Original Research

Journal Home page : www.jeb.co.in ★ E-mail : editor@jeb.co.in

Journal of Environmental Biology

JEB™

ISSN: 0254-8704 (Print)
ISSN: 2394-0379 (Online)
CODEN: JEBIDP

DOI: https://doi.org/10.22438/jeb/38/3/MRN-404

Assessment of natural radionuclides and chemical constituents in commonly used hair dyes in Saudi Arabia

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Key words

Activity concentrations, Chemical composition, HPGe spectrometer, Radiological hazard

Publication Info

Paper received : 12.07.2016
Revised received : 31.10.2016
Re-revised received : 30.01.2017
Accepted : 01.03.2017

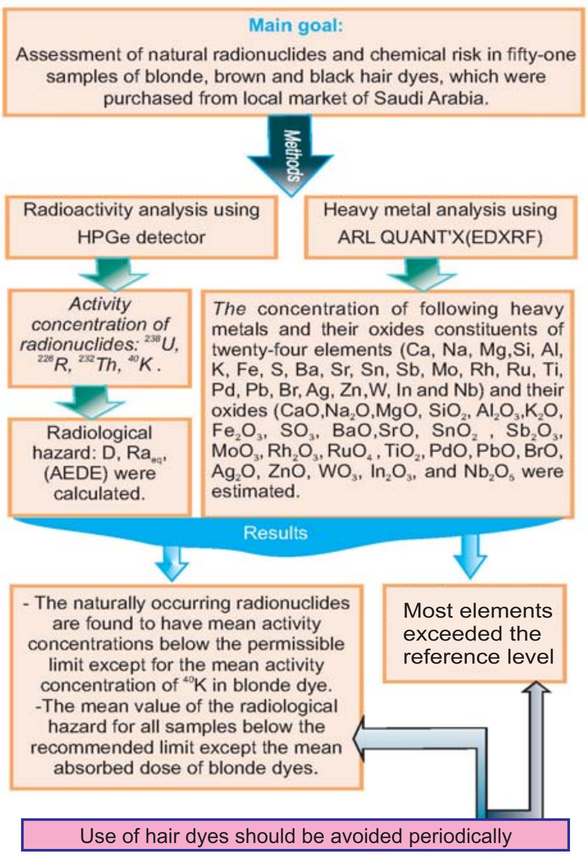
Abstract

Aim: Use of hair dyes has dramatically increased throughout the world, so there is an urgent need to human awareness of the radiological hazard potentially arising by using hair dyes periodically to reducing of use them. The main objective of the study was to estimate the radiological risk due to natural radionuclides and chemical constituents from the most common of hair dyes received by the consumer in Saudi Arabia.

Methodology: A total of fifty- one sample of seventeen hair dyes with common usage in Saudi Arabia imported from different countries. Radionuclides (^{40}K, ^{232}Th, ^{226}Ra and ^{238}U) in blonde, brown and black hair dyes were determined HPGe spectrometer. Twenty-four elements and their oxide concentrations were determined using ARL QUANT'X Energy-Dispersive X-ray Fluorescence spectrometer.

Results: The mean concentrations of ^{40}K in blonde dyes was above the permissible limit. Others naturally occurring radionuclides were found to have mean activity concentrations below the permissible limit. Uranium-238 was present in measurable values in most samples. The calculated radiological hazard, Absorbed dose rate, Annual effected dose rate and Radium equivalent for all samples were below the recommended value, except in one blonde dye sample. Most elements exceeded the reference level.

Interpretation: This is the first study for determining the radiological risks associated with usage the hair dyes (black, brown and blonde).From these measurements, it can be concluded that it should avoid the use of hair dyes periodically. Further, the obtained results will be of interest to those involved in health research through to compiling evidence on the subject



Introduction

The use of hair dyes has been traced back to thousands of years. Herbal dyes are generally safe, specifically Henna, *Buxus dioica* and *Isatis* (Nohynek *et al.*, 2004), but various health problems arises due to use of these chemical dyes, Commercial hair dyes are poor in quality and highly toxic (Haluk *et al.*, 2014). Some dye manufacturing companies may manipulate the consumer's health and add the synthetic organic compounds for coloration. Ammonia present in the chemical dyes open the hair cuticle to facilitate the oxidation process that lightens the natural color of the hair and it also helps in developing the added color. Hair dyes are amongst the most problematic pollutants because of their toxic effect on humans (Nohynek *et al.*, 2004; Gaffar *et al.*, 2014). The radiological risk in natural hair dyes come mainly from natural radionuclides ^{238}U, ^{232}Th series and ^{40}K through transmission of radionuclides from soil to plants (Chakraborty *et al.*, 2013).

