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Evaluation of lead and chromium in cosmetic products and detergents sold in Tripoli, Libya

Abdusalam S. Elaseer[1*], Mahasen AlKHabatt[2], K. Elhrishi[2], A.Abdulmonam[2] and Sohela Aboud[2]
[1]Tajoura Nuclear Research Center, Tajura, Libya
[2]Advanced Analytical Chemistry Laboratory, Tajura, Libya
a_khalf847@gmail.com

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Abstract

Assessment of the level of contamination with lead (Pb) and chromium (Cr) was carried out in cosmetic and detergent products collected randomly from Libyan market. Pb and Cr were determined in triplicate using continuum source graphite furnace Atomic absorption spectrophotometer. Both toxic metals were prominently detected in all tested samples. The mean ± SD concentrations of Pb and Cr in mg/kg are as follows: Pb 0.894±0.060µg/g and Cr 1.156±0.0023µg/g in cosmetic products samples, Pb 0.373±0.0035µg/g and Cr 0.367±0.0373µg/g in detergents samples, In Kohl samples the mean ± SD concentrations of Pb and Cr in mg/kg are 52.45±6.84µg/g and 1.564±0.042 µg/g respectively. The mean ± SD concentration of Pb was 1.007±0.00052µg/g and Cr was 2.339±0.00135µg/g in nail polishers. The mean results of 6 lipstick samples ranged thus: 1.02±0.050µg/g and 1.24±0.0388µg/g, Pb and Cr respectively. The mean ± SD concentration of Pb was 1.230±0.0016µg/g and Cr was 1.092±0.0023µg/g in eye shadow. Therefore, contamination of the tested products by Pb in descending order of Kohl > eye shadow > lipsticks > nail polishers >detergents > skin creams. The contamination of the tested products by Cr in descending order of nail polishers > Kohl > lipsticks > eye shadow > detergents > skin creams.

Keywords: Cosmetics and detergents, heavy toxic metals, atomic absorption.

Introduction

Cosmetic products and detergents believed to be used since the ancient civilization. It is evident that Ancient Egyptians used cosmetics containing large amounts of lead. Several types of these products intended to be rubbed, sprayed or applied in other ways to the human skin. These products were prepared to last longer in contact with the human skin to promote attractiveness and beauty on the person appearance. With the cosmetic products manufacturing, there is concern about the level of heavy toxic metals present in final products. People may be adding a bit more than a touch of color to their lips as proved by UC Berkeley's school study[1]. Toxic trace metals are introduced into cosmetics via the use of several raw materials for coloring, softness or final finishing of the products. Concern over the health risks has led many scientists to carry out researches to examine levels of chromium, lead, Arsenic, mercury and cadmium in the cosmetic products in the local market. In some literatures the overall mean metal composition of nineteen samples for lead and chromium were 3.78 and 1.33 mg/kg respectively[2], and in cosmetics were 6.03 and 93.3mg/kg respectively[3]. In June (1995), Robert Allen analyzed some cleaning products and he found Pb was 0.2mg/kg and Cr was less than 0.1mg/kg in powder Laundry detergent[4]. Cosmetic products such as eye shadow, nail polishers, eye linear, creams[5,6], lipsticks[7], and many body care products including shampoos, body lotions and hair colorings were all underwent careful analysis during last decades[8]. In September (2007) about 33 popular brands of lipsticks collected from five American states showed that 61% of the tested samples contained up to 0.65µg/g Pb^{2+}. However, the tested lipsticks samples were varied in lead concentrations and many exceeded the US Food and drug Administration's 0.1 µg/g Pb^{2+} limit in Candy[9]. Exposure of Libyan populist to heavy toxic metals from sources such as drinking waters, food, beverages, herbal preparations cosmetics and cleaning products have not been evaluated properly. The main objectives of this work is to lightening the cores of the content of some toxic heavy metals those may hidden as impurities in imported cosmetic and detergents to the Libyan market. The work is also aimed to ascertain the quality of cosmetics and detergents on the bases of heavy toxic metals concentration.

