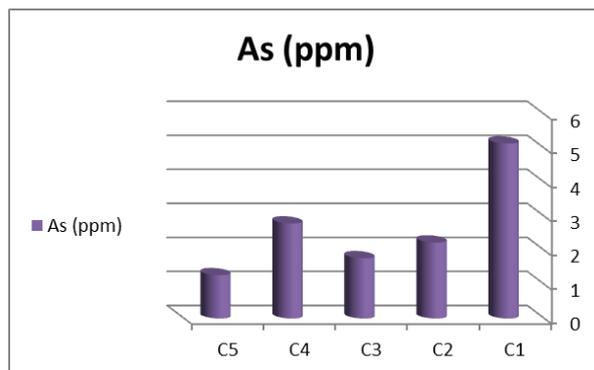


Figure 6: Levels of Arsenic in different brands of hair dyes.

Arsenic in all samples was detected, the highest concentration was obtained in Vatika 5.17 ppm above the limit (3 ppm) according to FDA.

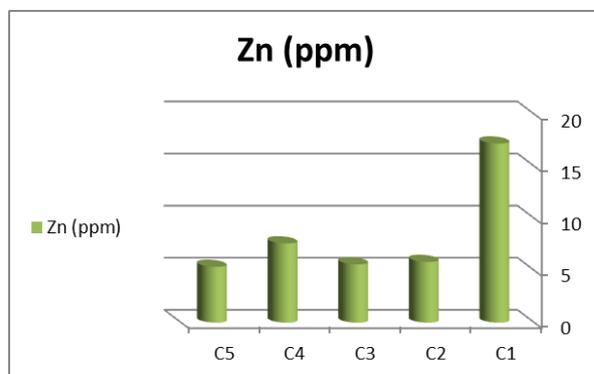


Figure 7: Levels of Zinc in different brands of hair dyes.

Hair dyes contain zinc combined with hydrogen peroxide, and other compounds or mixtures that release hydrogen peroxide, including carbamide peroxide as zinc peroxide. All samples contain zinc in different concentrations, the highest concentration (17.2ppm) obtained in Vatika, exceeding the FDA limit of 12ppm. Excessive Zinc exposure can be toxic. It is extremely rare to have high hair Zinc levels, which could indicate a zinc overload. gastrointestinal disorders, decreased heme synthesis (copper deficiency), tachycardia,, blurred vision, and hypothermia are all symptoms of zinc excess.

4. CONCLUSION

Heavy metals of Cd, Pb, Cu, Ba, Cr, Zn and As were found in all hair dye samples tested. The heavy metal content of hair dyes varied, but there was no significant difference in heavy metal concentration between dyes from different manufacturers. Heavy metal content in hair dyes was regulated in the EU by Directive; Regulation (EC) no 1223/2009 of the European Parliament and of the council, on cosmetic products, Hair dyes that produce darker shades of hair contain higher content of heavy metals than those that produce lighter shades.

low concentrations of toxic heavy metals Pb and Cd were detected in all of the analyzed samples, however, these heavy metals were strictly forbidden from being used as raw materials (EU Directive No 1223/2009) for the production of cosmetic products, including hair dyes, thus, these cosmetic products should not be used.

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