Determination of radioactivity in hair dyes is important for human health (Pietrzak-Flis *et al.*, 2001). As these hair dyes contain chemicals like p-phenylenediamine, hydrogen peroxide and resorcinol (Fernández-Vozmediano *et al.*, 2011; Al-Suwaidi and Ahmed, 2010). They can cause rash and dermatitis of eyes, throat, scalp, skin and respiratory system, hence while using them safety glasses, gloves, and good ventilation is essential. The dark colored dyes are more Toxic as they contain higher level of chemicals (Broides *et al.*, 2011; Le Coz *et al.*, 2000). Some hair dye products have been found to contain mutagenic & carcinoge nic compounds. Coal tar colors are derived from the tar found in bituminous coal. Some coal tar colors also contain heavy metals. In view of the above, the present study was carried out to estimate the radiological risks due to natural radionuclides and chemical constituents from the most common hair dyes used in Saudi Arabia.

Materials and Methods

Sample preparation and assessment of radioactivity : A total of fifty one samples of seventeen hair dyes of blonde, brown and black color were purchased from local market of Saudi Arabia and numbered as Hd1- Hd5 (blonde), Hd6-Hd 11(brown) and Hd12-Hd17 (black), respectively. The samples were dried at 110 °C. The homogenized powdered samples stored in Marinelli beaker were sealed for about one month to get secular equilibrium for ^{222}Rn and ^{226}Ra. Radioactivity was assessed by high resolution γ-ray spectrometry HPGe detector with 25% counting efficiency and high resolution of 1.29 keV (FWHM). at 662 keV and 1.70 keV (FWHM) Counting of the samples and background were carried out for 10 hrs. Each sample was measured at the same time for about 10 hrs.

The gamma background level was estimated with an empty polyethylene Marinelli beaker. The background was measured under similar above mentioned conditions. The net peak count rate of each sample was obtained by subtracting the gamma ray background. The energy and efficiency of gamma spectrometer was calibrated using standard sources: ^{232}Th, ^{152}Eu, ^{226}Ra, and mixed source (containing ^{57}Co, ^{241}Am, ^{60}Co, 88Y, 85Sr, ^{137}Cs ^{109}Cd, ^{203}Hg and ^{138}Ce) (Bajoga *et al.*, 2015). The activity concentration of ^{226}Ra and ^{232}Th was determined assuming the following gamma lines: 1764 keV, 11220 keV, 609 keV and 351 keV of ^{214}Bi and 186 keV of ^{222}Rn for ^{226}Ra, 860 keV and 582 keV of ^{208}Ti, 968 keV,911keV,338 keV, for ^{228}Ac and 238 keV of ^{212}Pb for ^{232}Th. The activity concentration of ^{40}K was determined using a single peak area of 1460 keV (Chandrashekara and Somashekarappa, 2016).

The absorbed dose rate (D_R) in air from external gamma radiation at 1 m above ground level due to the presence of uniformly distributed natural radionuclides in measured soils was calculated by the following formula (Beretka and Mathew, 1985): DR (nGy/h)=0.0417CK+0.462CU+0.604CTh (1).

Where, C_K, C_U, and C_{Th} are the activity concentrations (in $Bqkg^{-1}$) for ^{40}K, ^{238}U and ^{232}Th, respectively. Secular equilibrium was assumed for dose calculation. To assess the radiological hazard due to natural radionuclide ^{40}K, ^{232}Th and ^{238}U, radium equivalent activity was calculated by the following formula (Abdul hussein *et al.*, 2016):

Ra_{eq} ($Bqkg^{-1}$) = C_{Ra} + 1.43 C_{Th} + 0.077 CK …… (2) where, C_K, C_{Th} and C_{Ra} are the specific activities of ^{40}K, ^{232}Th and ^{226}Ra in $Bqkg^{-1}$. To evaluate the radiological hazard for consumers, indoor Annual Effective Dose Rate $(AEDR)_{indoor}$ was calculated by the following formula, considering indoor time occupancy factor as 80%(Saleh and El-Taher, 2016) AEDR (mSv/yr) = DR × 10-6 (mGy/h) × 8760 (h/yr) × 0.7 (Sv/Gy) × 0.8 …….(3) where, 0.7Sv/Gy was taken as conversion factor.

