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Determination of Heavy Metals and Trace Elements in Worldwide Branded Shampoo Available in Local Market of Bangladesh by Atomic Absorption Spectrometry

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Heavy and trace metals are certainly stirring elements which are existing with the environment. These substances go to the products by various process which we consume and use every day. In this analysis the heavy metals *i.e.* Cd, Pb and Hg with some trace elements, *i.e.* Al, Mg, Fe, Cu, Mn, As, Co, Zn, Cr and Ni were numerically assessed using atomic absorption spectrometry. The result indicates the concentration of Hg in the both synthetic and herbal shampoo was exceeded the WHO permissible limit. Aluminium value was nearly three times higher in synthetic shampoo than that of herbal shampoo. This study has revealed that the alarming amount of heavy metals and trace elements is present in most of the branded products including both of the synthetic and herbal. As a result, the continuous use of these cosmetics cause an adverse effects of heavy metal toxicity.

Keywords: Heavy metal and trace elements, Analytical methods, Flame and hydride furnace of atomic absorption spectrometry.

INTRODUCTION

Heavy metals and some trace elements are originated usually in the atmosphere by rock, water and soil. It existed in the production of colours and other raw materials in all industries with cosmetic industry. Nowadays cosmetics are two types, one is herbal and another is synthetics. Both of the cosmetics are available in all over the world.

In general, cosmetic products or it's related any substance are proposed to be placed in connection with several outer parts of the body *i.e.* skin, nails, lips and external organs or applied to the teeth and mucous membranes of the oral cavity which mostly used for beautification, scrubbing, protection, changing their entrance and keeping for fitted body[1,2]. Main ingredient of cosmetics are some surfactants, oils and other ingredients which are required to be active, long durable, sustainable and safe for human use[3]. Since the modern civilization, most of the cosmetics industries produce synthetic products because of easy manufacturing process and possibly to avoiding the dependency on the natural raw sources.

Nowadays, the cosmetics consumers are moving towards the herbal cosmetics instead of synthetic one because of their less side effects. Generally, herbal product are the rich source of vital trace elements, *i.e.*, aluminium, calcium, zinc, copper and magnesium and other useful minerals, which play an important role for skin nutritional requirements as well as effective anti poisonal materials[4,5], While herbal products have been used globally since prehistoric time. It is well known to the consumer that the chemical-based cosmetics are irritatives than the herbal cosmetics[6,7].

Metals or metal compounds are immersed into the herbal products that are not essential for the healthy skin[8]. Although the metal absorption through the skin is often ignored but analysis shows that lead actually can be absorbed through the skin[9]. Skin-absorbed lead can be detected in sweat, blood and urine within 6 h of skin application[10] in the body. Heavy metal *i.e.* Cr, Hg, Pb and As are identically noxious element, even in very small amounts. Environmental contamination by heavy metals employs physiological pressures that are clearly hindrance for survival of most species *i.e.* phenotypic plasticity or physiological acclimation rather than genetic adaptation[11].

On the other hand, research indicates the presence of toxicological metal in cosmetics is increasing in an alarming rate *i.e.*, arsenic, mercury and antimony[12,13]. The Canadian health organization reported that all cosmetic products tested positive for nickel and more than 90 % tested positive for both lead and beryllium. These products also contained at least four of eight metals of concern such as arsenic, cadmium, lead, mercury, beryllium, nickel, selenium and thallium[14]. Heavy metals are noxious for all living beings counting humans being due to their biotoxic effects. It would be acute, chronic, subchronic, neurotoxic, allergenic, carcinogenic, mutagenic and teratogenic diseases[15].

