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Trace Determination of Selected Heavy Metal Ions in Bleaching Creams in the Local Market of Saudi Arabia

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Bleaching cream and cosmetics products of skin have risk of toxicity and deleterious effects to the human health because of their multiplicative contamination with heavy metals and uncertain mixing of different components. Thus, the present study reports a comprehensive study on the trace selected heavy metal (Hg, Cd, Ti, Bi, Pb, As and Tl) determination in 16 samples of bleaching creams and samples mixture of bleaching creams simultaneously to get a double activity (shiny and faster) on the skin from the local market of Saudi Arabia. Samples were digested with high pressure microwave technique followed by direct determination by inductive coupled plasma - optical emission spectrometer (ICP-OES). Hg, Bi, Ti and Pb levels on samples were found equal 5739.16, 7013.53, 21407.73, 456.70 μg/g, respectively whereas other elements (Cd, As and Tl) were found less than 28.99 ppm. One sample of the mixtures showed high concentrations of Hg (13338.50 μg/g,) and Bi (619.23 μg/g). Thus, creams and cream mixtures containing heavy metals above the permissible limit must be blind. The lower detection limits (LOD) were achieved at 2.5-50 μg/g concentration level, RSD was less than 14.72%, and recovery percentage for cosmetics were in the range of 88.52 -99.62%. The proposed method for sample digestion and ICP-OES measurements was fast, precise, convenient and provided good recovery of the tested elements.

Keywords: Bleaching creams; Cosmetic products; Heavy Metals; Microwave digestion; ICP-OES determination.

Since the dawn of civilization, Cosmetic products e.g. care creams, lipsticks, kajal, mouth washesm, eye makeup etc.) have been used as routine body care[1, 2]. These products had a big boost and applied to the human body for beautification during the last few decades[3]. The significant route involves dermal exposure represents the most effective route since most of these complex species are directly applied to the skin[4]. Wearing of cosmetic cream that contain toxic metal ions as impurities can account for oral exposure[4]. The level of mercury measured in the cosmetic product of skin whitening cream from several Caribbean countries was 8%[5]. Thus, in recent years great attention of researcher and clinician has been oriented towards health awareness of the adverse effects of contamination by toxic metal ions in the cosmetic creams[6-11].

High concentrations of some essential elements become toxic[11]. Heavy metal ions get absorbed when come in contact with human body by forming complex species with the binding sites of proteins e.g. carboxylate, $-NH_2$ and -SH resulting in or cell death of the cells and lead to

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large varieties of diseases[11]. Intoxication by heavy metal ions has been achieved by chelation therapy forming complexes that can easily eliminated from the body[12]. Some cosmetic products are benign whereas others can cause many harmful effects e.g. allergic reaction, mutations, respiratory problems as well as development [13, 14].

Exposure to toxic metal ions through dermal contact is rare, and little information's are known on personal cosmetic products[15]. An increase in the trace levels of cadmium causes inhibition of DNA mismatched while zinc can also cause the same signs of illness as Pb, and can easily be mistakenly diagnosed as Pb poisoning[16]. exposure to a large dose of As cause skin and lung cancer and pigmentation of skin[17, 18]. Nine ingredients including coal tar colors, formaldehyde, glycol ethers, pB, hG, parabens, phenylenediamine, phthalates as highly toxic substances are banned in cosmetic products by US-EPA because of their toxicity[19]. In Canada concentrations of metal ions above 10 and 5 mg/kg for Pb and Sb and 3 mg/kg for As, Cd, Hg require special scrutiny[20]. In European Union (EU), a list of more than 1000 compounds are banned for use in cosmetic manufacturing[21].

According to (Saudi Standards, Metrology and Quality Org.) SASO//1953/2005, many heavy metals e.g. As, Cd, Hg, Tl, Pb or their compounds, except lead acetate are prohibited in the production of the cosmetics products even at trace levels[22]. FDA wariness to use bismacine drug containing large quantity of bismuth because of its toxicity [23]. The use of TiO_2 for skin protection from ultraviolet radiation has been reported[23]. A questioner study on 54 ladies use different bleaching creams on their faces and bodies has revealed that, more than 48% of them get different problems on their skins (redness, acne, pigmentation and allergies). Thus, it's necessary to precisely manage the amount of heavy metals used in cosmetic products to provide the customers with safe cosmetics. Hence, this article is focused on: i) Precise ICP-OES determination of selected heavy metal ions (Hg, Cd, Ti, Bi, Pb, As and Tl) in various bleaching creams and sample mixtures of bleaching creams simultaneously to get a double activity (shiny and faster) on the skin from the local market of Saudi Arabia ; ii) The results will be compared with the permissible limits for heavy metals set by world health organization (WHO) and SASO (Saudi Standards, Metrology and Quality Org.). The study helps the consumers in searching for other healthy products that not contains these toxic metal ions. The study also helps producers to provide the local market with cosmetics products that do not compromise human health under optimized conditions.