Heavy metal analysis : The concentration of following heavy metals and their oxides were estimated: Ca, Na, Mg, Si, Al, K, Fe, S, Ba, Sr, Sn, Sb, Mo, Rh, Ru, Ti, Pd, Pb, Br, Ag, Zn, W, In, Nb, Na_2O, MgO,Al_2O_3, SiO_2, SO_3, K_2O, CaO, TiO_2, Fe_2O_3, ZnO, SrO, Bro, Pbo, Nb_2O_5, MoO_3, RuO_4, Rh_2O_3, PdO, Ag_2O, In_2O_3, SnO2, Sb_2O_3, BaO and WO_3 by ARL QUANT'X Energy-Dispersive X-ray Fluorescence spectrometer (EDXRF). EDXRF provides a rapid and non-destructive method for the analysis of major and trace elements of across the broadest range of samples, including bulk solids, granules, powders, thin films, liquids, geological and biological samples. To detect the X-rays characteristic, a Peltier-cooled Si (Li) detector (PCD) with 15 re5eV FWHMsolution for 5.9keV X-rays at 1,500 cps and Beryllium (Be) Window ≤ 7.6 micron (0.3 mil) was used. The data acquisition was employed by using Multi-Channel Analyzer '32-bit, 4096 channel MCA (Budaka *et al.*, 2006). The samples were dried at 60^0C in an oven. The powder obtained was sieved through a 300 mesh sieve and the samples were then transferred onto a polyethylene myler film. A circular sample radius of approximately 3 cm was used. All the measurements were obtained by running each sample three times. The average concentration was obtained from the mean values of peak area.