Heavy metals are dangerous for all living beings. It has a non-biodegradable nature, long life time and accumulate in different parts of the body. It is easily soluble in water. Even at low concentrations of heavy elements have negative side effects to man and animals because there is no removal mechanism. Faridul Islam and his co-worker[16] showed that heavy metals are not only irritative for the soil, but also the aquatic environment and the living beings of the surrounding. Lead has diffused possible sources which could be from drinking water and mostly defendants were tap water and bore holes. Other sources are packaging materials, lead-deposited soils, use of agrochemicals during cropping season, use of leaded fuels, lead plate accumulators, alloys like solder, bearing metals and many type of metals *etc*.[17]. Lead is the most significant toxic heavy metals and it absorbed in our body through food and water as well as inhalation by inorganic forms[18]. The teratogenic effect of lead inhibits the synthesis of haemoglobin, dysfunctions in kidneys and joints, acute and chronic damage create to the chief nervous system, *etc*.[19]. The analysis showed that workers with chronic headache and dizziness have higher levels of Cr and Pb in the scalp hair samples who are working in a fireworks factory[20]. Arsenic toxicity symptoms depend on its chemical form which types are ingested in our body[21]. The high concentration of As could have resulted from the use of insecticides, doping agents in semi-conductors and some lead-based alloys *etc*.[17]. Chromium is an essential nutrient for our body that helps insulin to maintain normal glucose level. On the other hand, Chromium toxicity can cause stomach upsets, ulcer, kidney, liver damage and even death[18]. Omolaoye and his co-researcher[22] detected that the metal concentration levels are generally lower except chromium. The highest concentration of chromium obtained was 5470 μg g^{-1}. Shampoo is the essential goods in our daily life. At higher concentration of Cd was identified in shampoo with brand code A (S-A) monitored by soap with A and B brand (S-A and S-B)[12].

It is noticeable that the use of any cosmetic products exposes users to low concentrations metal which could constitute a potential health risk to users and also can accumulate in the biological system over time and are known to make skin problems or various diseases like as cancer. Islam *et al*. and Adepoju-Bello *et al*.[23,24] represented that the continuous use of high concentration heavy metals cosmetics exposes the users to create a heavy metal toxicity. For environmental contamination, Faridul and his collegues showed that the highest Zn value in pulse species of *Lathyrus sativus* is 29.50 μg/g in *Anowara upazila*[24] and the highest value of copper presented in *Colocasia esculenta* (*Patiya upazila*) is 50.0 μg/g respectively[25] of Chittagong region, Bangladesh.

According to the World Health Organization (WHO), the concentration of heavy metals of herbal products must be controlled in safety level[26-28]. In this circumstance, Health Canada has taken some initiative and instigated a few metal concentration in cosmetics and regulated the maximum acceptable limits such as lead-10 ppm, arsenic-3 ppm, mercury-3 ppm, cadmium-3 ppm and antimony-5 ppm[14].

The aim of this study is designed to determine the concentrations of heavy metals in cosmetic products like a different branded shampoo (herbal and synthetic shampoo) which is frequently sold in local shops in Bangladesh with a view of assessing the potential risks that such cosmetic may pose to consumers. The analysis was completed by atomic absorption spectrometry (AAS) followed of the recovery studies as a part of the method validation as per ICH guidelines.

EXPERIMENTAL

Forty nine branded shampoos (herbal and synthetic) samples were composed from the local market of Chittagong, Bangladesh. All the sample were levelling as from SS1 to SS41 for synthetic and HS42 to HS49 for herbal shampoo. Atomic absorption spectrophotometer (Model- iCE 3000, Thermo Scientific, USA) furnished with a deuterium lamp (D2) for background correction, which was used for determination of trace elements and heavy metals concentration. The hollow-cathode (HC) lamps for Fe, Co, Ni, Cu, Zn, Cd, Cr, Al, Mg, Pb, Mn, Hg, As and Ag were engaged as a radiation source. Hydride generator was used for As and Hg analysis. The flame used by air-acetylene, Argon and N_2O-acetylene gas.

Sulfuric acid, nitric acid, hydrochloric acid, hydrogen peroxide, potassium iodide, sodium borohydride and stannous chloride were analytical grade, manufactured by Fisher Scientific Company, USA. Water collected from Milli-Q-water purification system (Ranken Rion Ltd, India). All standard solutions were purchased from Fisher Scientific Company, USA.

Sample preparation: All the samples were prepared under standard procedure. Briefly, 100 g of each collected samples have been taken into evaporating dishes. Then, it dried in an oven at (100-110) °C about 4 h. The dried samples were ignited in a furnace at 600 °C. The temperature was increased gradually. The ashes of each sample were allowed to cool and transferred to 250 mL beakers. A small quantity of water and 25 mL of concentrated nitric acid were contacted with each sample. Then all of the samples were heated and added nitric acid as required until the digestion was completed. Finally, the samples were filtered into 250 mL volumetric flasks and dilute to the mark with deionized water.

