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ELEMENTAL COMPOSITIONS OF SOME COSMETIC PRODUCTS MARKETED IN TURKEY

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ABSTRACTS

The aim of this study was to determine elemental composition of various cosmetic products marketed in Turkey by X-Ray Fluorescence Spectrometry (XRFS). These cosmetic products ranged from blush, eye shadow, lipstick, nail polish, shampoo, hand cream, cellulite cream, baby powder, soap, to toothpaste (50 samples). Elements that were determined in these samples included V, Cr, Mn, Ni, Cu, As, Br, Mo, Ag, Sn, I, Hg, Pb and Bi. Metal concentration levels of Cr, As, Hg and Pb in certain cosmetic products are very important since these elements are toxic and dangerous for human health at high concentrations. In a few sample brands of cosmetic products As and Hg were detected at higher concentrations than limits defined by both German federal government and Health Canada regulations. In the majority of the samples, the concentrations of lead are higher than limits defined by both German federal government and Health Canada regulations. In lipsticks alone, 8 out of 11 brands contain Pb at concentrations higher than that of the maximum permissible concentration of $10 \mu\text{g g}^{-1}$ in cosmetics.

KEYWORDS:

Cosmetic products, toxic element, XRF, health hazard.

INTRODUCTION

Cosmetic products can be used on various parts of the human body such as the epidermis, nails, hairs and lips to look good or to change the appearance. Although cosmetic products are used by many people including children, young and elderly people, studies related to cosmetic products in the literature have been limited [1, 2]. The use of cosmetics is as old as human history, and almost all societies on earth have been used in many cosmetic products since very early on. The first archaeological data corresponding to the use of cosmetic products were found in the ancient Egyptians in BC 4000 years. Ancient Egyptians and

Romans were using lead and mercury to look beautiful but had no idea about the toxic effects of heavy metals. For example, HgS was used for many years by the Romans as a red colour pigment. This pigment was commonly used as wall decoration, sculpture dye, gladiator's body paint and as the lipstick of Roman women in the Roman [3]. Although there is no specific definition of heavy metals, it is often used as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or ecotoxicity [4]. Many of these products are in our homes and actually add to our quality of life when properly used. Heavy metals may enter the human body through food, water, air, or absorption through the skin when they come in contact with humans in agriculture and in manufacturing, pharmaceutical, industrial, or residential settings [5]. Although several adverse health effects of heavy metals have been known for a long time, exposure to heavy metals continues, and is even increasing in some parts of the world, in particular in less developed countries, though emissions have declined in most developed countries over the last 100 years [6].

As certain heavy metals such as lead, cadmium and mercury have been recognised to be potentially toxic, a considerable potential hazard exists for human exposure through consumer products. Therefore, the contents of the heavy or toxic metal of these products, including cosmetic products, should be investigated on a regular basis. Several important factors, for selection of analytical methods used for the elemental analysis, are reliability, good precision and accuracy (better than 10%), low detection limit and cost. The determination of heavy and toxic elements permits the study of their distributions, the pollution level as well as the risk assessment in the investigated ecosystems. Undoubtedly, the most popular methods for this purpose nowadays are X-Ray Fluorescence Spectrometry (XRFS), Atomic Absorption Spectrometry (AAS) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). However, the need for exhaustive the sample preparation for AAS and ICP-AES, has led

to increasing interest towards energy dispersive X-ray Spectrometry (EDXRF) in environmental investigations [7]. X-ray Spectrometry, in its various forms is now a powerful, well established and mature technique for environmental analysis. It is also one of the Atomic Spectrometric techniques that can be adapted for true field portable use [8]. It offers multi-element capability, low cost, high speed and easy operation, and its advantages and limitations are now well understood [9-11]. More specifically EDXRF has increasingly been applied, in the last 20 years, to the analysis of aerosols, waters, sediments, soils, solid waste and other environmental samples. EDXRF is a non-destructive and multi-elemental technique and can be applied to any kind of sample: liquid or solid (thick, intermediate or thin) and in many cases with sufficient sensitivity for the determination of many trace elements [12,13]. Element analysis and biological studies on ten oriental spices using XRF and ames test have reported [1] that the spices contained the following elements: Mg, Al, Si, P, S, C, K, Ca, Ti, Mn, Fe, Cu and Zn, with varying concentrations.

