DETERMINATION OF LEAD AND RADIOACTIVITY IN COSMETICS PRODUCTS: HAZARD ASSESSMENT

by

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In the proposed work, an investigation on hazard assessment by lead element and natural radioactivity in cosmetic samples collected from various countries is presented. These samples were face powder, eyebrow paint and henna. The lead element in cosmetic samples was determined using particle-induced X-ray emission. Maximum natural radioactivity concentrations of ^{226}Ra and ^{40}K were found in khol and make-up cosmetic samples, respectively. The qualitative analysis of cosmetic samples showed that lead is the most toxic element found in eyebrow paint samples.

Key words: traditional cosmetics, lead, particle-induced X-ray emission, khol

INTRODUCTION

The use of traditional cosmetics has a long history of over 10 thousand years when ancient Egyptians discovered the healing abilities of scented oils and black eye make-up. When cosmetics found their way out of Egypt, the industry flourished and became an important part of everyday life. Even though some of the cosmetic ingredients are poisonous, the use of cosmetic products spread with time and is connected with many beliefs and traditions. For example, there was a period in Rome when women were not considered beautiful if they did not use cosmetics. From time to time, cosmetics elicited a similarly harsh treatment in other civilizations as well. For example, in China common people were executed if they were caught wearing nail polish in public, and in Japan, noble women were forbidden to walk in public without full-body cosmetic treatment [1, 2].

An ancient cosmetic eye make-up called kohl (also: kuhl, kohhel, kohol, cohol, surma, cohol, and kajal) is widely used in south Asia, the Middle East, and Africa to darken the eyelids and eyelashes by mascara. It is worn mostly by women, but also by some men and children to make them attractive. Kohl is a mixture of soot and galena. Galena is a blue-grey natural mineral form of lead sulfide. There is also green eye make-up made from malachite, a copper ore, a carbonate mineral, copper carbonate hydroxide, which has a very vibrant green color. As for eye make-up or rouge, the Egyptians used a pigment that is made from naturally tinted clay called red ochre. Another traditional product with religious associations widely used by the Egyptians over the centuries for cosmetic and medical purposes was henna. In order to enhance its effect and give it a more vibrant color, various herbs and other substances are to this day added to henna. In ancient times henna served as nail polish prior to mummification. Several contemporary facial cosmetics contain heavy metals (lead, cadmium, chromium, nickel, zinc, and iron). Ancient cosmetics were prepared using lead palmitate ($C_{32}H_{62}O_4Pb$).

Lead is toxic, mainly entering the body through oral ingestion, inhalation of lead dust or by skin/hair exposure. Any fluctuation in the normal level of lead brings specific physiological disorders. Lead can reach the brain directly, especially via eyebrow paints, because eyes are very sensitive. Children are more susceptible than adults to lead intoxication. The blood lead level in children is considered poisonous if it exceeds 70 mg/dl. It may contribute to a reduction in pregnancy length and low birth weight. In adults, probably the most critical effect of lead is hypertension. Numerous reports and research papers have shown that lead affects almost every system of the body, causing lifelong adverse health effects. It is also known that skin-absorbed lead might not be detectable

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in the blood by the usual techniques. Thus, in some cases, skin absorption of lead may remain undetected. The critical effects of lead risk-assessment have been defined as the development of neurotoxicity in young children, cardiovascular effects, nephrotoxicity, and reproductive effects in adults. The continuous application of cosmetics may over time lead to health problems such as neurological damage and increased risk for lung cancer and stomach tumors. Lipstick and eye cosmetics provide a direct intake path of trace metals into the body. A major source of lead toxicity has been described by eye cosmetics in Arabian countries [3-6]. This has resulted in a growing interest for the role of lead present in human biological systems.

Since no data on a threshold for critical lead-induced effects exist, measures must be taken to limit human exposure to lead by all possible means, including the control of the lead content in consumer products [7-9] in use at present. Therefore, in the study presented here, the content of lead in cosmetic product samples collected from various countries was determined. In addition to lead element quantity, natural radioactivity elements for ^{226}Ra, ^{232}Th, and ^{40}K were also detected.

The trace elements in cosmetics are determined using neutron activation analysis (NAA), laser desorption ionization and electrospray ionization mass spectrometry, synchrotron radiation micro X-ray diffraction, atomic absorption spectroscopy, atomic absorption spectrophotometry, derivative potentiometric stripping analysis, synchrotron-based infrared microscopy, energy dispersive X-ray analysis (EDAX), inductively coupled plasma-optical emission spectrometry (ICP-OES), and cold vapor atomic absorption spectrometry. The proton X-ray emission (PIXE) method has been used for trace metal elements in lipsticks of different brands [10]. Detection limits for most elements are in the range of 100 ppb to 10 ppm. Various countries have prepared guidelines and incorporated them into their legislations. Nowadays, the performance of a cosmetic product is evaluated by its lead content.