Only for As and Hg, 10 mL of nitric acid was added to 2 g of accurately weighed dried sample in a 100 mL beaker and it was heated on a hot plate at 95 °C for 15 min. Next, the digest sample was cooled and 5 mL of concentrated nitric acid was added and heated for additional 0.5 h using the same temperature. Finally, this process was repeated and the solution was reduced to about 5 mL without boiling. The sample was cooled again and 2 mL of deionized water and 3 mL of 30 %

H_2O_2 was added. Then the sample in covered beaker was heated gently to start the peroxide reaction and follow to the gentle heat until the effervescence was subsiding. Next, 5 mL of concentrated hydrochloric acid and 10 mL of deionized water was added and the sample was heated at 15 min without boiling. Finally, the sample was cooled and filtered through a Whatman No. 42 filter paper and diluted to 50 mL with deionized water.

Sample analysis: Digested samples were analyzed for Fe, Co, Ni, Cu, Zn, Cd, Cr, Al, Mg, Pb, Mn, Hg, As and Ag used a flame atomic absorption spectrophotometer and for As, Hg uses hydride generation technique. The 1000 ppm standard solutions of elements were diluted in five different concentrations to obtain calibration curve for quantitative analysis immediately before use. All measurements were run in triplicate both for samples and standard solutions. The instrumental settings are listed in Table-1 giving details about parameters which are defined for respective metals.

Recovery studies: The standard method is used for method validation[29]. It has demonstrated the validity of our method. Hereafter, a recovery test was performed using standard methods. The standard solution having Fe, Co, Ni, Cu, Zn, Cd, Cr, Al, Mg, Pb, Mn, Hg, As and Ag were ready and spiked with digested samples. The average recovery ranged between 92 to 104 %.

RESULTS AND DISCUSSION

The heavy metal toxicity causes the short and long time effect on the living beings which exposure to common pollutants in our atmosphere, including food, air, water and many consumer products like cosmetics and toiletries. This toxic metal is associated with many chronic diseases. Many researchers have found that even low levels of lead, manganese, copper, chromium, mercury, cadmium, aluminum and arsenic create a number of health problems. The results of analytical investigation of heavy and toxic metal and other trace elements in 49 branded shampoo samples (both the herbal and synthetic shampoo) as shown in Table-2 respectively synthetic shampoo and herbal shampoo. In the present study, we determined Fe, Co, Ni, Cu, Zn, Cd, Cr, Al, Mg, Pb, Mn, Hg, As and Ag metal from 49 collected shampoo samples between 41 synthetic and 8 herbal shampoo.

The result shows (Table-2), the range of the target metals was found in the synthetic shampoo as: Fe from 5.9-0.02, Ni range was 0.24-0.05, Cu from 1.02-0.06, Zn from 5278.89-0.16, Cr from 0.61-0.04, Al from 28.04-0.83, Mg from 464.52-0.87, Mn from 1.21-0.03, Hg from 49.02-0.15, As from 0.42-0.003 and Ag from 1.4-0.21 mg/kg. Comparatively, the amount of Co, Cd and Pb was below the detection limit (BDL) for that of synthetic shampoo. In herbal shampoo the amount range of Fe was from 4.08-0.04, Ni range was 0.05-0.05, Cu from 0.41-0.1, Zn from 9.22-0.27, Cr from 0.38-0.2, Al from 9.85-1.04, Mg from 259.54-0.21, Mn from 0.3-0.02, Hg from 7.45-1.24 and As was 0.02-0.001 mg/kg and Co, Cd and Pb value were below the detection limit (BDL) as well. Table-2 also indicates that Ni and Ag metal was found in small amount only in few samples both of synthetic and herbal products. The amount of Zn metal was found extremely higher (5278.89 mg/kg) in one sample than those of other samples both of the synthetic and herbal shampoo. It was observed that the order of mean concentrations of metals in synthetic and herbal shampoos were, Zn (5278.89) > Mg (464) > Hg (49.02) > Al (28.04) > Fe (5.9) > Ag (1.4) > Mn (1.21) > Cu (1.02) > Cr (0.61) > As (0.42) > Ni (0.24) and Mg (259.54) > Al (9.85) > Zn (9.22) > Hg (7.45) > Fe (4.08) > Cu (0.41) > Cr (0.38) > Mn (0.3) > Ni (0.05) > As (0.02) mg/kg weight basis respectively. In comparison, the above all metals concentration in the synthetic shampoo is higher than those of herbal products.