MATERIALS AND METHODS

Samples collection

According to statistic studies on A 54 Saudi ladies were questioned to select the most bleaching creams they favored in the local market of Saudi Arabia. Based on the questioner, a sixteen samples of cosmetic creams were collected from the local market of Jeddah and their brand names were blinded and given the codes B_1 - B_{16}. Also, a 12 sells men from different cosmetic markets showed three mixtures of bleaching creams given the code B_{21}, B_{22} and B_{23}.

Instruments

Inductive coupled plasma - Optical emission spectrometer (ICP-OES) Optima 8300 – Perkin Elmer and a Milestone Ethos lab station with easy Wave or easy Control software HPR1000/10S high pressure segmented rotor were used. The optimum operational parameters of ICP-OES are: read delay time =10:0; sample flush time 20 s; flow rate = 1.0 mL/min; number of replicates =3 ; wash rate (2 mL/min) 2:00; wash time (s): 2:0 s and finally, resolution is normal. Ultrapure water were delivered from PURELAB classic purification system (ELGA, UK) was used for providing ultra-pure deionized water. Digital-micro-pipettes (Volac) were used for preparation of more diluted solutions.

Reagents and chemicals

Analytical reagent grade sulphuric acid (Sp.gr 1.84, 98%) and hydrofluoric acid (40%) (E. Merck) were used. The standard solutions were prepared at various concentrations. Standard solutions for each heavy metal were prepared freshly in the range from 0.5 to 10 ppm from High-Purity Standards ICP-MS-68B Solution (100 µg/mL in dilute nitric acid. Dilution correction was applied for samples diluted or concentrated during analysis. *C*alibration curves of the tested metal ions were prepared by diluting Hg and stock solutions

(1000 mg/L) (Accu Trace™ Reference Standard). Multi elements standard of Cd, As, Pb, Tl and Ti (1000 mg/L) (PerkinElmer Pure) was also used .

Microwave digestion of the cosmetic samples

In a closed conical flask, digestion of the cosmetic samples was performed using temperature control microwave heating as follows:

An accurate weight (0.2± 0.0 g) of cosmetic sample was placed in a TFM vessel, followed by adding 6 mL of concentrated H_2SO_4 (Sp.gr. 1.84, 98% m/v) and 2 mL of HF (40% m/v). The reaction mixtures were gently swirled to homogenize the sample with the acids[24]. The samples were then digested in the microwave digestion system at the specified program as follows:

Step	Time	Temperature	Microwave power
1	10 minutes	200°C	Up to 1000 Watt*
2	20 minutes	200°C	Up to 1000 Watt*

Table 1. Operational wavelength (nm) , calibration standard (µg/mL) and measured concentrations by ICP-OES

Analyte	Calib Std1	Calib Std2	Calib Std3
Hg 546.074nm		10:000	
Cd 226.502nm			10:00
Ti 337.279nm			10:00
Bi 190.171nm	10:00		
Pb 261.418nm			10:00
As 188.979nm			10:00
Tl 190.801nm			10:00

The samples were then left after complete digestion to cool at room temperature and the vessel was opened. The digested reaction mixtures were filtered through whatman paper no.1 into volumetric flasks (25 mL). Samples were then diluted to the mark with deionised water. The contents of Hg, Cd, Ti, Bi, Pb, As and Tl in the digested samples were determined by ICP-OES *versus* a reagent blank under the same experimental conditions and with the aid of calibration plot for each element. Calibration curve: The 1000 ppm standard solutions of elements were diluted in five d element. The concentration (mg/Kg) of each element was determined using the following equation[25]:

[C], mg/Kg = (Concentration mg/L × sample volume (mL)/mass, g) **(1)**

RESULTS AND DISCUSSION

The method of standard addition [26] was used for validation of the proposed method. Hence, the recovery percentage of standard solution of each tested element (10µg/mL) at the optimized wavelength for each element (Hg, Cd, Ti, Bi, Pd, AS and Tl) by the proposed digestion procedures is given in Table 1. The standard deviation (SD), relative standard deviation (RSD), recovery percentage and variation (S^2) of solutions spiked with standard Hg, Cd, Ti, Bi, Pd, AS and Tl at 5µg/mL were analyzed after digestion and dilution using the recommended procedures were critically determined. The results are demonstrated in Table 2. The recovery percent of Hg, Cd, Ti, Bi, Pb, As and Tl from last ranged from 88.52% to 99.62% (Table 2).