The aim of this work is to estimate naturally radioactive lead radioisotopes (^{210}Pb, ^{212}Pb, ^{214}Pb), so as to assess the hazards due to various colors and textures of cosmetic product samples originating from countries worldwide. The innocuous-looking kohl may actually be the cause of acute lead poisoning and radiation exposure from which sick children treated with traditional remedies suffer from. It is also possible that children exposed to small and infrequent amounts of lead-based kohls may show subclinical lead toxicity and lowered intelligence quotient levels.

MATERIAL AND METHODS

Preparation of samples

In this study 26 kohl, 15 make-up, and 15 henna samples of various colors and textures from China, Egypt, KSA, India, Iran, Italy, Germany, Oman, Pakistan, and Yemen were collected. Figure 1 shows how the studied samples are distributed by countries they originate from. Because the cosmetic material such as face powder and henna look like a fine and rather homogeneous dust, we prepared the targets by pressing

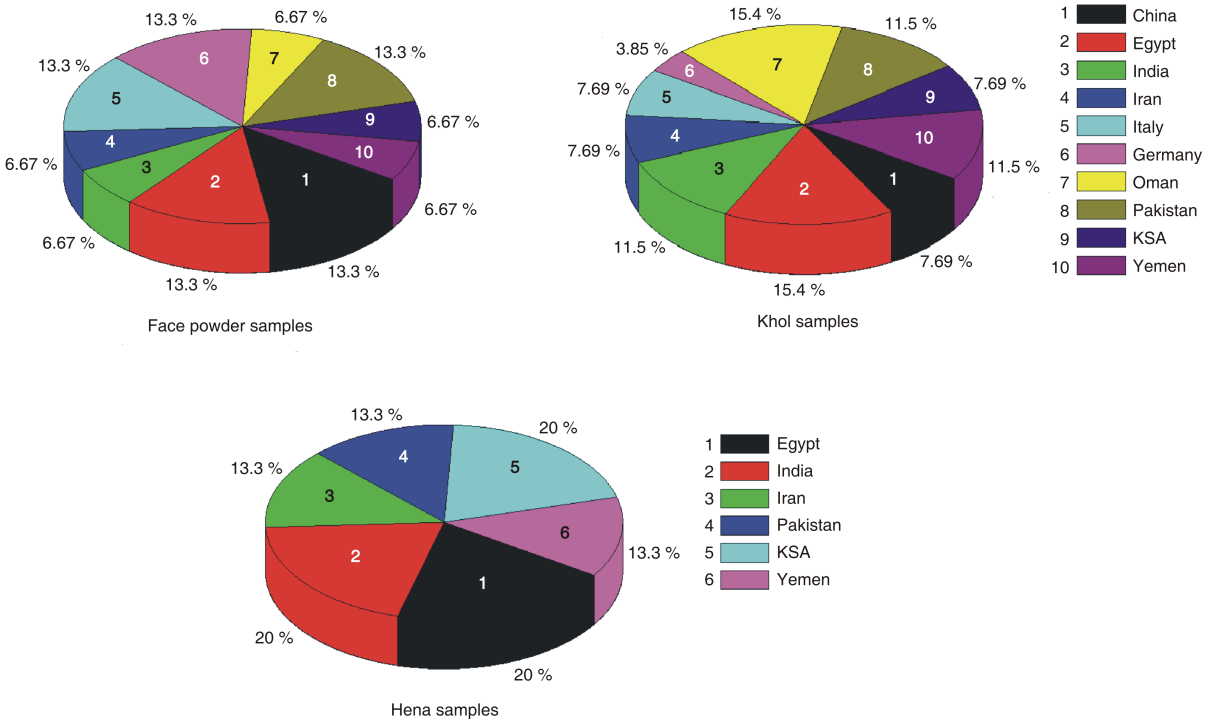

Figure 1. Origins of cosmetic samples studied

them to the form of tablets in a special steel container. The kohl samples were first ground to a fine powder and then pressed into tablets.

Natural radioactivity measurements

Natural radioactivity (concentrations of ^{226}Ra, ^{232}Th, and ^{40}K) in cosmetic samples was investigated to understand associated radiological hazards. The collected samples were dried at 105 °C in an oven for 24 hours so as to completely remove the moisture. Finally, samples were packed into plastic containers which were kept sealed for 4 weeks to achieve secular equilibrium. This step was necessary in order to ensure that radon was confined within the volume and the daughters remain in the samples.