The average concentration of heavy metals and trace elements was also found a higher range in the synthetic shampoo than that of herbal shampoo (Fig. 1). From Fig. 1, where as the Cu and Cr value in both samples is nearly same, the value of Al and Hg was found in both samples at higher percentages. On the other hand, some elements can accumulate in the body, so there is no truly safe exposure limit for those elements (*e.g.*, lead, mercury, cadmium)[14]. Less commonly, any metal with a potential negative health effect or environmental impact may be termed as heavy metal, such as nickel, copper, arsenic, chromium, aluminum and even iron, *etc*.[30]. Some of these elements are actually necessary for humans in small amounts (cobalt, copper, chromium, manganese, nickel) while others are carcinogenic or toxic effect which affecting the central nervous system (manganese, mercury, lead, arsenic),

TABLE-1
WORKING CONDITION OF ATOMIC ABSORPTION SPECTROMETRY DURING OPERATION TO DETECT HEAVY METALS IN SHAMPOO

Condition of AAS	Name of the detected metals						
	Mn	Ni	Co	Zn	Fe	Pb	Cd
Wave length (nm)	279.5	232	240.7	213.9	248.3	283.3	279.5
Band pass (nm)	0.2	0.2	0.2	0.2	0.2	0.5	0.5
Flame type	Air-C_2H_2	Air-C_2H_2	Air-C_2H_2	Air-C_2H_2	Air-C_2H_2	Air-C_2H_2	Air-C_2H_2
Hollow cathode lamp current (mA)	12	15	15	10	15	10	8
Fuel flow (L/min)	1.0	0.9	1.0	1.2	0.9	1.1	1.2
Condition of AAS	Name of the detected metals						
	Cu	Al	Mg	Ag	As	Hg	Cr
Wave length (nm)	324.5	309.3	285.2	328.1	193.7	253.7	357.9
Band pass (nm)	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Flame type	Air-C_2H_2	N_2O- C_2H_2	Air-C_2H_2	Air-C_2H_2	Air-C_2H_2 (vapour mode)	No heating (vapour mode)	Air-C_2H_2
Hollow cathode lamp current (mA)	5	10	4	4	12	6	15
Fuel flow (L/min)	1.1	4.3	1.1	1.1	1.0	0.2	1.4

