iJRASET
International Journal For Research in Applied Science and Engineering Technology

INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

Volume: 4 **Issue:** II **Month of publication:** February 2016

DOI:

www.ijraset.com

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Volume 4 Issue II, February 2016
ISSN: 2321-9653
International Journal for Research in Applied Science & Engineering Technology (IJRASET)

Risk Assessment of Heavy Metal Toxicants in Hair Oils

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Abstract— The hair oils were analyzed for heavy metal poisoning using Double Beam UV-Visible spectrophotometer and AAS. The hair oils were procured from the market and analyzed for heavy metals viz. Pb, Cu, Fe, Ni, Cr, Zn and Mn. It was reported that the concentration of lead, nickel and manganese exceeded the maximum permissible limits as specified by the various governing authorities and was found to be in the order, Zn> Ni >Mn> Cr >Cu >Fe >Pb. The concentration of lead, nickel and manganese in the hair oils was found to be very alarming which requires a high alert by the public as well as the government in order to prevent the common people from the ill effects of the heavy metal toxicity.
Keywords— Heavy metals, contamination, UV-Visible spectrophotometer, AAS, diseases

I. INTRODUCTION

Living organisms tend to take in and accumulate certain elements in their structures. The present study concerns with the analysis of heavy metals in hair oils because hardly any research has been done on hair oils due to which people are unaware about the toxicity of poor quality of hair oils. Heavy metals present above permissible limits in the body are not metabolized and accumulate in the body.[1] Heavy metal toxicity can cause malfunctioning of nervous system, kidneys, lungs and other organ. A number of heavy metals are carcinogenic or can cause gastrointestinal disorders.[2] They can also damage genetic material directly or indirectly causing many types of syndromes.[3] The presence of heavy metals in hair oils depends on many factors; they might originate from the soil, fertilizers and pesticides used in cultivating herbs which are used as hair oil ingredients, polluted environment, manufacturing and processing of mineral oil which is used as base in hair oil preparations or the manufacturing processes of hair oil as a whole and artificial colors and perfumes used in it. This has lead to the outbreak of low and medium priced cosmetics which comprises of nearly 60% of the total cosmetic market in terms of volume.[4]This requires a thorough study of the migration of trace elements and its compound or derivative at all the stages of ecological chain because these are immediate sources of heavy metals that reach the humans.[5] Many researchers have reported the seriousness and harmful effects of some toxic metals, especially cadmium, chromium, cobalt, nickel and lead.[6-10] It has been estimated that out of the total lead absorbed by the body, almost 95% goes in the bones where they cause serious problems. [11]In the present study, seven elements, Pb, Fe, Cu, Cr, Ni, Zn and Mn are estimated quantitatively in ten different brands of hair oils.

II. EXPERIMENTAL

A. Materials and methods

All the reagents are of analytical grade reagents having purities of more than 98% and were procured from Ases Chemical Works (India). Metal solutions were prepared by dissolving their appropriate standard salts in the de-ionized water. The methods used in the estimation of metals were taken from the manual of methods of analysis of metals. [12]

B. Collection, digestion and acid treatment of the sample

The hair oil samples were randomly selected from the local market. A weighed amount of hair oils were first volatilized on a soft flame of Bunsen burner and then digested in muffle furnace at 440-550 ºC for 4-5 hours.

C. Acid treatment and sample solution preparation

The digested samples were then heated along with dropwise addition of 1:2.5 HCl till all the residual matter dissolves in it. Then the solutions of each of the sample were completely transferred in separate 100ml volumetric flasks which were then made up to volume with de-ionized water and then analyzed for heavy metal contamination.

Volume 4 Issue II, February 2016
ISSN: 2321-9653
International Journal for Research in Applied Science & Engineering Technology (IJRASET)

D. Analysis of heavy metals

Pb, Fe, Cr, Cu, Ni were analyzed using Rayleigh Double Beam UV-Visible Spectrophotometer (UV-2601). Zinc and Manganese were analyzed using Atomic Absorption Spectrophotometer (nov AA400).