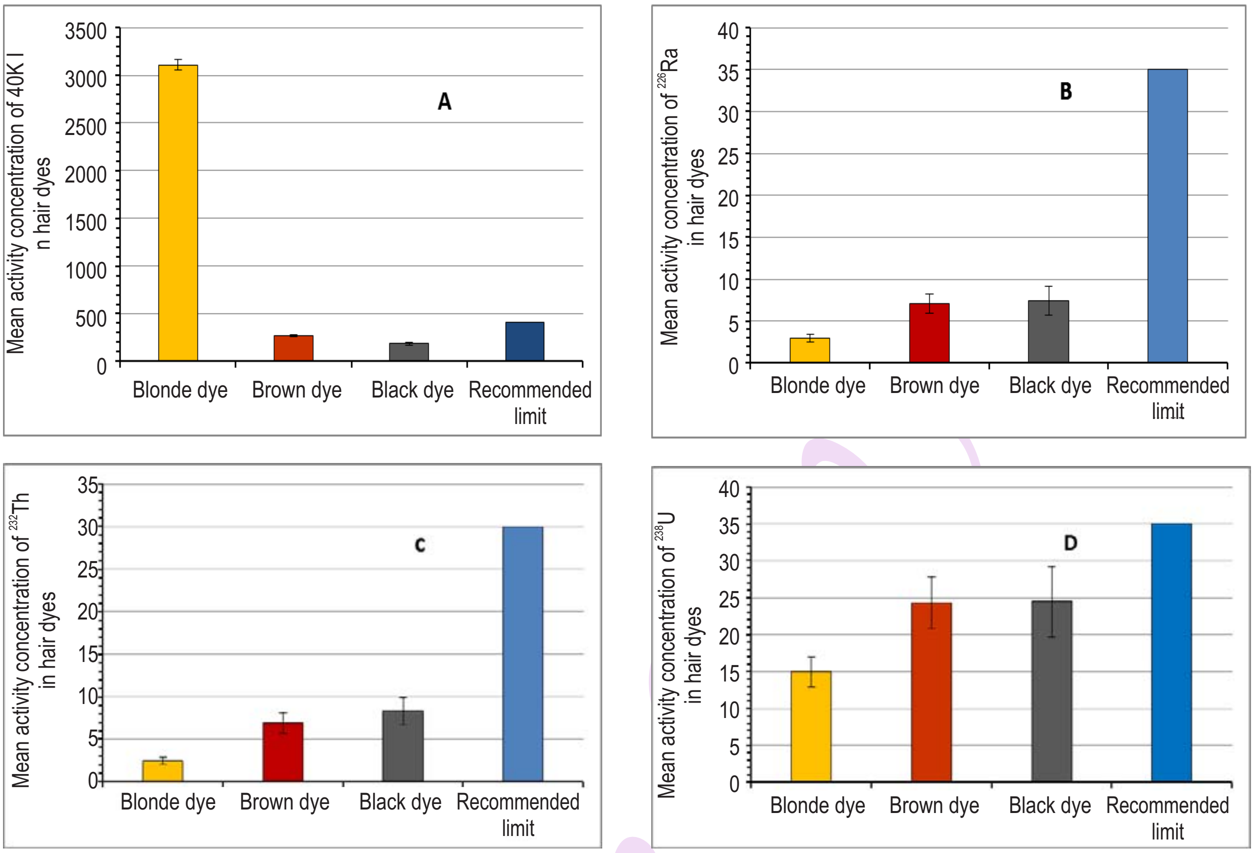


Fig. 1 : Comparison between the mean activity concentration of natural radionuclides in studied samples with the recommended limit (UNSCEAR, 2000)

Results and Discussion

Activity concentration in hair dye samples (Bq kg^{-1}): The average activity concentration due to ^{238}U, ^{226}R, ^{232}Th, ^{40}K radionuclides in brown, black hair and blonde hair dyes is given in Table1. Abdel Ghany *et al.*(2014) estimated radioactivity in textile dyes. The mean activity concentration of ^{40}K, ^{232}Th and ^{238}U were 565, 1.15 and 29.37 Bq kg^{-1}, respectively. The absorbed dose rates were below the maximum admissible value, except for yellow dye sample (166 nGy/h). Also, the radium equivalents for all the studied samples were lower than the International recommended limit (35, 35, 30, 400 Bqkg^{-1} for ^{238}U, 226Ra, 232Th and ^{40}K, respectively) (UNSCEAR, 2000).

A comparison between the mean activity concentration of natural radionuclides in the studied samples with the International recommended limit is shown in Fig.1 (A-D). The average activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th in blonde samples varied from ND to 6767.23 Bqkg^{-1}, ND to 5.86 Bqkg^{-1} and ND to 5.50Bq kg^{-1}. The results were found to be lower than the global median activity concentration of ^{226}Ra and ^{232}Th, respectively. Moreover, from Table1, it can be observed that the maximum of average activity concentration due to ^{40}K in sample Hd1, Hd4 and Hd5 was about 11, 17 and 10.7 times higher than the global median activity concentrations of ^{40}K. The average activity concentration of brown and black dyes was below the maximum worldwide values. The concentration of ^{40}K was also below the maximum worldwide acceptable values, except for Hd8, Hd9 and Hd14 dye samples, which was about 28.5%, 14.5% and 14% higher than the maximum permissible limit. As observed from Table 2, ^{238}U average concentrations ranged from ND to 27.72 Bqkg^{-1} in blonde dyes, 8.18to 41.37 Bqkg^{-1} in brown dyes and 8.18 to 27.26 Bqkg^{-1} in black samples, respectively. All the values were lower than the permissible limit (35 Bqkg^{-1}), except for sample Hd9 (41.37Bqkg^{-1}). A slight decrease in the mean activity concentration of ^{226}Ra and ^{232}Th was noted in brown hair dyes than in black hair dyes.

The estimated absorbed dose rate (Table 2) ranged from 3.12 to186.47 nGyh^{-1} in different hair dye samples. An increased dose rate was noted in blonde samples Hd1 (186.47), Hd4 (283.33) and Hd5 (180.80 nGyh^{-1}) due to higher radioactivity of ^{40}K. These values were higher than the permissible limit of 55 nGyh^{-1} (UNSCEAR, 2000). Therefore, the impact of radiation exposure on the workers and consumers for these samples cannot be ignored.