TABLE-2
HEAVY AND TRACE METAL CONCENTRATION IN SYNTHETIC AND HERBAL SHAMPOO

Sample ID	Heavy and trace metal concentration (ppm) in synthetic and herbal shampoo													
	Fe	Co	Ni	Cu	Zn	Cd	Cr	Al	Mg	Pb	Mn	Hg	As	Ag
SS	0.60	BDL	BDL	0.15	0.47	BDL	0.003	9.10	1.19	BDL	BDL	2.23	0.03	BDL
SS_2	0.20	BDL	BDL	0.20	0.36	BDL	0.02	5.87	1.67	BDL	0.22	BDL	BDL	BDL
SS_3	0.26	BDL	BDL	0.27	0.57	BDL	0.06	10.89	23.03	BDL	BDL	1.15	BDL	BDL
SS_4	0.45	BDL	BDL	0.49	BDL	BDL	BDL	1.17	6.18	BDL	BDL	BDL	BDL	BDL
SS_5	1.39	BDL	BDL	0.14	0.53	BDL	0.16	10.11	107.54	BDL	BDL	BDL	0.01	0.22
SS_6	1.65	BDL	0.01	0.27	2.82	BDL	BDL	2.19	8.34	BDL	0.28	0.6	0.01	BDL
SS_7	0.73	BDL	BDL	0.10	0.16	BDL	BDL	3.00	0.87	BDL	BDL	BDL	BDL	BDL
SS_8	0.55	BDL	BDL	0.17	0.30	BDL	BDL	0.93	5.78	BDL	BDL	BDL	0.02	BDL
SS_9	1.45	BDL	BDL	0.08	0.42	BDL	BDL	0.83	25.21	BDL	0.03	BDL	0.02	BDL
SS_{10}	1.09	BDL	BDL	0.24	1.98	BDL	0.04	9.32	14.78	BDL	BDL	2.07	BDL	BDL
SS_{11}	0.11	BDL	BDL	0.21	5278.89	BDL	0.14	7.53	9.66	BDL	0.27	BDL	BDL	BDL
SS_{12}	0.81	BDL	BDL	0.13	0.28	BDL	BDL	7.23	1.04	BDL	BDL	BDL	BDL	BDL
SS_{13}	0.42	BDL	BDL	0.09	0.92	BDL	BDL	0.94	2.77	BDL	0.03	BDL	BDL	BDL
SS_{14}	0.43	BDL	BDL	0.11	4207.2	BDL	BDL	5.12	464.52	BDL	0.07	BDL	0.01	BDL
SS_{15}	0.35	BDL	0.08	0.22	0.56	BDL	0.19	1.09	2.52	BDL	BDL	1.46	0.02	BDL
SS_{16}	0.45	BDL	BDL	0.18	5.18	BDL	0.16	16.32	29.4	BDL	BDL	BDL	0.05	BDL
SS_{17}	0.25	BDL	BDL	0.32	1.09	BDL	0.13	7.03	26.29	BDL	0.81	0.15	0.03	BDL
SS_{18}	0.55	BDL	BDL	0.23	3.08	BDL	0.21	11.66	3.93	BDL	BDL	49.02	BDL	BDL
SS_{19}	0.23	BDL	BDL	0.21	4840.32	BDL	0.34	10.54	3.46	BDL	0.27	BDL	0.01	BDL
SS_{20}	0.35	BDL	BDL	0.28	1.67	BDL	0.20	9.90	8.32	BDL	BDL	13.96	BDL	BDL
SS_{21}	5.90	BDL	0.24	0.47	10.00	BDL	0.61	14.77	28.42	BDL	0.34	BDL	0.012	BDL
SS_{22}	0.02	BDL	BDL	0.19	0.80	BDL	0.25	9.42	7.03	BDL	BDL	BDL	0.02	BDL
SS_{23}	0.69	BDL	BDL	0.14	0.24	BDL	BDL	0.99	1.78	BDL	0.03	26.2	0.004	BDL
SS_{24}	BDL	BDL	BDL	0.10	3.87	BDL	0.15	7.84	67.33	BDL	1	BDL	0.03	BDL
SS_{25}	1.55	BDL	BDL	1.02	5.58	BDL	0.16	28.04	13.74	BDL	0.51	BDL	0.42	BDL
SS_{26}	0.21	BDL	BDL	0.20	3.34	BDL	0.09	1.06	34.66	BDL	0.98	BDL	0.01	1.4
SS_{27}	1.88	BDL	BDL	0.16	63.1	BDL	0.16	10.40	51.01	BDL	1.21	0.76	BDL	BDL
SS_{28}	0.10	BDL	BDL	0.24	1.01	BDL	0.27	10.65	24.15	BDL	0.59	BDL	0.02	BDL
SS_{29}	0.06	BDL	BDL	0.37	2.42	BDL	0.28	10.91	9.99	BDL	BDL	BDL	0.05	BDL
SS_{30}	0.08	BDL	0.05	0.06	0.28	BDL	0.16	3.66	3.32	BDL	BDL	BDL	0.002	0.21
SS_{31}	0.11	BDL	0.07	0.28	0.42	BDL	0.22	6.70	17.12	BDL	BDL	3.57	0.02	BDL
SS_{32}	0.33	BDL	BDL	0.31	1.56	BDL	0.16	5.66	11.07	BDL	BDL	5.08	0.01	BDL
SS_{33}	0.28	BDL	0.05	0.26	0.47	BDL	0.22	6.39	9.69	BDL	BDL	8.33	0.01	BDL
SS_{34}	1.25	BDL	BDL	0.37	9.37	BDL	0.37	19.3	76.30	BDL	BDL	BDL	0.001	BDL
SS_{35}	0.48	BDL	BDL	0.36	1.16	BDL	0.20	6.72	36.46	BDL	BDL	BDL	BDL	BDL
SS_{36}	0.06	BDL	BDL	0.18	0.41	BDL	0.21	6.48	9.47	BDL	BDL	BDL	0.03	BDL
SS_{37}	0.99	BDL	BDL	0.23	1.08	BDL	0.31	8.50	27.11	BDL	BDL	7.15	0.01	BDL
SS_{38}	0.02	BDL	0.1	0.11	0.49	BDL	0.25	6.83	20.00	BDL	BDL	4.31	0.11	BDL
SS_{39}	0.01	BDL	BDL	0.29	0.46	BDL	0.23	6.46	7.98	BDL	BDL	BDL	0.01	BDL
SS_{40}	0.08	BDL	BDL	0.39	2.62	BDL	0.40	5.32	7.20	BDL	BDL	BDL	0.04	BDL
SS_{41}	0.14	BDL	BDL	0.19	0.83	BDL	0.23	6.16	11.85	BDL	BDL	1.47	0.003	BDL
HS_{42}	0.68	BDL	BDL	0.13	9.22	BDL	BDL	1.05	7.71	BDL	0.3	BDL	BDL	BDL
HS_{43}	0.70	BDL	BDL	0.14	0.27	BDL	BDL	1.04	0.21	BDL	0.02	BDL	0.02	BDL
HS_{44}	0.20	BDL	BDL	0.20	0.98	BDL	0.20	8.51	19.88	BDL	BDL	1.24	0.02	BDL
HS_{45}	BDL	BDL	BDL	0.10	0.50	BDL	0.23	7.42	6.93	BDL	BDL	BDL	0.01	BDL
HS_{46}	0.73	BDL	0.05	0.25	3.19	BDL	0.38	7.66	259.54	BDL	0.24	BDL	0.001	BDL
HS_{47}	4.08	BDL	BDL	0.41	7.59	BDL	0.31	9.85	24.37	BDL	BDL	7.45	0.02	BDL
HS_{48}	0.37	BDL	BDL	0.29	1.12	BDL	0.32	9.58	113.45	BDL	BDL	BDL	BDL	BDL
HS_{49}	0.04	BDL	BDL	0.14	1.27	BDL	0.26	7.74	26.06	BDL	BDL	BDL	BDL	BDL