The aim of this study has been the determination of elements and heavy metal concentrations in various brands in products of cosmetic such as lipstick, nail polish, blush, make-up materials, hand and cellulite cream, shampoo, soap, toothpaste and cleaning products. The EDXRF spectrometer (Epsilon 5, PANalytical, Almelo, the Netherlands) was used to determine the heavy metal concentrations in these samples.

MATERIALS AND METHODS

Sampling and sample preparation. The cosmetic samples were taken from different stores in Kahramanmaraş, Turkey 2010. All the samples were separately put into a box that was made of aluminium foil to protect from external effects. All the samples were dried at 105 to 350 °C for 10 h. Dried samples were homogenized using a mixer and stored in polyethylene bottles prior to analysis. All polyethylene bottles were cleaned by soaking overnight in 10% nitric acid solution and then were rinsed with water before the samples were placed. After that the prepared samples were placed in polyethylene bottles. Samples were compressed for 20 sec with 7 ton hydraulic press and reduced to 40 mm in diameter and the pellets at the mass of 500±3mg were prepared prior to analysis [14].

Measurement of elemental compositions in cosmetic samples. Measurements of cosmetic samples were performed with the EDXRF

Spectrometer (Epsilon 5, PANalytical, Almelo, the Netherlands) featuring a three-dimensional polarizing optical geometry. All the samples were measured at least three times and the averages of these results were obtained to minimize statistical errors. The measurement parameters of sample pellets were set up by using the Epsilon 5 EDXRF system's inbuilt software. The combination of features including a three dimensional, polarizing geometry, together with a 600 W Gd-anode, X-ray tube and 100 kV generator, up to 15 polarizing and secondary targets and a high resolution PAN 32 detector (typically 135 eV but ≤140 eV (2000 cps, MnK α)). Secondary targets were irradiated by X-rays from Gd tube under a vacuum equipped with a liquid nitrogen cooled PAN-32 Ge X-ray detector having a Be window thickness of 8 μ m together with crystal thickness of 5mm and area of 30 mm². Then, the sample pellets were irradiated by characteristic X-rays of the secondary targets. The power, current, and high voltage of the Gd X-ray tube was 600W, 6mA and 100 kV, respectively. The system's software (Epsilon 5 software) automatically analyzed the sample spectrum and determined the net intensities of element peaks as soon as the measurement was completed. A set of Auto Quantify, available from PANalytical, was used for the calibration of this application. Auto Quantify offers quantitative analysis without standards for the Epsilon 5 spectrometer. Epsilon 5's optional Auto Quantify routine easily handles the analysis of completely unknown samples. Based on Fundamental Parameter calibrations, it can handle concentrations from % to μ g g⁻¹ levels, in a variety of sample types including solids, powders and liquids (<https://www.panalytical.com>).

RESULTS AND DISCUSSIONS

Results of present measurements for trace metal contents in 50 cosmetic samples are listed in Tables 1-9. As presented in Tables 1-9, each cosmetic sample type is coded according to its group. The samples of blush, lipstick, eye shadow, nail polish, shampoo, hand cream, cellulite cream, soap and baby powder have been presented with the symbols of B, L, E, NP, SH, HC, CC, SO, and BP, respectively. The investigated samples consist of cosmetic products used for cleaning and make-up. All the samples examined contained various concentrations of V, Cr, Mn, Ni, Cu, As, Br, Mo, Ag, Sn, I, Ba, Hg, Pb and Bi.

The most important (most widely spread and toxic) heavy metals are known to be lead, mercury, nickel, manganese, chromium and cadmium. Some heavy metal limits in cosmetic are defined by

Health Canada regulation [15]. According to these regulations, some heavy metal limits are limited to 10 ppm for lead, 3 ppm for arsenic, 3 ppm for cadmium, 3 ppm for mercury and 5 ppm for antimony. The limit values for heavy metals in cosmetic by the German federal government are: 20 ppm for lead, 5 ppm for arsenic, 5 ppm for cadmium, 1 ppm for mercury and 10 ppm for antimony [16]. In addition to this, cosmetic regulation established by the government of the Republic of Turkey have been prepared in parallel with 96/335/EC Commission Decision with 76/768/EEC council directive of cosmetic regulations of the European Union. By this regulation the presence of some metals and their compounds mentioned below in cosmetic products are prohibited as follows: Antimony and its compounds, arsenic and its compounds, barium salts except for barium sulphate, beryllium and its compounds, bromine, cadmium and its compounds, chlorine, chromium, chromic acid and its salts, iodine, mercury and its compounds, lead and its compounds, radioactive materials, gold salts, selenium and its compounds, tellurium and its compounds, neodymium and its salts, tellurium and

its compounds, thallium and its compounds, zirconium and its compounds, cobalt sulphate, nickel monoxide, dioxide nickel, nickel and zinc salts. However, metals in cosmetic products are not currently regulated by the U.S. Food and Drug Administration (FDA). Acceptable limits for heavy metals vary according to the subpopulation of interest (for example, children are more susceptible to heavy metal toxicity than adults and have greater exposure potential due to hand-to-mouth activity), the amount of product used and the site of application (for example arms versus lips) [15, 16].