As tabulated in Table 2, radium equivalent activity varied from 7.09 to 523.53 Bqkg^{-1}. The highest value was detected in sample Hd4, which was 41.5% higher than the safety limit of 370

Table 1 : Average activity concentrations of 238U 226Ra, 232Th and 40K in hair dye samples

Sample code	^{238}U	^{226}Ra	^{232}Th	^{40}K
Hd1	23.67±3.44	3.58±0.60	ND	4411.84±95.58
Hd2	8.27±1.72	5.86±0.82	5.50±0.79	82.65±7.01
Hd3	15.24±1.92	2.94±0.44	2.92±0.45	ND
Hd4	27.72±3.04	2.45±0.40	ND	6767.23±100.60
Hd5	ND	ND	3.82±0.57	4280.36±80.66
Mean	14.98±2.03	2.97±0.45	2.448±0.36	3108.42±56.77
Hd6	30.34±4.04	3.46±.75	2.53±0.31	20.67±2.62
Hd7	26.63±3.11	5.96±0.71	4.25±0.50	12.59±1.40
Hd8	23.45±3.90	10.55±1.90	7.85±1.17	513.91±25.23
Hd9	41.37±6.90	6.64±0.48	10.72±1.74	458.01±17.44
Hd10	15.87±1.43	9.43±1.54	10.07±2.11	311.00±15.44
Hd11	8.18±1.20	6.49±1.20	6.04±1.25	304.64±13.11
Mean	24.31±3.43	7.09±1.10	6.91±1.18	270.14±12.48
Hd12	23.16±5.60	8.69±2.46	11.70±1.16	341.76±20.18
Hd13	26.79±4.20	3.97±0.91	3.07±0.29	DN
Hd14	27.26±5.61	10.49±2.51	13.60±3.51	455.86±23.21
Hd15	23.80±4.03	4.43±0.53	3.32±0.43	15.91±2.03
Hd16	22.98±4.51	8.00±2.01	16.45±2.51	284.74±13.51
Hd17	22.70±4.51	8.87±1.71	7.96±1.41	10.50±1.71
Mean	24.45±4.74	7.41±1.69	8.33±1.55	184.80±10.11

ND : Not detectable

Table. 2 : Radiological hazard effects: Absorbed dose rates (D), Radium equivalent activity (Raeq) and Annual effective dose rate $(AEDE)_{indoor}$

Sample code	D_R (nGy h^{-1}	Ra_{eq} (Bq kg^{-1})	$(AEDE)_{indoor}$ (mSvy^{-1})
Hd1	186.47	345.30	0.92
Hd2	9.48	20.08	0.05
Hd3	3.12	7.12	0.02
Hd4	283.33	523.53	1.39
Hd5	180.80	335.05	0.89
Mean	132.64	246.22	0.66
Hd6	3.99	8.67	0.02
Hd7	5.85	13.00	0.03
Hd8	31.05	61.35	0.15
Hd9	28.64	57.24	0.14
Hd10	19.05	38.45	0.10
Hd11	19.35	38.59	0.10
Mean	17.99	36.22	0.09
Hd12	25.34	51.74	0.13
Hdd13	3.17	0.09	0.02
Hd14	32.08	65.04	0.16
Hd15	4.72	10.40	0.03
Hd16	25.51	53.45	0.13
Hd17	9.35	21.06	0.05
Mean	16.70	34.80	0.09

Bqkg^{-1}. All the other estimated values were less than the permissible limit. Table 2 summarizes the results of the annual effective dose rate. The annual indoor effective dose rate ranged from 0.02- 1.39 mSvy^{-1}, 0.02- 0.15 and 0.02- 0.16 in blonde, brown and black samples, respectively, which were lower than the AEDR permission limit of 1 mSvy^{-1}, as reported by UNSCEAR (2000), except for Hd4 which was about 39% (1.39 mSv/y) higher than the average value. It was also observed that the $AEDR_{indoor}$ value for Hd1 and Hd5 samples were close to the maximum permissible limit. This implies that hair dyes products, if used for multiple times and longer duration may become a source of significant radiological hazards. As compared to the recommended values, the D_R value was about 2.41 times higher, while the mean values for each Ra_{eq} and $AEDE_{indoor}$ were less than the recommended level.

In the present study, twenty-four elements (Ca, Na, Mg, Si, Al, K, Fe, S, Ba, Sr, Sn, Sb, Mo, Rh, Ru, Ti, Pd, Pb, Br, Ag, Zn, W, In and Nb) and their oxides (Na_2O, MgO, Al_2O_3, SiO_2, SO_3, K_2O, CaO, TiO_2, Fe_2O_3, ZnO, SrO, Bro, Pbo, Nb_2O_5, MoO_3, RuO_4, Rh_2O_3, PdO, Ag_2O, In_2O_3, SnO_2, Sb_2O_3, BaO and WO_3) were determined. The study revealed that most of the elements present in each dye were higher than the maximum permissible limit (WHO, 2005). Table 3 summarizes the range of mean concentration of elements and their oxides, also it records the lowest and highest values of element concentration in the oxide composition