BDL = Below detection limit

the kidneys or liver (mercury, lead, cadmium, copper) or skin, bones, or teeth (nickel, cadmium, copper, chromium)[31]. The excess amount of Zn, Mg, Al, Fe and other metal affect the skin and also create the many Derma logic diseases[32]. The Zn, Mg and others metal concentration in synthetic and herbal shampoo are shown in Fig. 2. The Zn value is above 95 % in some synthetic shampoo. In addition, the Mg concentration in herbal shampoo is nearly 55 %, while synthetic shampoo contains below 40 % Mg. However, heavier and trace metal concentrations in both shampoos are nearly same.

Mercury is highly toxic to humans both inorganic and organic forms. Inorganic Hg, such as mercury vapour, is toxic if inhaled in large concentrations and can cause acute pneumonia[15]. Inhaled gaseous mercury is absorbed into the blood. By circulatory system, it can pass through the blood-brain barrier and accumulate in the brain which destructive the central nervous system. Gaseous mercury is oxidized to divalent mercury, which accumulates in the kidneys and can cause kidney damage[33]. The permissible limit (according to the WHO) for Hg in herbal preparation is 1 ppm[14], but we got

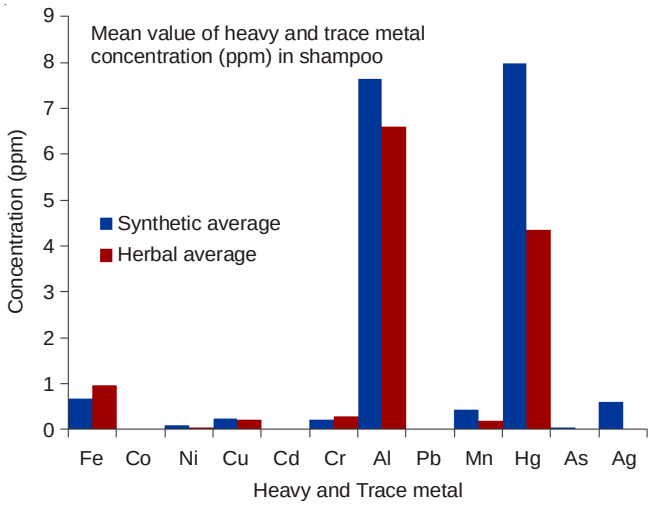

Fig. 1. Comparison of heavy and trace metal concentration in synthetic and herbal shampoo