This research work may provide clear data for the authorities to put certain measures for controlling the quality of the imported safe cosmetics and detergents.

Materials and methods

Samples: Thirty five different cosmetic products and detergents sold in Libya were purchased from retail stores in the capital Tripoli area. These products are imported to Libya by unauthorized companies without any certain specifications or regulations. The samples were of unknown qualities and popular brands taken in triplicate with the same name or lot number in order to obtain statistical evaluations and quality assurance. The

samples include thirteen shampoos, soaps and detergent powders, five skin creams, six lipsticks, four nail polishers, five eye shadows and two kohl samples.

Chemicals and reagents; Deionized water with conductivity less than 0.06µS/cm and pH 7 was used to prepare the working solutions. Analytical grade reagents including nitric acid (65%), perchloric acid (70%) purchased from sigma –Aldrich (Broendby, Denmark). Standard solutions of lead and chromium (1000ppm) used were provided by AAS company.

Instrumentation and software: ContraAA700 high resolution continuum source graphite furnace-AAS, The auto-sampler MPE60 was used to perfectly control injection volumes. Data acquisitions were accomplished automatically by built in microprocessor.

Calibration: From the stock solution, a concentration of 0.00, 5, 10, 15 and 20µg/l of each metal in 0.5%HNO_3, automatically prepare the above metal concentrations,15µl of the standard and 5µl of $Mg(NO_3)_2$ as a modifier. The analysis was carried out in triplicates with integration mode; area. Therefore, for quantitative analysis, five-point matrix-matched calibration curves were freshly automatically prepared for each run in order to avoid interferences using $Mg(NO_3)_2$ or $NH_4H_2PO_4$ modifier. Using these metal concentrations we obtained good linearity for both metals examined. The equation of the calibration line y=1.229x+0.046 and R^2=0.977. The method gave LOD (ppm) of 0.035µg/ml (lead) and 0.023µg/ml (chromium).

Sample digestion procedure: Approximately 1gram sample was weighed in glass beaker and 25ml of an acid mixture of nitric acid (65%) and perchloric acid (70%) at molar ratio 4:1was added. The mixture was wet digested at 130^0C in fuming hood near to dryness[10,11]. The procedure was repeated until the sample digestion process was completed as indicated by appearance of white fumes and residue almost getto dryness. The solutions were left to cool to room temperature, and each sample was filtered through Whatman no. 42 into a 50ml volumetric flask and was diluted up to the mark with double distilled water. The samples solutions were analyzed for Pb and Cr using a furnace atomic absorption spectrophotometer available at the Sadeem chemical laboratory, Tripoli.

Recovery procedure: In a series of 25ml long nick type Pyrex beakers, a one gram (close to four decimal numbers) of each selected known concentration cosmetic samples were weighed using an electronic analytical balance. To each sample, 1.0ml of 8.0µg/ml mixture of both Pb and Cr was added and homogenized carefully, then allowed to air dry for 48 hours before they were digested and analyzed with the applied procedure. Table-3, presents the recovery percentage of the applied method.

Table-1: The method parameters were.

Element	Wavelength, nm	Pyrolysis temp ^{0}C	Atomization temp,^{0}C	Modifier
Cr	357.8687	1300	2300	$Mg(NO_3)_2$
Pb	283.3060	800	1500	$NH_4H_2PO_4$

Table-2: The evaluation parameters were.

Element	Eva.pixels	Measurements time(s)	No. of spectra	Spectral width		Background correction
				[pixels]	[nm]	
Cr	3	5	68	200	0.4	Iterative baseline correction
Pb	3	5	68	200	0.32	