1) *Lead:* A suitable aliquot of the samples were taken from each of the flasks and neutralized with NH_3 sol. in presence of citrate. 10% KCN sol. was then added to each of them to complex the interfering metal ions and then lead was extracted as lead dithizonate into the $CHCl_3$. The $CHCl_3$ layer was then taken into another separating funnel containing dil. HNO_3 and shaken vigorously for 2-4 minutes. The $CHCl_3$ layer was discarded. Then the pH of the aqueous phase was buffered to 9.5 to 10 and finally the lead was re-extracted with dithizone in $CHCl_3$.The resulting red complex was read at 510nm.The appropriate volume and concentration of dithizone was chosen as per the data provided in the table I.

TABLE I
CONCENTRATION AND VOLUME OF DITHIZONE REQUIRED FOR LEAD EXTRACTION

Pb range (micrograms)	0-10	0-50	0-200
Concentration of dithizone in $CHCl_3$(mg of dithizone /L solution)	8	10	20
Volume of Dithizone solution to be taken (mL)	5	25	40

2) *Iron:* 10 mL aliquots of each of the digested solution were taken in separate 25mL volumetric flasks and 1mL $H_2NOH.HCl$ solution was added into each of them. The resulting solutions were kept for 5 min. and then 5mL buffer solution and 1mL o-phenanthroline solution were added to them to furnish a brown complex. Finally the solutions were made upto the mark and their absorbances were measured at 511nm.
3) *Copper:* Aliquots of the samples were taken in separating funnels containing 2N H_2SO_4. Then 10 mL citrate EDTA solution and two drops of thymol blue indicator were added into them. 6N ammonium hydroxide was then added dropwise till the solutions become blue-green. The resulting solutions were cooled on an ice bath and then 1 mL carbamate solution and 15 mL CCl_4 were added. The solutions were then shaken for 2 min. and then allowed to stand for the separation of layers. The CCl_4 layer of each of them were filtered through cotton pledget and then their absorbances were read at 400 nm.
4) *Chromium*: An aliquot of the sample was taken in a 50 mL volumetric flask into which 0.25 mL H_3PO_4 solution was added. 1mL diphenylcarbazide was then added into it and the volume make up was done with 0.05M H_2SO_4. The pH was adjusted to 2.0±0. The solution was then allowed to stand for 5-10 min. to form a red – violet complex which was read at 546 nm. The process was repeated for all the samples.
5) *Nickel:* A suitable aliquot of the sample was taken and neutralized with NH_3 sol. in the presence of citrate. 10% KCN sol. was added to complex the interfering metal ions and then Br_2 water was added to oxidize nickel. Finally 1% dimethylglyoxime was added which produced scarlet - red ppt. of nickel-dimethyl glyoxime. After filtration, the precipitate was washed with de-ionized water and was dissolved in 10 mL $CHCl_3$. A yellow complex is formed which was finally measured at 525 nm. The process was repeated for rest of the samples.
6) *Zinc and Manganese:* Zinc and manganese were analyzed using AAS (nov AA400) with the standard conditions as mentioned in table II.

TABLE II
STANDARD CONDITIONS FOR ANALYSIS OF ZINC AND MANGANESE USING AAS

Heavy Metal	Wavelength (λ) nm	Slit Width nm	Flame Composition
Zn	213.9	0.7	Air-Acetylene
Mn	279.5	0.2	

Volume 4 Issue II, February 2016
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III. RESULTS AND DISCUSSION

The concentration of the heavy metals in different brands of hair oils are tabulated in the table III. The statistical data covering the average, percentage, standard deviation, variance (standard deviation), population standard deviation, variance (population standard deviation) were also calculated and are tabulated in the table IV

TABLE III
HEAVY METAL CONTENT IN DIFFERENT BRAND OF HAIR OILS (in mg/kg)

S.No.	Brands of hair oils	Concentration of heavy metals (mg/kg)						
		Pb	Fe	Co	Cr	Ni	Zn	Mn
(i)	Nimson Amla	18	90	48	90	1298	1136	1178
(ii)	Vedic Amla	20	16	50	94	178	1304	1174
(iii)	Asha Almonds	16	14	44	76	158	1748	1054
(iv)	Neemcule	34	24	72	94	1394	1108	1314
(v)	Devratna	30	26	30	96	1704	1374	1148
(vi)	Nancy Amla	48	10	34	156	1886	1138	978
(vii)	Sangini	44	28	58	72	1686	912	738
(viii)	Ashakesh	26	44	18	50	1178	1138	1308
(ix)	Panchratna	14	64	2	28	972	1512	1114
(x)	Plush amla	18	36	6	92	1708	1374	1316