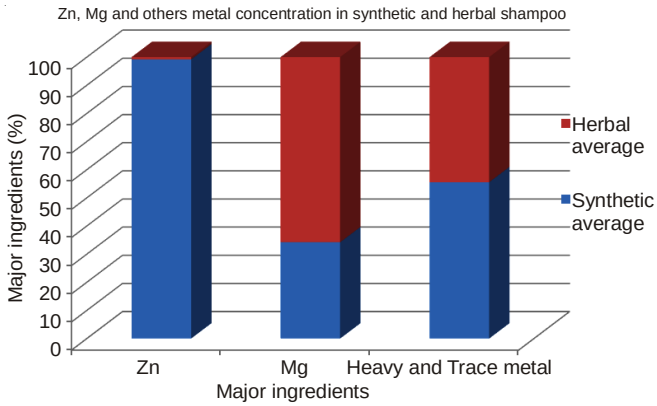

Fig. 2. Maximum (Zn, Mg) and minimum (heavy and trace metal) ingredients in synthetic and herbal shampoo

in highest value of synthetic and herbal shampoo is 49.02 and 7.45 ppm. Mercury also discolours the skin, which creates the carcinogenic effect on skin. It is used as a whitening cream in cosmetic products.

The overwhelming plague of aluminum means that your risk of disclosure is through the roof, which is also made of Al. Aluminum accumulates in the kidneys, brain, lungs, liver and thyroid, where it strives with calcium for absorption and affects the skeletal mineralization. Animal models have linked aluminum contact to mental impairments [34]. The result shows the highest value of Al (28.04 ppm) was determined in synthetic shampoo than those of herbal shampoo (9.85 ppm). Age-related Fe overloaded to multiple degenerative diseases, including liver fibrosis, heart attack and cancer[35].

Water insoluble Cr(III) compounds and chromium metals are not considered as a health hazard substances, while the Cr(VI) have been shown the toxicity effect for a long time[1]. Chromates are used to manufacture, amongst other things, leather products, paints, cement, mortar and anti-corrosives. This product can lead to allergic diseases, resulting in ulceration of the skin, sometimes referred to as "chrome ulcers". It available found in workers that have been exposed to the strong chromate solutions in electroplating, tanning and chrome-producing manufacturers[36].

In general, nickel occurs at low concentration in the environment and it also creates a variety of pulmonary adverse health effects, such as lung inflammation, fibrosis, emphysema and tumours[37]. In the present investigation the higher Ni concentration was found as 0.24 and 0.05 ppm in synthetic and herbal shampoo as well. Copper is an essential element for several enzymes and it is necessary for synthesis of hemoglobin[38]. Nevertheless, high intake of Cu has been known to cause of adverse health problem[39]. The higher value of Cu was available as 1.02 and 0.41 ppm of both synthetic and herbal shampoo. The Zn value in synthetic shampoo was 5278.89 ppm and herbal is 9.22 ppm. Some researchers reported that the chronic exposure of Cu and Zn related products are associated with Parkinson's disease[39] and these elements also might act alone or together over time to induce the disease[40].

In synthetic shampoo, the highest Mg value was observed, *i.e.*, 464 ppm and 259.54 ppm is in the herbal shampoo. Magnesium toxicity might be badly affect the cardiovascular system. Excess magnesium in the blood can also slow heartbeat or cause erratic heart rhythms, also known as arrhythmias. If high levels of magnesium gather in the blood the heart might stop beating completely, called cardiac arrest[41].

Arsenic is extensive in the environment for both anthropogenic and natural processes. The highest concentration in synthetic shampoo was 0.42 ppm and for herbal products was 0.02 ppm. Humans exposed to arsenic dust or fume inhalation are more pick to be encountered in mining and milling of ores. For industrial products such as smelting industry, which often produces irritation of the mucous membrane, resulting in laryngitis, bronchitis, rhinitis and tracheobronchitis, causing stuffy nose, sore throat, hoarseness and chronic cough *etc*.

Table-3 depicted the correlations between all analyzed heavy and trace metals, listing the Pearson product correlation coefficients. The considered metals in shampoos were significantly correlated with each other during both synthetic and herbal shampoo samples. The significant correlations were found between Ni and Fe (r = 0.787**), Ni and Cr (r = 0.585**), Cr and Fe (r = 0.380*), Cr and Cu (r = 0.311*), Al and Fe (r = 0.309*), Al and Cu (r = 0.617**), Al and Cr (r = 0.442**), Mg and Zn (r = 0.432**), As and Cu (r = 0.725**), As and Al (r = 0.607**) and Ag and Mn (r = 0.390*) at $p < 0.01$ indicates the double star and $p < 0.05$ indicates a single star level for synthetic shampoo. In herbal shampoo, Cu and Fe (r = 0.798*), Fe and Hg (r = 0.955**), Hg and Cu (r = 0.787*) and Al and Cr (r = 0.890**) were significantly correlated (Table-3). The results might indicate that the distributions of these pairs were regulated by common local inputs and similar dispersion processes in this study, except for Zn, Mg and Mn in synthetic shampoo and Zn, Cr, Mg, Mn and As in herbal shampoo.