Singh *et al.* (2007) reported the toxicological effect and risk evaluation of nanostructured materials on human health and their safety assessment. Human exposure to these materials is inevitable as they can enter the body via drink, food and medicine. They may affect various tissues and organs such as liver, brain, heart, colon, kidney, blood, spleen, bone etc., and may cause cytotoxic effects like inhibition and deformation of cell growth leading to several diseases in humans. Their toxicity grades and interactions with biological systems hugely depend on upon their properties like concentration, size, solubility, stability and biological and chemical properties.

Nagajyoti *et al.* (2010) investigated the occurrence and toxicity in plants due to accumulation of zinc, cadmium, copper, mercury, chromium, lead, arsenic, cobalt, nickel, manganese and iron. These metals at excessive level are toxic to plants and affect the ecosystem. Sixty-three samples of henna products were analysed by Bernth and Hansen (2005). Pb has been observed in several samples with concentration ranging from 0.00005% to 0.0002 %. Also p-phenylenediamine was observed in three samples varying from 0.003% to 17%. The highest concentration exceeded the limit stated in the Directive on Cosmetics.

Sulphur and its oxide were recorded in eleven samples. The concentration of sulphur varied from 1.60% (Hd14, black dye) to 98.86% (Hd7 brown dye). The SO_3 content ranged from 3.545% - 99.66%. Highest concentration was reported in brown sample (Hd8) and the lowest value was observed in brown dyes

Table 3 : The range of mean concentrations of elements and their oxides (%) hair dyes

Element	Range	Oxide	Range
Na	14.006-45.49	Na_2O	16.45-38.97
Mg	2.52-32.78	MgO	3.40- 31.79
Al	1.31-13.58	Al_2O_3	1.95-11.28
Si	1.93-40.20	SiO_2	2.923-38.27
S	1.60-98.86	SO_3	3.545 - 99.66
K	2.61-34.56	K_2O	0.31-15.79
Ca	0.141-85.76	CaO	0.192 -78.75
Ti	0.183-2.98	TiO_2	0.080-4.205
Fe	0.281-10.45	Fe_2O_3	0.075-5.1275
Zn	4.81-28.45	ZnO	1.04-13.28
Br	ND-0.187	BrO	ND
Sr	0.055-0.587	SrO	0.0368-0.3064
Nb	0.022-0.308	Nb2O5	0.0067- 0.227
Mo	0.0127-0.224	MoO_3	0.0078-0.174
Ru	0.0062-0.115	RuO4	0.0034-0.0777
Rh	0.0042-0.092	Rh_2O_3	0.0023-0.0547
Pd	ND-0.0132	PdO	0.0086-0.0189
Ag	0.0083-0.014	Ag_2O	0.0064-0.0150
In	0.0085-0.113	In_2O_3	0.0031- 0.051
Sn	0.006-0.067	SnO2	0.0027-0.0219
Sb	0.0046-0.055	Sb_2O_3	0.0017-0.0150
Ba	0.73-68.85	BaO	0.243-53.93
W	ND-2.02	WO_3	ND-0.98
Pb	0.0215-0.044	PbO	ND

ND : Not detectable

sample (Hd14)kg^{-1} where S concentration in their oxides was 39.91% and1.42%, respectively. The concentration of sulphur in the present study exceeded the calculated mean sulphur value of 17.266 mgkg^{-1} (≈ 0.001726%) (Pednekar and Raman, 2013). Sulphur exposure causes skin allergy and irritation of eyes, respiratory, moreover occupational exposure to sulphur has been associated with lung damage (Pean *et al.*,1995).

Silicon was detected in all the dye samples ranging from 1.93% to 40.20%, except in Hd6, Hd7, Hd13 and Hd17. Silicon dioxide SiO_2 was present in all the samples varying between 2.923-38.27%, except for Hd6,Hd8, Hd13 and Hd17. All these values exceeded the range value 0.0017-0.10% of silicon concentrations as reported by Bernth and Hansen (2005). Chang *et al.* (2007) examined the biological activity of normal fibroblast and tumor cells with varying doses of amorphous silica or composite nanoparticles of silica and chitosan. The silica nanoparticles were found to be nontoxic at low doses while high doses decreased cell viability. High dose of silica also damage cell membrane. The fibroblast cells were more susceptible to damage caused by silica exposure than tumor cells. The silica–chitosan composite nanoparticles caused lower inhibition in cell proliferation, as well as lower membrane damage.