As seen from Table 1, the blush samples of the nine different brands were analyzed and V was determined in samples coded as B1, B2, B6, B7 and B9; Cr was determined in samples coded as B3, B4, B5, B8 and B9; Mn, Ni and Zn were determined in all samples; Cu was determined in all samples except for B6; Ba was determined in all samples except for B5; Br was determined only in B1 and B4; Sn was determined in all other samples except for B4 and B6 samples; I was determined in B3, B7 and B8; Pb was determined in all samples except for B1, B3 and B4, and As was determined in B2, B7 and B8.

TABLE 1
The results of elemental analysis of blush samples (ppm), ($\bar{x} \pm \sigma$, number of measurements n=3)

	B1	B2	B3	B4	B5	B6	B7	B8	B9
V	N.D.	N.D.	149.114 ± 5.779	41.956 ± 6.318	89.007 ± 35.795	N.D.	N.D.	61.057 ± 19.243	N.D.
Cr	N.D.	N.D.	21.822 ± 1.946	149.346 ± 2.794	22.060 ± 4.316	N.D.	N.D.	12.500 ± 1.261	N.D.
Mn	89.180 ± 6.454	88.298 ± 2.550	325.455 ± 3.882	205.547 ± 4.220	35.483 ± 2.97	129.307 ± 5.685	108.008 ± 2.405	278.319 ± 3.143	110.380 ± 6.378
Ni	14.889 ± 0.279	5.192 ± 1.031	18.718 ± 1.720	15.791 ± 1.673	13.276 ± 0.0977	66.337 ± 1.890	9.437 ± 1.267	17.248 ± 1.800	N.D.
Cu	24.293 ± 0.991	60.462 ± 1.311	10.891 ± 1.376	23.580 ± 0.986	N.D.	N.D.	9.716 ± 0.715	91.783 ± 2.112	13.469 ± 0.503
Zn	144.888 ± 0.507	50.360 ± 1.011	3200 ± 0.001	8190 ± 0.003	8980 ± 0.006	68.578 ± 1.628	35.618 ± 1.824	8630 ± 0.001	9380 ± 0.002
As	N.D.	0.369 ± 0.045	N.D.	N.D.	N.D.	N.D.	2.694 ± 0.577	0.199 ± 0.010	N.D.
Br	128.739 ± 1.251	N.D.	N.D.	3.766 ± 0.512	N.D.	N.D.	N.D.	N.D.	N.D.
Sn	35.546 ± 3.024	32.680 ± 3.189	185.908 ± 4.283	N.D.	7.122 ± 1.868	N.D.	35.919 ± 0.724	8.622 ± 0.543	12.420 ± 1.303
I	58.162 ± 4.782	57.577 ± 0.517	N.D.	60.486 ± 0.501	35.874 ± 5.278	61.691 ± 2.312	N.D.	N.D.	47.299 ± 2.066
Ba	629.733 ± 5.454	229.762 ± 1.048	88.438 ± 3.907	114.767 ± 1.410	N.D.	85.764 ± 0.911	87.062 ± 0.849	401.356 ± 2.003	81.089 ± 3.255
Pb	N.D.	24.769 ± 0.179	N.D.	N.D.	24.156 ± 0.387	6.364 ± 0.319	11.482 ± 1.220	59.042 ± 0.468	9.929 ± 0.096

Not detected=N.D.

The average Pb concentration in blush samples was determined to be 22.62 ppm which is higher than the limit defined by Health Canada regulations. Arsenic concentration in the B7 sample (a blush sample) was also determined to be higher than the limit defined by the German federal government. V, Cr, Mn, Ni, Cu, Zn, Br, Sn, I and Ba concentrations found in most of the blush samples are greater than that which can be tolerated by the body. As an example, Cr was found in 4 out of 9 blush samples, at concentrations higher than 10 ppm.

