

Heavy Metals Determination in Hair Dye Samples Selected from Iraqi Markets

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ABSTRACT

Heavy metals play an important role in human organism and are called essential metals, while others are not known as being useful for our health, or more precisely they are toxic. High concentrations of heavy metals may cause health problems. Hair dye (K303/66, K303/4 and K307/1) were selected as common brands in Iraqi markets. All these samples were treated with digestion acids (2.5:1 nitric acid: hydrochloric acid) to free the elements from organic components in order to be tested as prepared solutions in atomic absorption. EDX analysis for hair dye samples shows that there was a large proportion of the sulfur element and none of the toxic and health-related elements in the selected samples. Atomic absorption analysis shows that the method of acid digestion by means of a mixture of nitric acid to hydrochloric acid was not effective enough to dissolve all the elements as evidenced by the presence of some elements in the precipitation resulting from acid digestion. Several treatments may be needed to insure the optimum extraction for the elements from the selected samples.

Keywords: Heavy Metal, Hair Dye, Henna, Toxic Element

INTRODUCTION

Heavy metals are a term that covers a group of elements with similar chemical properties. Some of them, including copper, iron, zinc, play an important role in human organism and are called essential metals, while others are not known as being useful for our health, or more precisely they are toxic. High concentrations of heavy metals may cause health problems [1]. Hair, just like the fat tissue, is the organism's storage of toxic and other matters, and the longer the hairs, the longer the period over which the analysis can determine the organism's status. Hair analysis is very important because it indicates the actual status of organism and the actual nutritional status, as well as the quantity of stored and accumulated toxins, all of which can be reliably determined only by the hair mineral analysis [2]. Hair is employed as a biomarker of environmental and occupational exposure to essential and trace elements [3,4].

The definition of a cosmetic identifies the site of application (epidermis, hair system, nails, lips, eyes) and the intended functions (cleaning, perfuming, changing the appearance, correcting body odors, protecting and, keeping in good condition) [5]. Herbal cosmetics are the valuable products consist of botanicals or their bioactive ingredients/extracts which enrich the skin with

trace (nutrient) elements and other useful minerals, prevent from infection and hence responsible for their cosmetic effects. Although they are used worldwide since ancient time, but in the last decade, there has been a renewed craze of herbal cosmetics and personal care products, especially in the skin care segment with the growing belief that chemical-based cosmetics are harmful and herbal cosmetics are safe being natural [6, 7]. According to the World Health Organization (WHO), heavy metals concentration of herbal medicines must definitely be controlled [8]. But WHO is silent regarding the maximum permissible limits of heavy metals in herbal cosmetics. In this case, Health Canada has taken the initiative and implemented a few measures to control heavy metal concentration in cosmetics and determined the maximum acceptable limits i.e. Lead (10ppm), Arsenic (3ppm), Mercury (3ppm), Cadmium (3ppm) and Antimony (5ppm). Cosmetic and hair dye has been one of the pollution resources of heavy metals. Dyeing hair can change the content of heavy metals in hair, but the degree of effect is different for different element: contents of Mn, Fe, Ni, Cu, Cd and Sb in hair of dyed group were higher than that of non-dyed group, but contents of As, Cr, Zn, Ag, Pb and Hg were lower. The cause of the above results could be that hair dye contains