In general, the analysis of heavy and trace metals are performed using atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS), X-ray fluorescence spectroscopy (XFS) and inductively coupled plasma atomic emission spectrometry (ICP-AES). Nevertheless, the instrumental methods of ICP-MS, ICP-AES and XFS are usually more costly and their use is not as candid and appropriate as atomic absorption spectrometry. In this

TABLE-3
CORRELATION BETWEEN HEAVY AND TRACE METAL IN SYNTHETIC AND HERBAL SHAMPOO

Synthetic shampoo

	Fe	Ni	Cu	Zn	Cr	Al	Mg	Mn	Hg	As	Ag
Fe	1	0.787	0.29	-0.115	0.38	0.309	0.04	0.151	-0.042	0.088	-0.067
Ni	0.787**	1	0.183	-0.064	0.585	0.166	-0.02	0.04	-0.053	0.006	-0.047
Cu	0.29	0.183	1	-0.112	0.311	0.617	-0.134	0.099	-0.059	0.725	-0.083
Zn	-0.115	-0.064	-0.112	1	0.018	0.012	0.432	0.032	-0.1	-0.081	-0.056
Cr	0.380*	0.585**	0.311*	0.018	1	0.442	-0.101	0.01	0.003	0.037	-0.107
Al	0.309*	0.166	0.617**	0.012	0.442**	1	0.026	0.141	0.017	0.607	-0.198
Mg	0.04	-0.02	-0.134	0.432**	-0.101	0.026	1	0.053	-0.11	-0.054	0.027
Mn	0.151	0.04	0.099	0.032	0.01	0.141	0.053	1	-0.168	0.154	0.39
Hg	-0.042	-0.053	-0.059	-0.1	0.003	0.017	-0.11	-0.168	1	-0.08	-0.072
As	0.088	0.006	0.725**	-0.081	0.037	0.607**	-0.054	0.154	-0.08	1	-0.058
Ag	-0.067	-0.047	-0.083	-0.056	-0.107	-0.198	0.027	0.390*	-0.072	-0.058	1

Herbal shampoo

	Fe	Cu	Zn	Cr	Al	Mg	Mn	Hg	As
Fe	1	0.798	0.611	0.217	0.239	-0.061	-0.071	0.955	0.499
Cu	0.798*	1	0.349	0.607	0.608	0.338	-0.146	0.787	0.337
Zn	0.611	0.349	1	-0.14	-0.206	-0.053	0.628	0.5	-0.017
Cr	0.217	0.607	-0.14	1	0.89	0.678	-0.164	0.272	-0.258
Al	0.239	0.608	-0.206	0.890**	1	0.325	-0.459	0.409	-0.033
Mg	-0.061	0.338	-0.053	0.678	0.325	1	0.415	-0.178	-0.394
Mn	-0.071	-0.146	0.628	-0.164	-0.459	0.415	1	-0.253	-0.443
Hg	0.955**	0.787*	0.5	0.272	0.409	-0.178	-0.253	1	0.572
As	0.499	0.337	-0.017	-0.258	-0.033	-0.394	-0.443	0.572	1

**P < 0.01; *P < 0.05

study, a simple, reliable, sensitive and suitable atomic absorption spectrometry method has settled for quantitative estimation of heavy, trace and other metal which can conveniently be utilized for quality control of synthetic and herbal product preparations at industrial level.

Conclusion

This study has revealed that there are considerably high concentrations of Fe, Cu, Zn, Cr, Al, Mg, Mn and Hg in some of the shampoo products investigated. Many metals are no guideline. The metal concentration value of synthetic shampoo is higher than that of herbal shampoo. Mercury, Al, Zn and Mg value are higher in the both shampoo samples. These elements are commonly used for cosmetic products and their continual usage may render the users at high risk of heavy metal toxicity. In view of this, regulatory guidelines on good manufacturing practice, good analytical practice with using sophisticated instrument in the manufacturing and importation of cosmetics should be formulated and enforced by relevant authorities. In the same vein, the extensive or excessive use of cosmetics should be discouraged by public awareness. This project will help to aware the mass people to use of cosmetics.

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