Table-3: Recovery percentage of lead added to the real cosmetic samples

Sample type	Sample colour	Predetermined Pb^{2+} value in µg/g	Total Pb^{2+} value in µg/g	Conc. of Pb^{2+} found in µg/g	Recovery
Lipstick	Copper	1.180±0.0023	9.18	9.51±0.022	103.6%
Eye shadow	Red	1.043±0.00053	9.043	8.76±0.020	96.9%
Kohl Arab	Black	99.60±10.58	107.60	102.86±0.01	95.6%
Kohl At mad	Red	5.483±0.539	13.483	13.70±0.06	101.6%
Eye liner	Black	1.63±0.0058	9.63	8.47±0.032	88.0%
Nail polisher	Green	1.308±0.00053	9.308	9.11±0.025	97.8%

Method of analysis: All measurements were performed with the contr AA700 high resolution continuum source graphite Atomic Absorption. All instrument parameters are shown in Table-1. And the evaluation parameters are given in Table-2. The volume of each analyzed sample was 20µL. Triplicate sample preparations with the same procedure was used for the calibration standards and analyzed.

Results and discussion

Heavy metals are those with a specific gravity (density) greater than about 5g/Cm^3 including Lead 11.345g/Cm^3 and chromium 7.15g/cm^3. Both metals have toxic properties. Despite its toxicity, trace level of chromium was found an essential metal for human body. In this study, we determined these metals in a total of 35 individual products, including 13 shampoos, soaps and detergents, 7 eye shadows, eye liners and kohl, 6 lipsticks, 5 skin creams and 4 nail polishers. These samples were carefully examined for lead and chromium content as impurities. All examined products had detectable lead and chromium content. The average concentration of lead was 0.3134±0.053µg/g and chromium was 0.179±0.0023µg/g.

The obtained results are tabulated in Tables-4 to 8, for skin creams, lipsticks, nail polishers, eye shadows, and shampoos, soups and detergents respectively. The concentration of lead ranged from 0.177 to 0.423µg/g in skin creams and from 0.37 to 1.31µg/g in lipsticks. In nail polishers lead concentration ranged from 0.875 to 1.308µg/g and from 0.941 to 1.63µg/g in eye shadow samples. Lead is high in the two kohl samples and ranged from 5.483 to 99.60µg/g. In shampoos, soaps and detergents lead concentration ranged from 0.081 to 1.818µg/g. Chromium in skin creams ranged from 0.143 to 0.221µg/g and from 0.154 to 2.962µg/g in lipsticks. In nail polisher, chromium concentration ranged from 0.211 to 2.588µg/g and from 0.519 to 1.401µg/g in eye shadow. The concentration of chromium in kohl samples range from 1.465 to 1.662µg/g. In shampoos, soaps and detergents chromium concentration range from 0.167to 0.858µg/g. Figure-1 shows comparison view of lead and chromium in varies types of the samples analyzed in this study. It indicates that both metals were higher in cosmetics than in detergents and skin creams. Chromium is seen to be higher in lipsticks and nail polishers at average 1.246 and 2.34µg/g respectively, which suggests that Cr being used as colorant might have been contaminated or not adequately purified. Eye shadow and lipstick products have been reported to contain relatively high concentration of toxic metals[12]. The average lead concentration in cosmetic and detergent products was 0.3134±0.00053µg/g which is in agreement with that of 0.36± 0.39 µg/g obtained by Sa Liu et al[7]. However, Campaign for safe cosmetics (2007) reported the lead value 0.65µg/g[9]. Grosser. Zeo et al determined six metals in cosmetics including lead and chromium[3]. They found the average Pb was 0.618µg/g and Cr was 12.05µg/g in lipsticks, 0.062µg/g Pb and 0.040µg/g Cr in skin creams, 1.997µg/g Pb and 3.98µg/g Cr in nail polisher.

The results obtained in the present work for chromium is far less than those obtained by Muhammed et al[13]. Asaffar.et. al, analyzed 40 eye shadow samples and found the average lead concentration was 4.465µg/g and the range from 0.00 to 25.57µg/g[14]. Previous study by Abulude et al, estimated that maximum the lead content of about 9 folds and therefore, the content of Pb and Cr were 5.8 and 2.7mg/kg respectively[2]. Atkins et al, in (1911) analyzed lipsticks and found Pb mean concentration 0.993µg/g and range from 0.0609 to 2.39µg/g and Cr mean concentration 2.22µg/g with range from 0.059 to 31.45µg/g[15], Canadian environmental group was found unreported levels of heavy metals in lip gloss that contained seven of eight metals tested for. The products contained more than 10 times the lead limit in cosmetic products set out in a draft Health Canada guideline[16].Gondal et al detected 15–20 ppm lead and 20–30ppm chromium in the talcum powder sample[17].