more Mn, Fe, Ni, Cu, Cd and Sb, but less As, Cr, Zn, Ag, Pb and Hg, and dyeing hair could restrain the metabolism and excretion of As, Cr, Zn, Ag, Pb and Hg from human body [9]. For years, researchers believed that hair dye could cause cancer, especially in women who used the darker colors. In fact, some studies even showed that using hair dye repeatedly could increase the risk of non-Hodgkin's lymphoma and multiple myeloma. But, despite scores of studies, the results linking hair dye to cancer were often contradictory and inconclusive until now. New research in the American Journal of Epidemiology has found that women who have spent years coloring their hair do indeed run a greater risk of developing non-Hodgkin's lymphoma, a cancer of the lymph system that claims about half of all its victims. The main ingredients of the dye are paraphenylenediamine, resorcinol, propylene glycol, sodium ethylene diamine tetra acetic acid (EDTA), preservatives, and perfumes. The main compound responsible for the toxicity is paraphenylenediamine (PPD) [10]. While many people use coal-tar hair dyes, FDA (U S Food and Drug Administration) is aware of the following problems: Eye injuries, Hair dyes have caused eye injuries, including blindness, when used in the eye area. Eyebrow and eyelash dyeing are not permitted uses of coal-tar hair dyes. Color additives approved for use on hair include henna (from the Lawsonia plant) as well as lead acetate and bismuth citrate, both of which are used in "progressive" hair dyes that darken hair gradually with repeated applications. The chemicals in hair dye may include ammonia, ethanolamine, sodium carbonate, hydrogen peroxide, p-phenylenediamine, toluene diamines, naphthylamine, and other chemicals. Some of the heavy metals in hair coloring agents may include lead, mercury, silver, bismuth, and arsenic causes of hair dye poisoning [11]. Data available in the literatures shows that toxic metals are present in various types of cosmetics at concentrations varying within relatively wide ranges from almost undetectable values to as high as 3.76 g Pb kg⁻¹ in lipsticks [12] or sometimes even higher in body care products (790 g Pb kg⁻¹; CDC, 2005), 65.133 g Hg kg⁻¹ in skin-lightening creams, 6.259 g Cd kg⁻¹ in kohl as well as 50.0 g Al kg⁻¹, 359.44 mg Ni kg⁻¹ and 11.1 mg As kg⁻¹ in eye shadows [13]. Elements such as Ni, Co and Cr are accumulated in the stratum corneum and may cause allergic contact dermatitis, whereas Hg, Pb, Cd and Al pass through the skin layers to blood vessels and are

transported into various organs where they are accumulated and exert toxic effects [23]. Increased Pb, Cd, Hg and Al concentrations in the blood, urine or internal organs noted in individuals in whom the use of cosmetic products was the only source of excessive exposure to these metals confirm their absorption through the skin. Although absorption of these metals by the skin is less effective than by the gas inhalation, some amounts of them may enter the body by this way as a result of the use of cosmetics. Hg enters the skin mainly through appendages [14]. This work aims to determine the toxic metals in popular brands hair dyes available in local cosmetics markets Iraq using (EDX) and atomic absorption instruments for metal detection and determination. This article is mainly concerned with safety matters. Researches on chemical safety has been of interest to the researcher and has published many articles in such subjects, several important recommendations was stated in these articles [15-26].

EXPERIMENTAL PART

Sampling

Three samples of common hair dye brands we select from local markets in Baghdad (K303/66, K 303/4 and K 307/1).

Reagents and Chemicals

Analytical grade nitric acid (65%, Sigma Aldrich) and hydrochloric acid (37%, Sigma Aldrich) were used for sample preparation. Standard solutions for calibration of Magnesium, Zinc, Potassium, Copper, Chromium, Nickel, Cobalt, Cadmium, Lead and Iron were prepared from 1000 mg/l Standard Stock Solution of GFS Fishers' AAS Reference Standard. All the solutions were prepared in de ionized water. Dilution correction was applied for samples diluted or concentrated during analysis.

Hair Dye Acid Digestion

A 0.51g of each hair dye samples were weighted and placed into 25ml conical flask separately. 6ml of 65% HNO₃ with 4ml of HCL was added [27]. The contents were mixed well by stirring thoroughly. The beaker was placed on a hot plate. Heating continued until the contents dissolved, then filtered (use what man filter paper No.41). The filtrate solution diluted with de ionized water to 50ml. The resulting solution was used for spectrophotometric determination of various metal analyses. According to safety rules in chemical laboratory, this procedure was carried out in fume hood.

RESULT AND DISCUSSION

Hair Dye Analysis

Energy-dispersive X-ray spectroscopy (EDS, EDX, or XEDS) Bruker model (XFlash6110), sometimes called energy dispersive X-ray analysis (EDXA), is an analytical technique

used for the elemental analysis or chemical characterization of a sample. Common brands hair dye (K 303/66, K 303/4 and K 307/1) was tested in EDX instrument for elemental determination. Results obtained for this test illustrated in the figures 1, 2 and 3 respectively.