Presented in Table 2, are the results of eleven different brands of lipstick samples marketed in Kahramanmaraş, Turkey. In these lipstick samples V was determined in L3, L8 and L9; Mn was determined in L3, L6, L8, L9 and L10; Cr was determined in L3, L9 and L10; Ni was determined in L1, L2, L8, L9 and L10; Cu, was determined in all samples except for L6; Zn was determined in all samples except for L1 and L2 ; Br was determined only in L3, L5 and L9; Sn was determined in samples L1, L8, L9, L10 and L11; I was determined in samples L1, L2, L7, L8, L9, L10 and L11; Ba was determined in samples L3, L4, L6, L7, L8, L9 and L10; As was determined only in L1, L7 and L10; and Pb was determined in all samples except for L2, L5 and L6.

It can be inferred from Table 2, that the average Pb concentration in lipstick samples was 20.35 ppm which is higher than the limits defined by both the German federal government and Health Canada regulations. Arsenic was found only in 3 lipstick samples but all of these samples had concentrations higher than 1 ppm which is higher than the limit defined by Health Canada regulations. In general, most of the lipstick samples contained V, Cr, Mn, Cu, Zn, B, Sn, In and B in concentrations higher than 10 ppm. These findings are in agreement with most of the previous reports [17-19]. In a previously reported study, the measurement of Pb in 26 brands and in 72 lipstick samples from China, Germany, Thailand, USA and Taiwan was performed [17] and it was reported that the mean value of Pb in the lipstick samples as an average of two batches with the same LOT number was 117.40 ppm wet wt. Lipstick samples in four different brands have been investigated in another study and Al (10.98- 694.5ppm), Cr (1.30-81.60ppm), Mn (0.89- 48.89ppm), Ni (4.94ppm), Cu (118.6ppm), Zn (10.62- 345.8ppm), Cd (0.14 ppm), Ba (10.37- 1895 ppm), Pb (1.32- 15.92 ppm) and Bi(21.3- 698.1ppm) metals in the lipstick samples were reported [20]. A study of 20 lipsticks conducted by the United States Food and Drug Administration showed Pb impurity levels averaged 1.07 ppm, where Canada's current draft guideline

for lead impurities is 10 ppm, which is considerably high by comparison [21]. The analyses of the trace metal of facial (eyeliners, eye pencils and lipstick) cosmetics used extensively in Nigeria were reported [22] and who found Pb, Cd, Cr, Ni, Zn and Fe at various concentrations. They reported that continuous use of these cosmetics could result in an increase in the trace metal levels in the body beyond acceptable limits [22]. It has been reported that investigated trace metals such as Cr, Ni, As, Cd, Sb, Hg and Pb in lipsticks produced in various countries and they reported levels of Pb, Cd, Ni, Cr, Hg, Sb, and As to be 13, 15, 10, 10, 0, 11, and 23 ppm, respectively [17]. The heavy metals such as Al, Ti, Cr, Mn, Co, Ni, Cu, Cd and Pb concentrations in 8 lipsticks and in 24 lip glosses were measured previously [18]. In addition, a research related to presence of lead (Pb) in lipsticks sold in the United States has been done using inductively coupled plasma-mass spectrometry (ICP-MS) and it was reported that Pb levels found by the FDA are within the range that might be expected from lipsticks formulated with permitted colour additives and other ingredients prepared under GMP conditions [23]. Concentration determination of heavy metals such as Pb, As, Cr, Co, Cd, Ni and Cu in lipstick samples of the various brands were performed and it was reported that almost all brands contained safe levels of Pb, As, Cr, Co, Cd, Ni and Cu but in several cases the presence of Pb and As exceeded permissible limits rendering the product unsafe for human consumption and cosmetic application [19].

As seen in Table 3, six different brands of eye shadow samples were analyzed. The investigated samples contained V, Mn, Ni, Zn, As, Br, Sn, I, Ba, Hg, Pb and Bi in various concentrations. V was determined in E3 and E6; Mn was determined in all samples; Ni was determined in all samples except for E4; Cu was determined in all samples except for E3 and E6; Br was determined only in E4; Sn was determined in all samples except for E2 and E4; I was determined in all samples except for E2; As was determined only in E1; Hg was determined only in E2; Pb was determined in all samples except for E2 and E4, and Bi was determined only in E1. Four out of six eye shadow samples contained Pb and the average concentration of Pb in four eye shadow samples was 19.65 (4.548-45.859) ppm which is higher than the limits defined by both the German federal government and Health Canada regulations. Most of the concentrations (27 out of 28) determined for V, Mn, Cu, Br, Sn, I and Ba in eye shadow samples are too great to be tolerated by human body. The measurement of lead in the eye shadows in the eight different brands were done [17] and it has

been reported an average 1.38 (0.944-1.854) ppm Pb in the eye shadows samples. It has been reported [20] heavy metal contents of various types of cosmetics such as lipsticks, Kohl (eyeliner), henna (hair dye or temporary tattoo), eye shadows, cream; freckles, moisturizing and foundation, and face

powders. Nine brands of mascara and eyeshade purchased from the Saudi market were analysed by Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and a flow injection mercury system (FIMS) and twenty eight elements in the mascara and eyeshade samples were determined [24].