Table 2. Analytical results of recovery %, standard deviation, RSD, and variance*

Element	Spiked con, µg/mL	Measured con, µg/mL	Recovery, %	S	RSD, %	S^2
Hg	5	4.458	89.16	0.434	9.734	0.188
Cd	5	4.898	97.96	0.035	0.716	0.001
Ti	5	4.898	97.96	0.192	3.943	0.036
Bi	5	4.426	88.52	0.009	13.724	0.0001
Pb	5	4.981	99.62	0.075	1.497	0.006
As	5	4.793	95.86	0.039	0.808	0.002
Tl	5	4.816	96.32	0.025	0.510	0.001

* Variance =S^2.

Table 3. Heavy metals content in cosmetic products (B_1- B_{16}) and 3 mixtures of bleaching creams (B_{21}-B_{23})

S. no.	Hg (25 ppm)*	Cd(2.5 ppm)*	Bi(50 ppm)*	Pd(25 ppm)*	As(25 ppm)*	Tl(25 ppm)*	Total toxic elements	Ti(2.5 ppm)*	TiO_2%
B_1	466.91 ± 33.56	0.24 ± 0.01	470.35 ± 55	96.48 ± 15.11	8.63 ± 0.45	3.31 ± 10525	1045.92	2248.34 ± 157.28	0.38
B_2	BDL	0.165 ± 0.11	BDL	BDL	6.5 ± 0.51	0.95 ± 0.09	7.615	31.07 ± 2.22	5.18×10^{-3}
B_3	3964.31 ± 105.11	BDL	BDL	456.70 ± 4.98	28.99 ± 1.29	15.47 ± 9.7	4465.47	15906.58 ± 119.22	2.65
B_4	513.55 ± 37.09	0.06 ± 0.01	5.563 ± 0.09	19.43 ± 4.45	6.00 ± 1.52	6.40 ± 3.13	551.003	2728.92 ± 32.17	0.46
B_5	1594.72 ± 93.06	0.14 ± 0.03	BDL	BDL	14.9 ± 1.49	6.98 ± 1.74	1616.74	7264.92 ± 73.97	1.21
B_6	5739.16 ± 109.47	BDL	BDL	6.93 ± 4.75	36.31 ± 2.68	13.69 ± 5.06	5796.09	21407.73 ± 404.21	3.57
B_7	730.28 ± 37.79	0.51 ± 0.09	7013.53 ± 149.12	111.85 ± 6.37	11.26 ± 2.85	5.47 ± 1.29	7872.9	3709.80 ± 17.91	0.62
B_8	18.57 ± 18.57	0.4 ± 0.19	BDL	BDL	5.85 ± 2.28	4.51 ± 1.78	29.33	32.93 ± 9.41	5.49×10^{-3}
B_9	BDL	0.11 ± 0.01	BDL	BDL	3.70 ± 0.68	2.63 ± 1.3	6.44	41.43 ± 4.65	6.91×10^{-3}
B_{10}	BDL	0.27 ± 0.01	0.70 ± 0.70	BDL	3.68 ± 0.88	2.00 ± 1.84	6.65	38.24 ± 0.24	6.38×10^{-3}
B_{11}	229.73 ± 33.59	BDL	BDL	56.58 ± 1.85	2.14 ± 0.39	0.92 ± 0.92	289.35	1707.50 ± 12.99	2.85
B_{12}	BDL	0.57 ± 0.02	917.45 ± 154.90	226.47 ± 8.65	7.34 ± 0.69	6.42 ± 0.50	1158.25	40.56 ± 1.16	6.77×10^{-3}
B_{13}	BDL	0.06 ± 0.06	BDL	BDL	3.00 ± 1.57	1.22 ± 0.38	4.28	56.50 ± 0.00	9.42×10^{-3}
B_{14}	BDL	0.12 ± 0.12	BDL	BDL	4.67 ± 0.61	2.73 ± 0.29	7.52	38.89 ± 3.13	6.49×10^{-3}
B_{15}	BDL	0.07 ± 0.07	BDL	BDL	3.60 ± 3.60	1.84 ± 0.33	5.51	47.02 ± 4.39	7.84×10^{-3}
B_{16}	BDL	BDL	BDL	21.10 ± 21.10	2.26 ± 2.26	0.44 ± 0.44	23.8	39.55 ± 1.23	6.60×10^{-3}
B_{21}	1338.53 ± 84.07	BDL	619.23 ± 160.88	94.18 ± 5.05	10.17 ± 8.51	7.53 ± 7.47	2069.64	7193.85 ± 14.3	1.20
B_{22}	BDL	0.18 ± 0.14	70.71 ± 22.78	16.26 ± 11.36	10.05 ± 3.96	4.43 ± 0.12	101.63	265.80 ± 7.36	0.4
B_{23}	BDL	0.06 ± 0.06	BDL	2.78 ± 2.78	1.23 ± 1.23	0.60 ± 0.60	4.67	189.81 ± 39.76	0.3

