DETERMINATION OF ZINC AND CADMIUM IN ANTI-DANDRUFF SHAMPOOS AVAILABLE AT THE LIBYAN MARKET BY ATOMIC ABSORPTION

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Abstract

The present study is carried out to measure zinc and cadmium in twenty samples of anti-dandruff shampoo products commercially available in the local cosmetic markets in Libya. Detection of zinc and cadmium were done by Flame Atomic Absorption Spectrophotometry (FAAS) method. The results showed that cadmium concentration ranged between 0.017 and 9.37 $mg.kg^{-1}$ while zinc concentration ranged between 25.9mg $kg^{-1}$and 8300$mg.kg^{-1}$. These measurements indicated that cadmium and zinc contents in the investigated samples were higher than WHO limits; suggesting that chronological use of these shampoo products would impose serious health risks to human users. Therefore, quality control and concentration optimism should be implemented to assure the safety of cosmetic products. This also can be achieved by improving the processing and manufacturing practices in the industry.

Keywords: zinc, cadmium, spectrometry, cosmetic shampoos, anti-dandruff

Introduction

Dandruff is a condition in which white scales of dead skin are shed by the scalp. It develops as a natural process of renewing epidermal cells in the skin of the scalp. Dandruff is the remains of dead skin cells that can be replaced by new cells (Amartey *et al*., 2011). The development of dandruff is usually associated with itching and redness to human skin. To overcome this health problem, human use cosmetic and body care products. However, in the last few decades, cosmetic industry has grown rapidly over the world and produced wide range varieties of cosmetics for the care and beautification of the skin, hair, nails, teeth and body. These products can also be found in different forms to meet the customer requirements, such as screams, soaps, powders, lotions, oils, dyes, perfumes and lipsticks (Amartey *et al*.,2011; Iwegbue *et al*., 2015). However, scientific research has shown that these products might have adverse effects on human health. This includes reproduction, neurological and

dermal ailments (Umar & Caleb, 2013: Iwegbuea *et al.*, 2016b). Heavy metal contaminants are responsible for these problems. Heavy metals such as lead, zinc and cadmium are common contaminants in different types of cosmetic products (Nnoromet *et al*., 2005: Chauhan *et al*., 2010). For instance, cadmium is a highly persistent pollutant and categorized by the Agency for Toxic Substances and Disease Registry (2012) as one of the top-ten hazardous chemicals. Metallic compounds in hygienic products, such as shampoos are known for their antidandruff effect. Similarly, zinc pyrithione and selenium sulfides have fungi static and fungicidal action against Pityrosporum, and they play a pathogenic role in seborrhea dermatitis and dandruff. Selenium and cadmium formulations are useful adjuncts in the treatment of *tinea capitis*, a common cause of dandruff. Increased concentrations of zinc pyrithione or and selenium sulfide are restricted to pharmaceutical end points due to their allergic effects on skin (Nnorom *et al*., 2005). For cadmium sulfide, it is toxic and not widely used in cosmetic formulations (Salvador *et al.*, 2000). Therefore, the establishment of content of these metals in cosmetic products is imperative in order to protect human health and to improve the quality of the products. According to the directions set by the European Community Directives (ECD), cosmetic formulations containing more than 1% of selenium sulfide, 0.5% of zinc pyrithioneup, and 1% of other zinc salts are prohibited in the cosmetic industry (Esemedafe & Ogagaoghene 2016; Karimi & Ziarati, 2015). The maximum allowable limit for Cd, as an impurity in cosmetic products is set at 3.0 µg/g in Canada (Health Canada, 2012; Iwegbuea *et al.*, 2017: Dghaim*et al.*, 2015), and 5.0 µg/g in Germany; compared to WHO limit of 0.3µg/g (Iwegbue *et al.*, 2015; Iwegbuea *et al.*, 2017; Faruruwa & Bartholomew 2014). For zinc, WHO recommends the concentrations of 100µg/g and 200µg/g to be used as minimum and maximum allowable limits (BfR, 2006; Iwegbue *et al.*, 2016a)