TABLE 2

The results of the elemental analysis of the lipstick samples (ppm) ($\bar{x} \pm \sigma$, number of measurements n=3)

	L1	L2	L3	L4	L5	L6	L7	L8	L9	L10	L11
V	N.D.	N.D.	17.352 ± 5.731	N.D.	N.D.	N.D.	N.D.	835.355 ± 118.133	559.611 ± 26.823	N.D.	N.D.
Cr	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	30.287 ± 1.030	12.446 ± 0.859	71.197 ± 3.183	N.D.
Mn	N.D.	N.D.	362.625 ± 12.511	170.058 ± 3.433	N.D.	193.978 ± 8.572	N.D.	254.757 ± 7.956	272.807 ± 12.051	131.429 ± 8.236	49.500 ± 2.735
Ni	32.795 ± 2.813	34.755 ± 2.541	N.D.	N.D.	N.D.	N.D.	N.D.	46.315 ± 4.526	51.734 ± 6.150	19.597 ± 1.887	N.D.
Cu	164.458 ± 3.902	100.242 ± 3.343	143.158 ± 2.463	35.250 ± 0.891	39.244 ± 5.480	N.D.	36.688 ± 4.095	41.553 ± 4.166	28.862 ± 2.711	36.308 ± 2.449	22.853 ± 2.362
Zn	N.D.	N.D.	203.174 ± 3.468	560.342 ± 7.919	813.484 ± 0.095	1372.130 ± 17.816	1812.604 ± 68.081	575.365 ± 4.878	160.534 ± 4.835	254.693 ± 8.968	513.975 ± 1.912
As	3.228 ± 0.317	N.D.	N.D.	N.D.	N.D.	N.D.	2.200 ± 1.689	N.D.	N.D.	4.591 ± 0.933	N.D.
Br	N.D.	N.D.	334.886 ± 1.861	N.D.	33.074 ± 8.123	N.D.	N.D.	N.D.	11.705 ± 0.829	N.D.	N.D.
Ag	1.295 ± 0.014	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
Sn	115.928 ± 17.029	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	457.244 ± 21.620	24.381 ± 3.752	N.D.	20.325 ± 2.348
I	397.668 ± 2.080	119.816 ± 0.543	156.605 ± 1.008	N.D.	177.072 ± 45.113	N.D.	55.760 ± 48.30	136.336 ± 118.077	82.699 ± 1.567	123.710 ± 8.584	86.610 ± 0.368
Ba	N.D.	N.D.	180.316 ± 4.624	278.458 ± 4.650	N.D.	297.078 ± 5.377	1007.107 ± 30.629	144.576 ± 4.380	90.589 ± 0.523	133.244 ± 8.304	N.D.
Pb	22.091 ± 0.675	N.D.	31.487 ± 5.474	23.367 ± 1.314	N.D.	N.D.	13.533 ± 0.537	25.530 ± 0.503	20.228 ± 1.446	16.161 ± 3.014	10.397 ± 0.531

TABLE 3

The results of the elemental analysis of the eye shadow samples (ppm), ($\bar{x} \pm \sigma$, number of measurements n=3).