Tin and Antimony were present in all the dye samples, ranging from 0.006% to 0.067% and 0.0046% to 0.055%, except in Hd10, Hd11, Hd12 and Hd16, samples. Tin dioxide and antimony trioxide were noted in all the samples ranging from 0.0027% -0.0219% and 0.0017% to 0.0150%, respectively, except in Hd9, Hd10, Hd11, Hd12 and Hd16. The concentration of Sn and Sb was far greater than the range of Sn (0.00005-0.000089)% and Sb concentration. The average concentration of In and Nb varied from 0.0085% to 0.113% and 0.022%to 0.308%. Indium (III) oxide (In_2O_3) and Niobium pentoxide (Nb_2O_5) ranged from 0.0031% to 0.051% and 0.0067% to 0.227% and were detected in all hair dye samples. All the samples accumulated Indium and Niobium elements above mention value (Bernth and Hansen, 2005).

Niobium and its compounds may be toxic, however no reports of human intoxication has been reported. The study on laboratory animals have revealed that inhalation of Nb_2O_5 or NbN leads to fibrosis of lungs at exposure level of 40 mgm^{-3}. Nb_2O_5 decompose on heating and emits toxic vapors of niobium (Nowak and Ziolek, 1999).

Bromine was only present in sample Hd8 (0.187%). Debrah *et al.* (2011) recorded Br concentration between BDL to (0.001395)%. Bromine can damage the nervous system and thyroid gland. Few compounds of organic bromine like ethylene bromine are carcinogenic. Tungsten and its trioxide was only reported in sample Hd13 (2.02% and 0.98%), which was much higher than the range of permissible limit (0.000005-0.000017)% as reported by Bernth and Hansen (2005). Ruthenium and Rhodium were monitored in all samples except in Hd3 (blonde hair dye), Hd8 (brown hair dye) and Hd14 (black hair dye). Highest concentration of them was noted in Hd12, whereas lowest value was detected in sample Hd1. Ruthenium tetroxide (R_uO_4) and Rhodium sesquioxide (Rh_2O_3) were detected in all the samples, except for Hd3, Hd7, Hd14 and Hd15 samples. The highest concentration of RuO_4 and Rh_2O_3 was found in H16 (0.0777% and 0.0547%. The lowest value of RuO_4 (0.0034%) and Rh_2O_3 (0.0023%) was noted in Hd1, Mo and MoO_3 was present in all samples, except to two black hair dye samples (Hd13 and Hd15), ranging from 0.0127% to 0.224% and from 0.0078% to 0.174%, respectively. However, Mo average concentration exceeded the values reported by Bernth and Hansen (2005), while MoO accumulated Mo below the limit except, hair dyes samples Hd9, Hd10, Hd11, and Hd16. The MoO_3 concentration varied from 0.0078% (Hd1) to 0.174% (Hd10). Zinc was found only in two samples Hd13 and Hd15 (28.45% and 4.81%). ZnO was noted in Hd7, Hd13 and Hd15 samples (1.040, 13.280% and 1.041%) respectively. Zinc content was lower than the maximum permissible limit of Zn (0.005) % (Shah *et al.*, 2013). Jeng and Swanson (2006) assessed the toxicity profile of metal nano oxides (ZnO, TiO_2, Fe_3O_4 and Al_2O_3) in mammalian cells. The microscopic studies showed that nanoparticle-exposed neuro-2A cells were abnormal in size, displaying cellular shrinkage and detachment from the surface of flasks. ZnO was highly toxic, whereas Al_2O_3 was moderately toxic and Fe_3O_4 and TiO_2 exhibited slight toxicity at high concentration. Pb, Ag and Ti metals were present in few samples only. Pb appeared only in sample Hd11 (0.044%) and Hd16 (0.0215%) which was above the acceptable limit of Pb in (0.0005-0.001)%. PbO was not present in any of the dye samples. Ag was found in sample Hd11 (0.014%) and Hd16 (0.0083%) only. Silver oxide (Ag_2O) was found only in sample Hd11 (0.0104%), Hd14 (0.0150%) and Hd16, (0.0064%). Ag concentration exceeded the permissible limit (0.000001-0.00008)% as recommended by WHO (2005). Ti was present in four samples Hd3(1.10)%, Hd6 (0.183)%, Hd9 (2.54)% and Hd14 (2.98)%. Titanium dioxide (TiO_2) was found in sample Hd3 (0.460%), Hd6 (0.080%) and Hd14 (4.205%).