Experimental Work

Method and Materials

The chemical analysis method used in this study was the flame atomic absorption spectrometry (FAAS). A Varian AA-10 FAAS instrument was used to measure Zn and Cd contents. This spectrometer is widely used in testing antidandruff shampoos as prescribed by previous workers (Iwegbuea *et al.*, 2016c; Faruruwa & Bartholomew, 2014). Other laboratory materials used for the analysis included concentrated nitric acid HNO_3 %65, concentrated sulfuric acid H_2SO_4 %98 and sodium chloride NaCl. All of the materials were of analytical grade quality. The concentration of elements was calculated in mg/kg units using the following equation (Zainy, 2015):

Concentration mg/kg = (Concentration mg/l × volume l ÷ weight kg)……. (Eq. 1)

Sample preparation

Twenty-two antidandruff shampoos of different origin were collected from local markets in Libya. In these samples, zinc content was present in the pyritionateor sulfate form, whereas cadmium content was in the sulfide form. Other components found in the formulations of the samples included ten bioactive, diverse organic polymers, fragrance agents, softening creams, aluminum–magnesium silicate (only in cadmium samples)and water.

The sample preparation done in the lab was in accordance with the procedure undertaken by Bocca *et al.*(2014). A sample fraction of 0.1 g, weighed by an electronic balance, was added to 2ml digestion solution (70% nitric acid, 30% sulphuric acid). The mixture was capped tightly and placed in an oven at 60^{o} C for 12 hours. The mixture then was cooled before a volume of 6 mL distillated water was added to. Finally, 2 mL NaCl solution was added to the mixture.

Results and Discussion

Table 1:Concentrations of heavy metals in some antidandruff shampoos obtainedin the Libyan markets.

Sample NO	Country of made	Zn (mg/kg)	Cd (mg/kg)
1	Algiers	1940	4.5
2	USA	37	3.3
3	India	39	2.9
4	Saudi Arabia	8300	3
5	Tunisia	1560	3.3
6	Turkey	71.1	3.1
7	Malaysia	1436	4.1
8	Tunisia	27	3.5
9	P.R.C	46.4	3.1
10	Libya	34.1	3.7
11	Saudi Arabia	31.3	3.9
12	Turkey	38.5	3.7
13	Germany	32.5	3.5
14	Turkey	26.5	2.9
15	Tunisia	142.2	3.5
16	Turkey	1332.87	0.017
17	Spain	36.2	4.4
18	Italy	25.9	3.5
19	Bahrain	28.9	3.9
20	EU	42.0	3.6
21	Libya	106.68	0.058
22	U.A	40.1	9.37

Table 1 shows the results of the collected samples. The results showed that the sample concentration levels vary between 0.017 to9.37 mg/kg for Cd and 25.9 to

8300 mg/kg for Zn, respectively. For cadmium concentration, the majority of the samples had higher values than the WHO permissible limit (0.3 µg/g), with the highest in sample number 22 and the lowest in sample number16 (Figure 1). For Zn concentration, all of the sample values (25.9 - 8300 mg/kg) exceeded the WHO permissible limit (100µg/g), with the highest in sample number 4 and the lowest in sample number 18. (Figure 2).