* Detection limit of element [25]; BDL= Below limit of detection and value are expressed as arithmetic mean ± SD (n=3)

The contents of heavy elements in the screened samples as a mean of triplicate determination are summarized in Table 3. Mercury concentration varied from 18.57 to 5739.16 ppm for eight samples (B_1, B_3, B_4, B_5, B_6, B_7, B_{11} and B_{21}). Sample B_6 has the highest mercury concentration (5739.16 ± 109.47µg/g) and sample B_8 has the lowest Hg content (18.57 ± 18.57µg/g). In some other samples (8 samples), mercury content was found below the lower detectable limit. In cosmetic products, the permissible limit for mercury set by WHO is 1.0 µg/g[27]. Thus, B_1, B_3, B_4, B_5, B_6, B_7, B_{11} and B_{21}samples contain mercury concentration above the permissible limit.

Cadmium concentrations in 12 samples varied from 0.06 to 0.57 µg/g. Concentrations of Cadmium concentration in sample B_4 and B_{13} were the lowest, while sample B_{12} has the highest cadmium concentration. According to the WHO[27] , the permissible limit for cadmium in cosmetic products is o.3 µg/g. Sample B_7, B_8 and B_{12} were found to contain Cd concentration above the permissible limit. Regarding Bi, the bismuth content varied from 0.70 and 7013.53 µg/g thus, these samples must be blend. In 11 samples, Bi content was found below the detectable limit.

Lead concentrations varied from 6.93 to 456.70 µg/g where sample B_3 has the highest content (456.70 ± 4.98µg/g) and sample B_6 has the lowest (6.93 ± 4.75µg/g). In the other 8 samples, Pb content were found below the detectable limit. According to the WHO[27], the permissible limit for lead in cosmetic is 10 µg/g. The Pb content in samples B_1, B_3, B_4, B_7, B_{11} and B_{12} were found above the permissible limit. In all samples, arsenic was found in small quantities and varied from 2.14 to 36.31 µg/g. Sample B_6 has the highest As content (36.31 ± 2.68µg/g) and sample B_{11} has the lowest (2.14 ± 0.39µg/g). According to the WHO, the permissible limit for As in cosmetic products set at 10 µg/g. The As content in samples B_3, B_5, B_6 and B_7 were found above the permissible limit i.e. > 10 µg/g.

Thallium was found on all samples In all samples, Tl was found with small quantities in the range 0.44 -15.47 µg/g. The highest Tl content (15.47 ± 9.7µg/g) was found in sample B_7 whereas the lowest content (0.44 ± 0.01µg/g) was found for sample B_{16}. Ti was found in the 16 samples and the level content varied from 31.07 to 21407.73 µg/g, where, sample B_6 has the highest Ti concentration (21407.73 ± 404.21µg/g) and sample B_2 was the lowest (31.07 ± 2.22µg/g). Titanium present as titanium dioxide (TiO_2) in cream matrix where, the content of TiO_2% varied from 5.18×10^{-3} to 3.57%. According to the (SASO//1953/2005), the level of TiO_2 presents at a level below the permissible limit 25%.

The total toxic metals concentrations on the tested cream samples were found up to 1000 µg/g were found in samples B_1, $_{B3}$, B_5, B_6, B_7 and B_{12} and varied from 1045.92 to 7872.9 µg/g. Bleaching mixture no. B_{21} composed of $B_1 + B_2 + B_3 + B_4 + B_5 + B_6 + B_7 + B_7$ creams has 1338.53, 619.23 and 94.18 µg/g Hg, Bi and Pb, respectively. This cream mixture was found above the permissible limits, thus it must be blended. Bleaching mixture no. B_{22} consists of $B_2 + B_8 + B_9 + B_{10} + B_{11} + B_{12} + B_{16}$ creams has 70.71 and 16.26 µg/g Bi and Pb, , respectively. These values are above the permissible value set by WHO[27]. Thus, this sample must be blinded. Bleaching mixture no. B_{23} consists of B_{13} + B_{14} + B15 + B_{16} creams has small quantities of different elements under permissible limits, so it no blinded and satisfactorily approved.

CONCLUSION

Based upon the content of the heavy metal (Hg, Cd, Ti, Bi, Pd, AS and Tl) in16 bleaching creams and 3 mixtures of bleaching creams, it can be concluded that, mercury, bismuth and lead are present in high quantities in samples. Both arsenic and thallium present in small quantities ranged from 0.44 to 36.31 µg/g. On the other hand, TiO_2 determined under the permissible limit of SASO. Two of bleaching mixtures have high quantities of total heavy metals up to the permissible limit. Continued use of cosmetic creams that highly contaminated with these elements are known to release of these toxic elements into the body of the human and subsequently harmful effects. The quality of the products can be improved if careful selection of the raw material is made keeping in view the heavy metal contents and save the beauty of the environment.

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