Lead exposure can cause various biological effect depending on the duration and level of exposure. It is one of the most toxic elements that may affect the central nervous system, reproductive system and endocrine system (ATSDR, 1999).

Exposure to titanium may be harmful to brain, where titanium nanoparticles can directly access the brain through olfactory bulb present in the nose. Although titanium dioxide is used as an additive in the pharmaceutical and food products, but on the other hand, it has also been classified as a possible carcinogenic to humans by the International Agency for Research on Cancer (Flamm,1985).

Calcium was observed in all the samples, except for Hd1, Hd4, Hd5 and Hd13. Ca content varied from 0.141 % for black hair dye (Hd15) to 85.76% for blonde hair dye (Hd2). It was observed that the calcium level in hair dye samples exceeded the permissible range (0.0005-2.40)%, except for Hd6, Hd7 and Hd15 (Bernth and Hansen, 2005). Calcium oxide was present in eleven samples, in range of 0.192% -78.75%, except for Hd1, Hd4, Hd5, Hd7, Hd13 and Hd15.

Sodium was observed only in four samples Hd1 (14.006%), Hd3 (45.49%), Hd6 (42.70%) and Hd7 (22.60%). Na_2O was also observed in four samples Hd3, Hd6, Hd8 and Hd15 varied from 16.45%-38.97% Na level in the hair dyes exceeded the permissible range of (0.0001-0.5)% (Bernth and Hansen, 2005). The highest Al and Mg content was found in brown hair dye (Hd9;13.58%) and black dye (Hd15; 32.78 %), however the lowest content was found in brown hair dye. (Hd10 ;1.31%) and in blonde hair dye (Hd2; 2.52%).

The highest concentration of Fe and Sr was observed in brown hair dye sample Hd8 (10.45) % and (0.587) % where the lowest concentration were observed in black hair dye sample Hd15 (0.281) % and blonde hair dye Hd2 (0.055) %. The highest Al_2O_3 concentration of 11.28% was found in Hd_2 (blonde dyes) and the lowest value was recorded in brown dyes Hd10 (1.95%). The concentration of MgO ranged between 3.40% (Hd2)- 31.79% (Hd4), while Fe_2O_3 ranged between 0.075% (Hd7) - 5.1275 % (Hd14). Strontium oxide (SrO) varied from 0.0368% (Hd2) to 0.3064%(Hd16).

Huda (2015) evaluated the level of toxic metals in twelve samples of hair dyes from the local store for various brands in Baghdad. The concentration of heavy metals ranged from 0.41 to 0.91 $mgkg^{-1}$ for lead, 0.26 to 0.31 $mgkg^{-1}$ for copper, 0.64 to 1.36 $mgkg^{-1}$ for iron and 0.11 to 0.16 $mgkg^{-1}$ for cadmium (1$mgkg^{-1}$ =0.0001%). It is obvious that heavy metals causes skin problems and cancer due to long term exposure .

In regard to Ba and BaO, all Ba concentrations in samples were found to be higher than the calculated value (0.0027-16.7786) % (Ghanjaoui *et al.* 2014), except in sample Hd3 (0.73%), where the highest Ba concentration was noted in sample Hd12 (68.85%). BaO was observed in the range of 0.243% - 53.93%).

Palladium was found only in one sample Hd2 (0.0132%), however, PdO was detected in two samples Hd2 (0.0086%) and Hd16 (0.0189%). The permissible limit of Pd is 0.002 $mgkg^{-1}$. All palladium compounds are highly toxic and carcinogenic. It may cause skin sensitization, eye or respiratory tract irritation. In general, people with known palladium allergy should not work with palladium compounds. Personal protective equipment should be used to prevent skin contact with palladium compounds, but no specific guideline to palladium exposure has been published (WHO, 2002). Potassium was present in ten samples. The concentration of potassium varied between 2.61% to 34.56%. Potassium oxide (K_2O) was present in nine samples, ranging between 0.31% to 15.79%.

The results indicate that the toxicity resulting due to regular use of hair dyes can not be ignored.

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