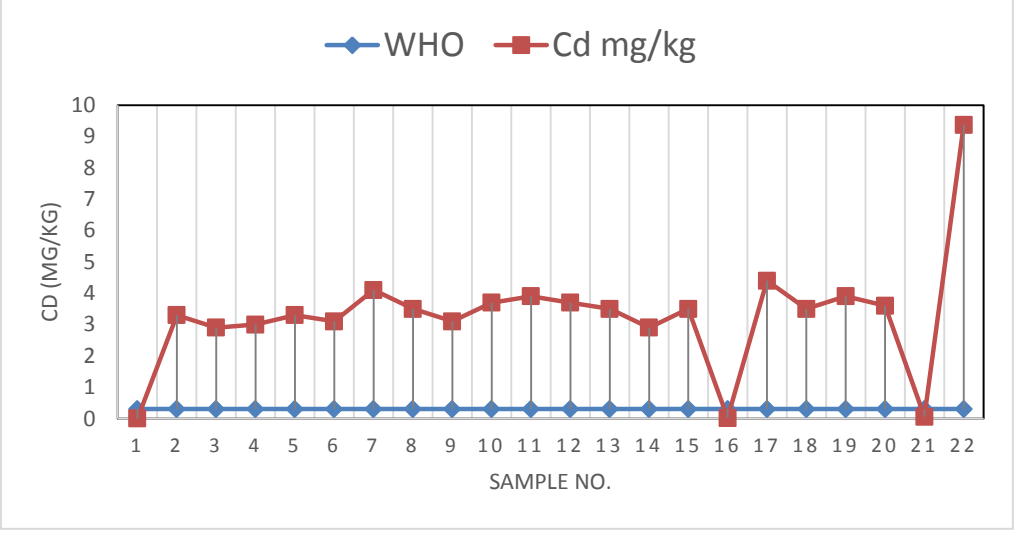


Figure 1: Cadmium concentration in sample antidandruff shampoos compared with WHO limit

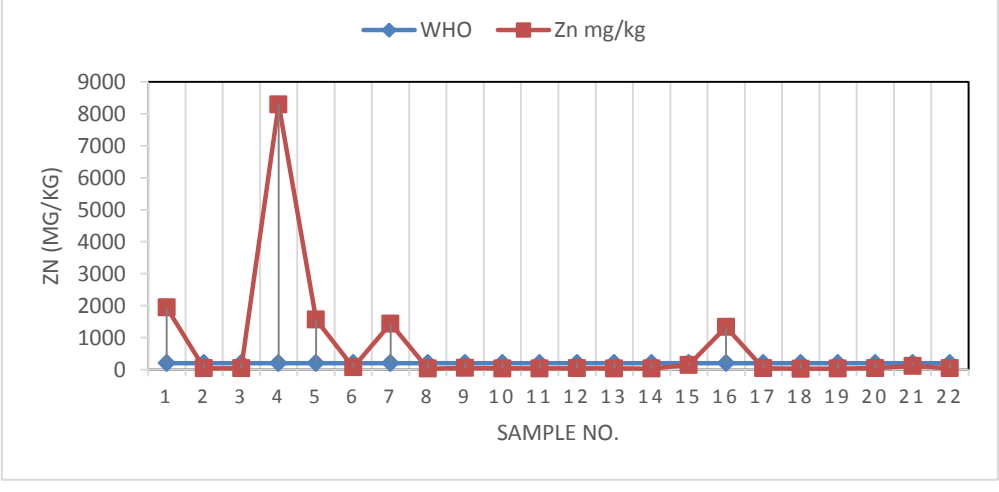


Figure 2: Zinc concentration in sample antidandruff shampoos compared with WHO limit

The results indicated that the obtained Cd concentration was generally higher than the levels found in shampoo products widely marketed in Middle East and Asia

regions (see Table 2). Ullah *et al.* (2013) conducted a FAAS analysis for 15 cosmetic products from imported sources as well as locally manufactured items in Pakistan. The investigated products included three ordinary shampoos, three talc powders, three lipsticks, three kohl samples, and three cream samples. Chauhan *et al.* (2010) investigated shampoo samples by FAAS, and the values ranged between 0.9 and1500μg/g for Zn, and 0.33 and 0.042 µg/g for Cd. Although the cadmium in some of the samples was in trace amount, the chronic exposure to more than 0.005 ppm of Cd might potentially impose risk to human health (Iwegbuea *et al.*, 2016b). However, the severity of Cd hazard exposure depends on multiple factors, such as rate of product use, age, body sensitivity, and others (Ullah *et al.*, 2013; Al-Qutob *et al*., 2013).