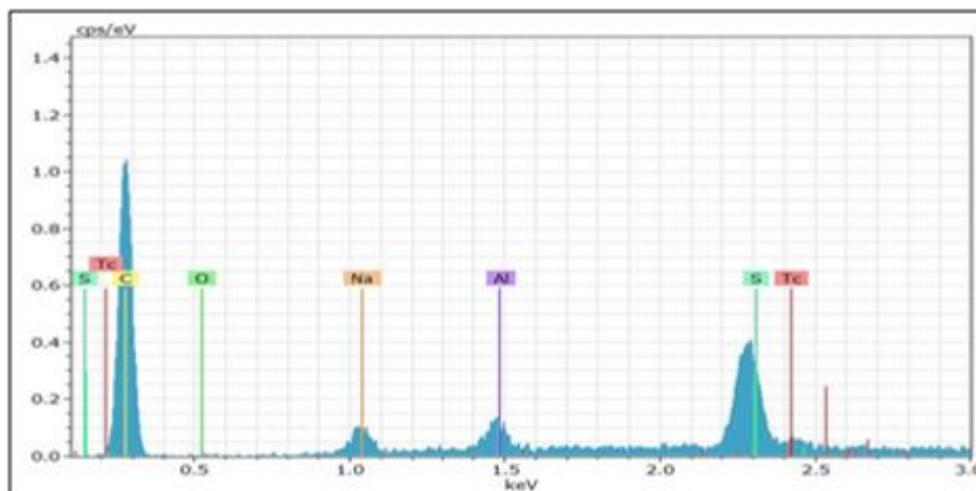


Figure1. EDX spectrum for hair dye brand (K 303/66)

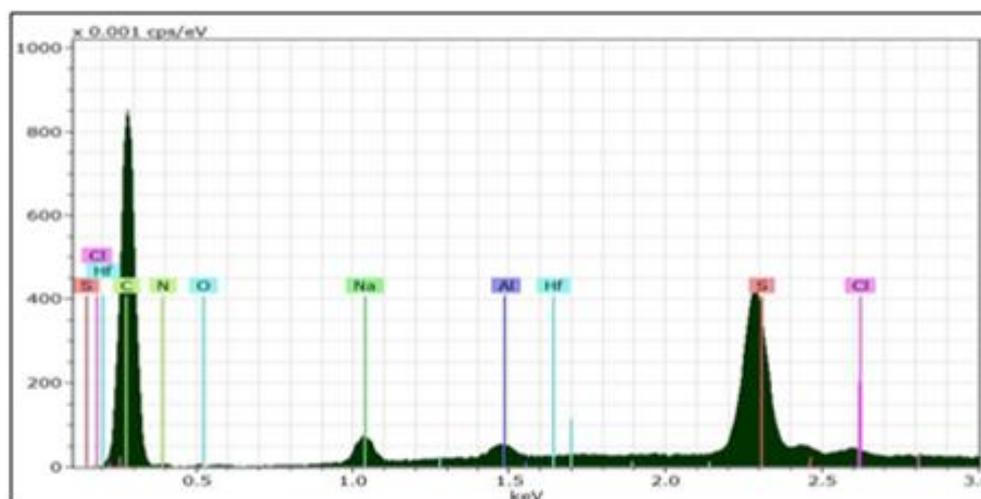


Figure2. EDX spectrum for hair dye brand (K303/4)

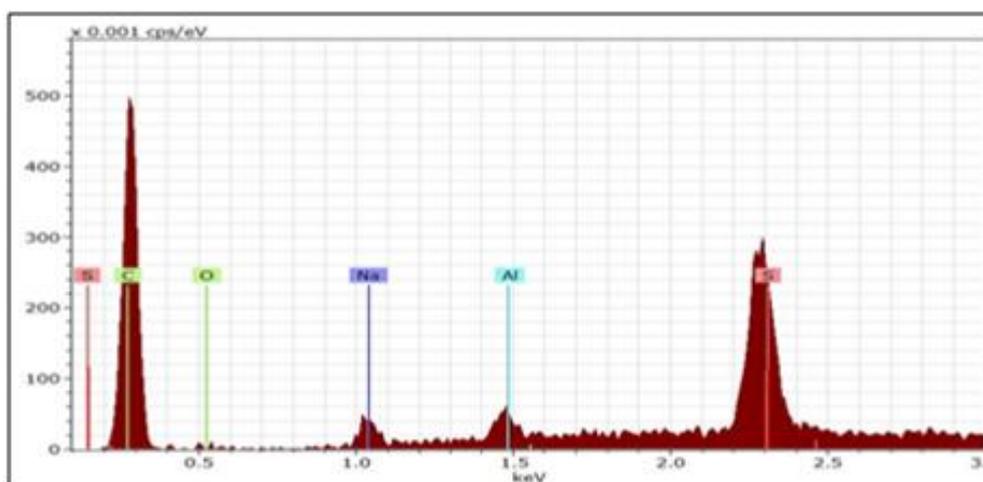


Figure3. EDX spectrum for hair dye brand (K 307/1)

Heavy Metals Determination in Hair Dye Samples Selected from Iraqi Markets

Results obtained for these tests illustrated in the figures 1, 2 and 3 shows the presence of elements: aluminum, sodium and a large proportion of sulfur. In OTC (Over-the-Counter) drug products, Sulfur is used as an ingredient to reduce the number of acne blemishes, acne pimples, blackheads, and whiteheads, and to help to control dandruff, seborrheic dermatitis, and psoriasis. In cosmetics and personal care products Sulfur is used to enhance the appearance and feel of hair, by increasing hair body, suppleness, or sheen, or by improving the texture of hair that has been damaged physically or by chemical treatment and to enhance the appearance of dry or damaged skin by reducing flaking and restoring suppleness [28].