	E1	E2	E3	E4	E5	E6
V	N.D.	N.D.	353.978 ± 5.201	N.D.	N.D.	190.678 ± 0.587
Mn	192.389 ± 4.023	316.55 ± 3.668	205.071 ± 3.547	33.336 ± 4.561	206.626 ± 4.335	94.477 ± 7.145
Ni	13.709 ± 2.957	9.494 ± 0.904	10.841 ± 0.717	N.D.	7.319 ± 0.277	12.540 ± 1.056
Cu	8.936 ± 0.285	15.215 ± 0.336	N.D.	35.076 ± 4.002	102.099 ± 3.540	N.D.
As	0.058 ± 0.003	N.D.	N.D.	N.D.	N.D.	N.D.
Br	N.D.	N.D.	N.D.	160.377 ± 1.383	N.D.	N.D.
Sn	53.684 ± 4.298	N.D.	720.904 ± 2.282	N.D.	182.330 ± 0.750	193.242 ± 1.031
I	60.150 ± 0.646	N.D.	84.629 ± 1.876	67.542 ± 0.505	21.783 ± 0.396	51.253 ± 1.192
Ba	878.230 ± 4.544	425.921 ± 2.436	108.185 ± 1.454	N.D.	156.993 ± 1.110	97.957 ± 2.941
Hg	N.D.	1967.704 ± 37.835	N.D.	N.D.	N.D.	N.D.
Pb	19.544 ± 1.095	4.548 ± 0.923	N.D.	N.D.	45.859 ± 0.837	8.638 ± 0.212
Bi	1.186 ± 0.080	N.D.	N.D.	N.D.	N.D.	N.D.

As seen from Table 4, four different brands of hand creams samples were found to contain various concentrations of V, Cr, Mn, Ni, Cu, As, I, Hg and Pb. Hg was determined in all samples except for HC4; Pb and As were determined in HC2 and HC3. In addition, I was determined only in HC3; Ni and Cu were determined in all samples; Cr was determined in all samples except HC3; V was determined in all samples except HC1; Mn was determined only in HC2 and HC4. As seen from Table 4, Hg and Pb concentrations in hand cream samples are detected to be higher than the limits defined by Health Canada regulations. As concentrations in hand cream samples are found to be lower than the limits defined by both the German federal government and Health Canada regulations.

Since As, Hg and Pb are toxic elements for human health, they should not be present even in trace levels in cosmetic products. In addition to these, V, Cr, Mn, Ni, Cu and I concentrations are also found to be large enough to cause toxic effects on the body. In addition to these results in a previously reported study, a moisturizing cream has

been analyzed and the various concentrations Al (15.31ppm), Cr (4.30ppm), Mn (0.70ppm), Ni (2.89ppm), Cu (0.84ppm), Zn (996.3ppm), Mo (0.51ppm) and Ag (0.07ppm) were found [20]. The elemental analysis of epidermal creams by using X-Ray Fluorescence Spectrometer (XRF) have been done and in these creams Ca, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Rb, Sr, Y, Zr, Nb, Mo and Pb were determined [2].

As shown in Table 5, the samples of the cellulite creams of the four different brands were investigated and in the investigated samples V, Cr, Mn, Ni, Cu, As, Br, I, Ba, Pb and Bi elements were determined at various concentrations. In all samples except for the CC2 sample, As and Pb were found which are accepted to be toxic to human body. As shown in Table 5, Hg was not detected in any cellulite cream samples. However the Pb concentration in one cellulite cream sample (CC4) was found to be higher than the limit defined by Health Canada regulations. V, Cr, Mn, Ni, Cu, I, Br, I and Ba concentrations were found high enough to be harmful to human health.

TABLE 4

The results of elemental analysis of hand cream samples (ppm), ($\bar{x} \pm \sigma$, number of measurements n=3).

	HC1	HC2	HC3	HC4
V	N.D.	817.717±58.968	4.651±0.638	34.353±0.561
Cr	49.677±2.141	234.483±26.953	N.D.	10.436±0.512
Mn	N.D.	26.140±3.248	N.D.	28.419±1.814
Ni	12.265±2.773	64.446±4.231	13.134±1.632	4.955±0.628
Cu	61.330±44.965	235.304±6.231	112.016±5.256	366.962±4.422
As	N.D.	2.644±0.204	0.654±0.051	N.D.
I	N.D.	N.D.	101.269±1.103	N.D.
Hg	8.427±0.559	5.360±0.555	7.388±1.297	N.D.
Pb	N.D.	20.210±2.145	10.586±1.648	N.D.

TABLE 5

The results of elemental analysis of the cellulite cream samples (ppm), ($\bar{x} \pm \sigma$, number of measurements n=3).