TABLE IV

STATISTICAL EVALUATION OF HEAVY METAL CONTENT IN HAIR OILS

S.No.	Heavy Metal	Average	Percentage	Standard deviation	Variance (Standard deviation)	Population Standard deviation	Variance (Population Standard deviation)
1.	Lead	26.8	0.704	11.97	143.29	11.36	128.96
2.	Iron	35.2	0.925	25.00	625.07	23.72	562.56
3.	Copper	36.2	0.951	22.62	511.51	21.46	460.36
4.	Chromium	84.8	2.228	33.54	1124.62	31.81	1012.16
5.	Nickel	1216.2	31.956	618.79	382911.51	587.04	344620.36
6.	Zinc	1274.4	33.486	239.64	57428.27	227.34	51685.44
7.	Manganese	1132.2	29.749	178.72	31939.07	169.54	28745.16

Health Canada's Natural Health Products Directorate (NHPD) [13] suggest the upper limit of lead as 10 ppm but the studied samples showed lead concentration in the range 14-48 mg/kg with the mean concentration of 26.8 mg/kg which was greater than the normal value.

According to the European Medicine Agency's [14] guidelines the Permissible Daily Exposure (PDE) of iron is 13mg/day or 260µg/kg/day for a 50 kg person. The iron content in the studied samples was found in the range of 10-90 mg/kg of which the mean was found to be 35.2 mg/kg .If 5g of hair oil is used per day by women with long hairs then the mean PDE comes out to be 3.52 µg/kg/day which was well within the limit.

The PDE for copper is 50µg Cu/kg/day in a 50 kg person. The copper content in the samples ranged between 2-72 mg/kg having the mean concentration of 36.2 mg/kg. The estimated PDE with this result was found to be 3.62 µg Cu/kg/day which was below the specified value.

According to WHO (1996) [15], the Cr concentration should not exceed the supplementation of 250 µg/day. A report by a Dutch RIVM I 2001[16] determined a provisional Tolerable Daily Intake (TDI) of 5µg/kg/day for oral exposure to Cr (VI). Chromium in the samples was reported in the range of 28-156 mg/kg with the mean concentration of 84.8 mg/kg which was within the limits.

Nickel has not been considered as an essential for human body by European Food Safety Authority (EFSA). Skin eczema has been reported in nickel sensitized people. Some studies on nickel has reported that 8-12µg/kg of body weight has provoked such reactions.[17] The PDE for Nickel is 6µg/kg/day in a 50 kg person while WHO recommends a Tolerable Daily Intake (TDI) of 5µg/kg/day. In the analyzed samples, Nickel ranged between 158-1886 mg/kg with the mean value of 1216.2 mg/kg which gives a value of 121.618µg/kg/day which was higher than the permissible limit.

The PDE for zinc is 13000 µg/ day or 260 µg/kg/day in a 50 kg person while WHO recommends a Tolerable Daily Intake (PMTDI) of 0.3-1.0 mg/ day. The studied samples showed zinc concentration in the range 912-1748 mg/kg respectively with the mean concentration of 1274.4 mg/kg which gives an estimated value of 127.44 µg/kg/day. Davias et al [18] has suggested a NOAEL of 50mg/day. Thus, it was found that the analyzed samples were not contaminated with zinc.

WHO (1996), has set a range of 0.1-1mg/ kg for manganese, above which the neurological effects are seen in the body while the US National Research Council [19] has suggested the Estimated Safe and Adequate Dietary Intake(ESADDI) of manganese as 2.5 mg/day. In the analyzed samples, manganese ranged between 738-1316 mg/kg with the mean concentration of 1132.2 mg/kg which corresponds to the daily intake of 5.66 mg/day which was higher than the ESADDI value.

IV. CONCLUSION

The average of these heavy metal was found to show the following order, Zn> Ni >Mn> Cr >Cu >Fe >Pb.The analyzed samples showed a high concentration of manganese, nickel and lead which may be attributed to the contamination in hair oil before i.e. in raw materials or manufacturing steps and after the processing i.e. in storage and packaging. These heavy metal contaminant causes irritation, rashes, itching, skin eruption and many other serious alternations in metabolic processes leading to serious disorders in the human body and the environment. This should necessarily be controlled in order to lead life smoothly, happily and healthy. This is only possible by alertness and attention paid by the government and also by the consumers.