Sulfur, one of the main minerals found in the human body, plays an important role in the body's overall health and its ability to heal. Sulfur primarily transports oxygen, and thus

aids in cellular regeneration, which is important to the health of skin, nails and hair -- external features of the body become healthier when they are able to consistently regenerate. Therefore, sulfur is often referred to as the (beauty mineral). Any type of cellular regeneration requires the transportation of oxygen, and sulfur is one of only three minerals that facilitate this process. When hair follicles are oxygenated, much needed nutrients are released into the hair shaft, which supports healthy hair growth [29].

Atomic Absorption Analysis

AAS Agilent FS240 model was used in determining the content of heavy metals and its concentration in one kind of the previously acid digested samples. Selected elements were tested using atomic absorption apparatus for the prepared solutions as explained in sec.2. (See table 1,2,3 and 4).

Table1. Some prepared samples with a brief description

Sample No.	Sample description	Extracted solution(ml)
1	Hair dye K303/66 acid digestion	50
2	Hair dye K303/66 acid digestion for ash	60
3	Hair dye K303/66 acid digestion for ppt.	100

Table2. Concentration of selected elements in mg/kg (p.p.m) for some prepared samples

Sample No.	Zn	Pb	Cd	Fe	Mg	Cu	K	Cr	Ni	Co
1	0.45	none	none	2.75	0.50	none	0.23	none	none	none
2	0.43	none	none	10.75	0.60	none	1.17	none	none	none
3	0.04	none	none	1.25	0.21	none	0.17	none	none	none

Table3. Weight of selected elements in (mg) for some prepared samples in the total extracted solutions

Sample	Zn	Pb	Cd	Fe	Mg	Cu	K	Cr	Ni	Co
1	0.023	none	none	0.14	0.03	none	0.23	none	none	none
2	0.026	none	none	0.65	0.04	none	1.17	none	none	none
3	0.004	none	none	0.13	0.02	none	0.17	none	none	none

Table4. Weight % of selected elements for some prepared samples with respect to total sample weight

Sample	Sample wt. (g)	Zn	Pb	Cd	Fe	Mg	Cu	K	Cr	Ni	Co
1	0.51	0.005	none	none	0.03	0.03	none	0.002	none	none	none
2	3.02	0.0009	none	none	0.02	0.04	none	0.002	none	none	none
3	0.15	0.003	none	none	0.09	0.01	none	0.01	none	none	None

From Table-4 we can conclude the following:

The process of Hair dye K303/66 acid digestion(sample-1) refer to the percentage of zinc element higher than the method of burning (sample-2) which indicates the loss of part of the element by burning. When zinc (melt at 419.53 °C) is raised to a high temperature (at or above its boiling point around 900°C), it burns and forms zinc oxide smoke [30]. The presence of elements (Zn, Fe, Mg and K) in large percentages in the precipitate resulting from digestion by acid of Hair dye K303/66 (sample-3) which was further extracted by acid

digestion process for the precipitate indicates that the main digestion process was not very effective.

CONCLUSION

Hair dye (K 303/66, K 303/4 and K 307/1) was selected as common brands in Iraqi markets. These samples were treated with digestion acids to free the elements from organic components in order to be tested as prepared solutions in EDX instrument for elemental determination and atomic absorption. From EDX analysis for hair dye samples two main things can be concluded:

First, there is a large proportion of the sulfur element (Sulfur is used as an ingredient to reduce the number of acne blemishes, acne pimples, blackheads, and whiteheads and to help to control dandruff and psoriasis) and the other, none of the toxic and health-related elements in the selected samples.

Atomic absorption analysis shows that the method of acid digestion by means of a mixture of nitric acid to hydrochloric acid was not effective enough to dissolve all the elements as evidenced by the presence of some elements in the precipitation resulting from acid digestion. Several treatments may be needed to insure the optimum extraction for the elements from the selected samples.

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Heavy Metals Determination in Hair Dye Samples Selected from Iraqi Markets

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