Table-4: Presents the concentration of lead and chromium (mean±SD and RSD%) in skin creams.

Sample name	Concentrations of the metal Mean±SD			
	Pb	RSD%	Cr	RSD%
Vatika with almond	0.259±0.00060	2.70	0.143±0.00004	0.70
Vatika with olive oil	0.177±0.00063	2.20	0.166±0.00037	8.10
Dove	0.304±0.00079	10.30	0.221±0.00069	3.10
Fair & lively	0.423±0.00049	7.10	0.186±0.00021	0.81
PONDS	0.404±0.00014	1.50	0.180±0.0100	73.0

Table-5: Presents the concentration of lead and chromium (mean±SD and RSD%) in lipsticks.

Sample name	Concentrations of the metal Mean±SD			
	Pb	RSD%	Cr	RSD%
Red	0.931±00083	1.63	2.465±0.00060	0.86
Blue	0.875±00039	1.08	2.193±0.00078	3.90
Green	1.308±0.00053	0.96	2.588±0.00016	4.60
Violet	0.914±00033	2.91	2.111±0.0038	9.80

Table-6: Presents the concentration of lead and chromium (mean±SD and RSD%) in nail polishers.

Sample name	Concentrations of the metal Mean±SD in µg/g			
	Pb	RSD%	Cr	RSD%
MIC	0.37±0007	1.25	0.154±0.0015	2.04
Brown	1.31±0018	1.18	0.878±0.0082	2.40
Copper	1.18±0.0023	0.90	0.184±0.0046	1.03
Pink	1.12±0017	0.48	2.962±0.0035	3.40
Violet	1.13±0.0142	4.40	2.324±0.190	2.38
Orange	1.02±0004	1.41	0.916±0.00060	1.06

Table-7: Presents the concentration of lead and chromium (mean±SD and RSD%) in eye shadows.

Sample name	Concentrations of the metal Mean±SD			
	Pb	RSD%	Cr	RSD%
Blue	1.361±00083	3.60	1.401±0.00563	0.93
Green	1.175±00039	6.80	0.888±0.00037	7.33
Red	1.043±0.00053	7.66	0.519±0.00044	8.60
Gold	0.941±00033	5.41	1.307±0.0037	1.87
Eye liner	1.63±0.0058	3.30	1.345±0.00120	4.07
Kohl black (Arabic)	99.60±10.58	10.30	1.465±0.039	3.99
Kohl red (Athmod)	5.483±0.539	3.34	1.662±0.042	9.09

Table-8: Presents the concentration of lead and chromium (mean±SD and RSD%) in Shampoos, soaps and detergents.

Sample name	Concentrations of the metal Mean±SD			
	Pb	RSD%	Cr	RSD%
Johnson	1.818±00094	12.10	0.731±0.00013	1.40
Azzurra	0.148±00036	3.10	0.197±0.00073	8.10
Head and shoulders	0.503±0.00023	2.60	0.278±0.00048	5.10
Souplesse	0.332±00022	2.40	0.188±0.00056	6.70
Palmolive	0.110±0.00115	11.90	0.199±0.00109	13.20
Clear	0.223±00050	17.90	0.172±0.00071	9.80
Dove	0.085±00082	10.80	0.211±0.00016	2.10
Johnson	0.081±00097	12.80	0.167±00010	1.00
Johnson	0.186±00085	14.60	0.283±00098	3.10
LUX soap	0.349±00069	9.40	0.858±0.00062	4.60
OMO powder	0.356±00078	1.60	0.539±0.00050	31.5
Tide powder	0.414±00025	2.00	0.734±0.00016	2.10
Persil powder	0.238±00026	2.10	0.215±0.000	0.00