V. ACKNOWLEDGEMENT

The authors are greatly acknowledging the UGC, New Delhi, for providing the financial assistance for the findings of the paper. The authors also thanks the Department of Chemistry, J.N.V.U, Jodhpur for providing the instrumental facilities and constant guidance in the research work.

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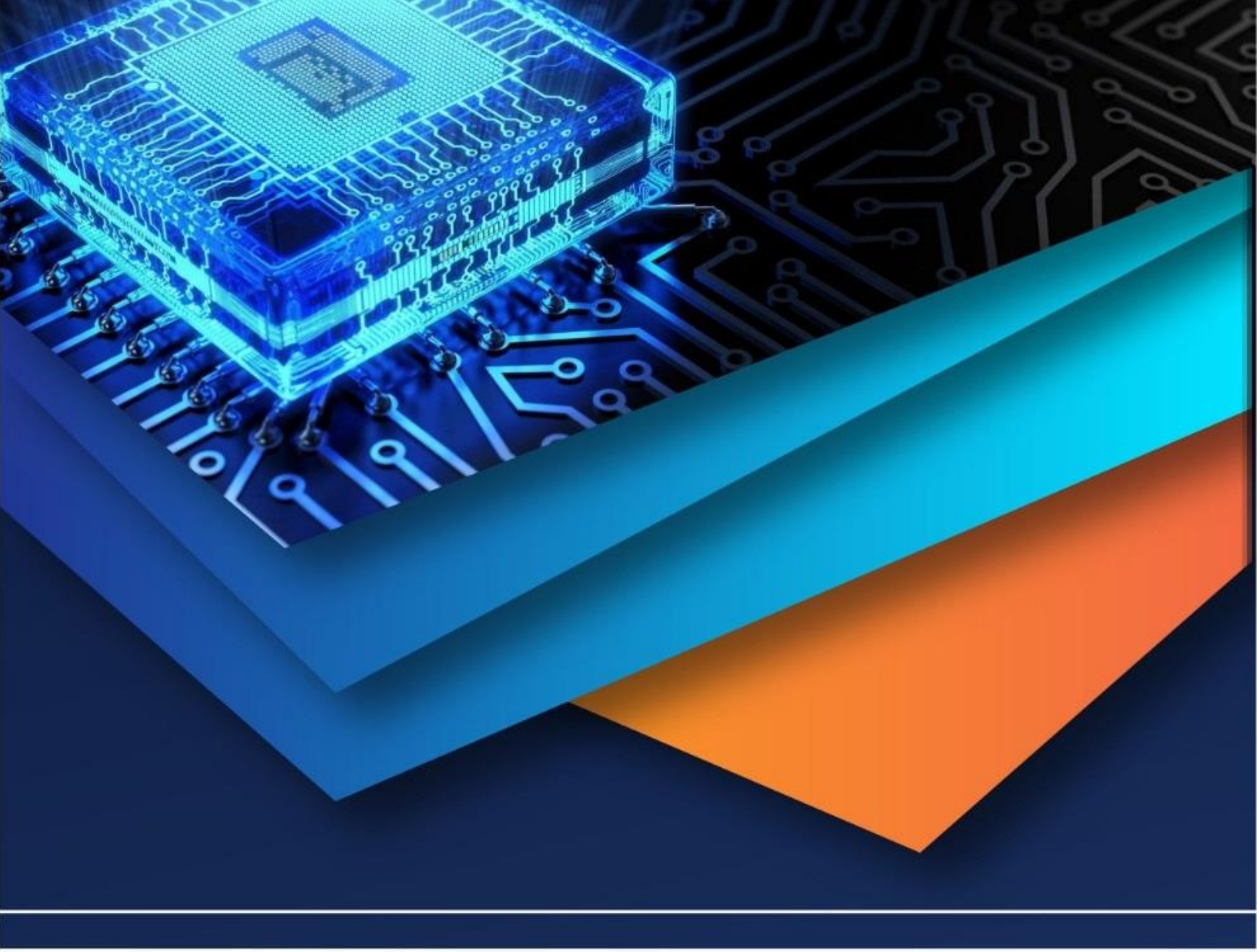

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