Table 2: Comparison of the results of the present study with previous studies in the world

Heavy metal	Concentration range (µg/g)	Product name	References
Zn ,Cd	25.9 to 83000.017 (Zn) 0.017 to 9.37 (Cd)	Antidandruff shampoos	This work
Cd	0.09 to 5.2	Skin whitening creams	ALqadamiet *et al*. (2013)
Cd	0.625 to 1.875	Oily preparations	Sukender *et al.* (2012)
Zn , Cd	0.496 to 1500 (Zn) 0.058to -0.203 (Cd)	Shampoo	Ullah *et al.* (2013)
Zn , Cd	1.600 to 89.500 (Zn) 4.200 to 6.800 (Cd)	Hair pomade	Amartey *et al*. (2011)
Cd	Less than 10 to more than 50	Eye shadow	Nourmoradi *et al.* (2013)
Cd	0.08 to 8.14	Eye shadow	Alsaffar *et al.* (2014)
Cd	0.033 to 0.042	Shampoo	Chauhan *et al.* (2010)
Cd	Less than 0.002 to 3.48	Lip products	Liu *et al.* (2013)
Zn , Cd	18 to 320 (Zn) 3.1 to 8.4 (Cd)	Face Powder	Liu *et al.* (2013)
Zn , Cd	0.7 to 185.0 (Zn) 0.8 to 18.6 (Cd)	Henna	Nouioui *et al.* (2016)
Cd	0.01 to 0.2	Soap	Orisakwe & Otaraku (2013)
Cd	0.0472 to 0.7321	Personal care products	Karimi & Ziarati (2015)
Zn , Cd	28.33 to 342.22 (Zn) 1.67 to 8.89 (Cd)	Personal care products	Faruruwa *et al.* (2014)
Zn , Cd	3.2 to56.57 (Zn)	Personal care products	Ibrahim *et al.*

	0.07 to 3.5 (Cd)		(2016)
Zn , Cd	1.676 to 996.3 (Zn) 0.08 to 0.96 (Cd)	Personal care products	Al-Qutobet *et al.* (2013)
Zn , Cd	17.3 to 372.0 (Zn) 0.25 to 6.3 (Cd)	Skin moisturizing creams	Iwegbue *et al.* (2015)
Zn , Cd	0.7to 2.7% (Zn) 0.75to8.6% (Cd)	Antidandruff shampoos	Salvador *et al.* (2000)
Zn , Cd	25.5 to 1000 (Zn) Less than 0.06 to 3.4 (Cd)	Bathing soaps and shower gels	Iwegbuea *et al.* (2017)
Zn , Cd	30.0 to1080 (Zn) 0.6 to 2.7 (Cd)	Antidandruff shampoo	Iwegbuea *et al.* (2016b)
Cd	2.58 to 6.95	Hair care products	Umar & Caleb (2013)

A wide concentration range of Zn has been reported for cosmetic products in the literature (Iwegbue *et al.,* 2015). For instance, Iwegbuea *et al.* (2016b) reported Zn concentrations of 17.3 – 372 µg/g were detected in skin moisturizing and whitening creams in Nigeria, and30.0 - 1080 µg/g in antidandruff shampoos. The high levels were attributed to the zinc enrichment in the antidandruff formulation agent, which may pose health hazards, e.g., allergy, neurological, gastric ailment (Iwegbuea *et al.*, 2016b; Iwegbuea *et al.*, 2016c). Compared with our study, Zn concentration was comparable with those reported in shampoos tested in Pakistan (Ullah *et al*., 2013) and hair pomades in Ghana (Amartey *et al*., 2011).

Conclusion

The work in this study indicated that the tested antidandruff products available in the Libyan market have Zn and Cd contents higher than WHO limits. When used over long time, these shampoos may impose serious risk on human health. The findings of this study were generally similar to those established in previous works done in different countries. Therefore, there is a need for the establishment of regulations for heavy metals in personal care products, as well as imply some modifications in industry qualities to avoid human users any adverse effects imposed by these products.

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.

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