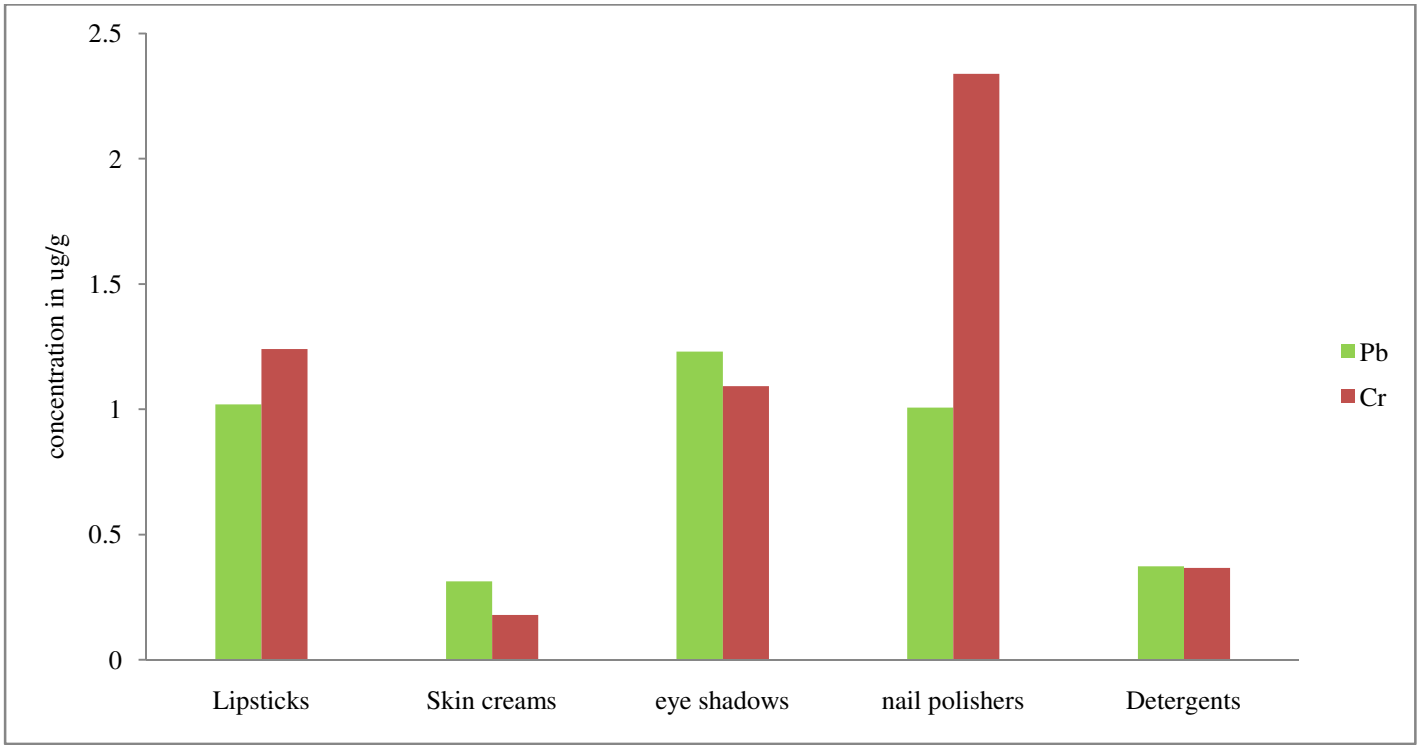

Figure-1: Graphical comparison of lead and chromium in cosmetics and detergents.

Conclusion

We were able to evaluate the extent of contamination by lead and chromium in all cosmetics and detergent. It is however the minute concentrations of the two metals did not exceed the world health organization limitation. Therefore, the continuous use of cosmetics containing trace toxic metals may result in health complications. Kohl (Arabic) should be completely discarded from use.

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