	CC1	CC2	CC3	CC4
V	N.D.	708.540±16.611	88.164±14.451	3.478±0.501
Cr	30.557±0.509	N.D.	107.221±6.802	211.180±17.407
Mn	N.D.	54.314±0.344	20.123±3.481	18.375±0.545
Ni	N.D.	27.999±2.891	N.D.	45.140±2.199
Cu	92.191±2.683	156.459±2.086	85.945±2.704	32.668±3.606
As	2.417±0.121	N.D.	2.905±0.145	1.044±0.155
Br	8.199±0.491	24.871±1.742	N.D.	N.D.
I	75.358±0.557	91.634±0.551	98.436±1.005	94.696±2.570
Ba	N.D.	N.D.	105.053±3.486	N.D.
Hg	N.D.	N.D.	N.D.	N.D.
Pb	8.090±1.889	N.D.	9.983±2.241	14.374±1.445
Bi	8.035±0.498	N.D.	N.D.	N.D.

Not detected=N.D.

As shown in Table 6, three different brands of baby powder samples were analyzed for their V, Cr, Mn, Ni, Cu, As, I, Hg and Pb contents. In a few of these baby powder samples toxic elements such as As in BP3, Hg in BP2 and BP3, and Pb in BP3 were found. Pb and Hg concentrations in baby powder samples are lower than the limits defined by both the German federal government and Health Canada regulations. However, the As concentration in BP3 is higher than the limit defined by Health Canada regulations. In most of the analyzed samples Cr, Mn, Cu and I concentrations are found high enough to be harmful to human health. In a previous study, elemental contents of talcum baby powder have been analyzed by using X-ray fluorescence and fast neutron activation techniques [25] and it was reported that the samples were found to contain Mg, Si, Al, Fe, Zn, and Ba. In another study, analysis of the trace metals (such as Pb, Cd, Co, and Cr) in cosmetic facial talcum powders marketed in Nigeria were performed and it has been reported that the mean concentrations of the trace metals to be 5.0-1.0 mg/kg for Pb, 2.1-0.3 mg/kg for Cd, 0.7-0.1 mg/kg for Co, and 0.2-0.1 mg/kg for Cr [22]. Both of these previously

reported studies contain similar results to this study [22, 25].

As shown in Table 7, five different brands of nail polish samples were analyzed and V, Mn, Ni, Cu, Zn, As, Br, Ag, I, Ba, Hg, Pb and Bi were observed in various concentrations. In a few of these nail polish samples, toxic elements such as As (NP1, NP4 and NP5), Hg (NP4) and Pb (NP1, NP3, NP4 and NP5) were found. V was found in all samples except for NP3; Mn, Cu and Zn in all samples; Ni only in a NP1; Br in all samples except for NP3 and NP5; Ag only in NP3; I and Ba in only two of the samples (NP2 and NP3) and Bi only in NP2 were determined. Pb concentrations in a majority of the nail polish samples were found to be higher than the limits defined by both the German federal government and Health Canada regulations. In addition to this, V, Mn, Cu, Zn, Br, I, and Ba concentration were also found to be large enough to cause toxic effects to human health. Ten lipsticks and ten nail polishes sold at a cosmetic store were investigated using Atomic Absorption Spectrophotometer (AAS) by Ouremi and Ayodele and the concentrations of six heavy metals, including Pb, Ni, Cd, Mn, Cr and As were reported [26].

TABLE 6
The results of elemental analysis of baby powder (ppm), ($\bar{x} \pm \sigma$, number of measurements n=3)

	BP1	BP2	BP3
V	7.853±0.300	21.144±4.677	N.D.
Cr	14.665±2.208	N.D.	N.D.
Mn	25.697±2.116	35.687±0.497	42.0022±0.303
Ni	13.329±3.805	N.D.	3.101±0.155
Cu	25.493±0.500	17.036±1.144	11.614±0.431
As	N.D.	N.D.	3.194±0.160
I	37.144±1.031	49.286±0.623	N.D.
Hg	N.D.	1.221±0.018	2.276±0.477
Pb	N.D.	N.D.	6.477±0.879

As seen from Table 8, two different brands of shampoos (SH1 and SH2) and three different brands of baby shampoos (BSH1, BSH2, and BSH3) were analyzed for their metal content and V, Cr, Ni, Cu, Zn, Br, I, Hg, Pb and Bi were found in various concentrations. In the three different brands of baby shampoos V, Ni, Cu, Zn, Br, I, Hg, Pb and Bi elements were measured. Arsenic was not detected in any shampoo samples that were

analysed. However, Cu and Zn were detected in all shampoo samples. In addition Pb was detected in SH2, BSH1 and BSH3. As seen from Table 8, Hg concentrations in S1 and BSH3 were higher than the limits defined by both the German federal government and Health Canada regulations. Most of the determined concentrations (19 out of 22) for V, Cr, Ni, Mn, Cu, Zn, Br, Ag, I, Bi and Ba are also found to be too high to be tolerated by the body.

TABLE 7
The results of elemental analysis of nail polish samples (ppm), ($\bar{x} \pm \sigma$, number of measurements n=3)

	NP1	NP2	NP3	NP4	NP5
V	47.988±9.791	849.787±49.683	N.D.	13.959±4.027	207.171±0.154
Mn	71.296±4.593	140.625±0.545	59.266±1.101	22.267±1.387	51.322±2.715
Ni	18.270±1.388	N.D.	N.D.	N.D.	N.D.
Cu	34.120±4.627	24.342±4.053	27.825±3.285	49.448±2.004	40.663±2.873
Zn	2010±9.849	182.178±6.383	67.284±1.146	43.008±2.384	298.350±6.115
As	7.965±0.461	N.D.	N.D.	7.858±0.891	3.216±0.189
Br	11.013±0.071	1544.268±2.967	N.D.	182.504±1.932	N.D.
Ag	N.D.	N.D.	11.403±0.363	N.D.	N.D.
I	N.D.	184.953±4.929	157.397±1.028	N.D.	N.D.
Ba	N.D.	384.976±9.544	2040±18.788	N.D.	N.D.
Hg	N.D.	N.D.	N.D.	0.998±0.004	N.D.
Pb	26.878±3.117	N.D.	11.677±0.586	9.927±0.064	14.826±0.283
Bi	N.D.	9.736±3.281	N.D.	N.D.	N.D.

As shown in Table 9, three different brands of soap samples were investigated for their metal content. After completing the analysis of these soap samples only V, Cu, Zn, As, I, Hg and Pb were detected. V was determined in SO1; while Cu and Zn were determined in all soap samples; As was determined in SO2; I was determined in SO1 and SO3; while Hg was determined only in SO1, and Pb

was determined in SO2 and SO3. Concentration values of As, Hg and Pb in soap samples were found to be less than the limits defined by the German federal government and by Health Canada regulations. However, it is important to note that all the concentrations for Cu, Zn and I are higher than 10 ppm.

TABLE 8
The results of elemental analysis of shampoos and baby shampoos (ppm) ($\bar{x} \pm \sigma$, number of measurements n=3).

	SH1	SH2	BSH1	BSH2	BSH3
V	N.D.	N.D.	N.D.	13.435±0.513	14.473±3.913
Cr	19.500±1.356	N.D.	N.D.	N.D.	N.D.
Ni	4.465±0.399	N.D.	7.736±1.646	N.D.	N.D.
Cu	27.782±1.305	56.679±0.327	27.226±2.024	33.364±1.849	50.020±1.881
Zn	803.312±2.535	131.787±1.325	1073.982±13.393	11160±20.000	676.872±3.305
Br	278.867±3.416	N.D.	3.416±0.104	10.445±0.374	12.553±0.514
I	N.D.	48.654±1.166	71.457±0.505	N.D.	36.432±1.689
Hg	3.376±0.464	0.410±0.014	2.121±0.626	N.D.	N.D.
Pb	N.D.	5.597±0.611	9.339±0.573	N.D.	9.595±1.204
Bi	N.D.	N.D.	N.D.	51.080±2.599	N.D.

CONCLUSION

This study has investigated the levels of trace metals in nine different types of cosmetic and cleaning products (50 samples) marketed in Turkey. A total of 20 samples contained Pb at elevated concentrations (more than 10 ppm) of the 33 samples that contained Pb. In addition, 17 samples

contained As and 11 samples contained Hg out of 50 samples analyzed. These results suggest that toxic metals in cosmetics should be regulated and good manufacturing practice must also be followed to protect women's health in Turkey, as has already undertaken by German federal government and by Health Canada regulations.

TABLE 9
The results of elemental analysis of soap samples (ppm), ($\bar{x} \pm \sigma$, number of measurements n=3).

	SO1	SO2	SO3
V	19.401±0.529	N.D.	N.D.
Cu	36.299±2.404	15.668±1.754	14.964±0.413
Zn	28.243±0.670	53.511±0.598	23.049±0.228
As	N.D.	0.385±0.022	N.D.
I	48.380±0.451	N.D.	12.476±1.610
Hg	0.136±0.005	N.D.	N.D.
Pb	N.D.	4.598±0.528	4.638±0.119

Not detected=N.D.

Our results indicate the need for further studies to evaluate toxic metal concentrations in blush and lipstick products with different form of instrumentation methods, as well as other cosmetics, and their related health risks.

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