The assay of the samples were carried out with a gamma ray spectrometry system consisting of HPGe detector (Canberra model) with the relative efficiency 40 % coupled with a PC-based multichannel analyzer (MCA) along with Genie software installed in the PC. Genie 2000 software (Canberra Industries, Meriden, USA) was used to acquire and subsequently analyze the information provided. The detector was kept in a cylindrical cavity shielded with 5 cm lead to reduce background in gamma ray spectra. Head of the detector was placed nearly at the centre of the cavity. Energy calibration of the system was done initially with ^{241}Am, ^{57}Co, ^{137}Cs, and ^{60}Co gamma ray point sources. Resolution (FWHM) of the system was 1.9 keV at 1332.5 keV gamma peaks of ^{60}Co point source kept at a distance of 10 cm in front of the detector face. The measuring time ranged from 12 to 24 hours depending on the activity. To determine the background counts, an empty container of the same geometry was counted in the same manner.

Activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in cosmetic samples are given [11]

$$A \quad \frac{P}{\varepsilon f m} \tag{1}$$

where A [Bqkg^{-1}] is the activity of the isotope, P – the net count rate under the most prominent photo peaks, ε – the full energy peak efficiency, f – the absolute transition probability of gamma decay, and m [kg] – the mass of the sample. The uncertainty of activity concentration was calculated by

$$\frac{\Delta A}{A}^2 \quad \frac{\Delta P}{P}^2 \quad \frac{\Delta \varepsilon}{\varepsilon}^2 \quad \frac{\Delta m}{m}^2 \tag{2}$$

A range of gamma ray transitions from a number of the decay chain members of the ^{238}U and ^{232}Th primordial decay chains were utilized in order to obtain consistent values for the activity concentrations of these nuclei and their decay daughter products are given in tab. 1. The gamma ray transitions of 351.9 keV (^{214}Pb) and 609.3 keV (^{214}Bi) were used to determine the activity concentration of the ^{226}Ra series. The strongest gamma ray energies of 911.1 keV (^{228}Ac) and 583.1 keV (^{208}Tl) were used to determine the activity concentration of the ^{232}Th series in order to ovoid experimental errors in the measurements. The activity concentrations of ^{40}K were measured directly through the gamma energy emission at 1460.8 keV. The concentration of ^{210}Pb is below the minimum limit of detection.

Table 1. Gamma ray energies and their emission probability used for activity concentration determination

Radionuclide	Energy [keV]	Intensity [%]
^{238}U series		
^{226}Ra	186.0	3.2
^{214}Bi	609.3	46.2
	768.4	5.0
	1120.3	15.1
	1238.0	5.9
	1764.0	15.8
^{214}Pb	295.2	19.2
	351.9	37.2
^{232}Th series:		
^{228}Ac	338.0	11.3
	911.1	27.7
	969.1	16.6
^{212}Pb	238.6	44.6
^{208}Tl	583.1	30.0
	2614.5	35.6

Figure 2. shows a typical gamma spectrum of some khol samples due to natural radioactivity.

PIXE measurements

The samples were analyzed via the particle-induced X-ray emission or proton-induced X-ray emission (PIXE) technique. The experiments were carried out at the Van de Graff accelerator, Joint Institute of

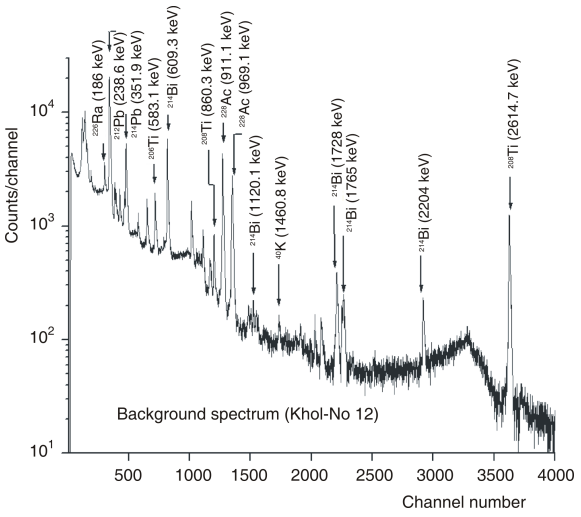

Figure 2. Gamma ray spectrum of a selected khol sample with the highest natural radioactivity concentrations

Nuclear Research, Dubna, Russia, and a 2 MeV proton beam was applied for the analysis of the cosmetic samples. The samples were placed in the vacuum chamber and positioned under the beam, without disrupting the vacuum. The dimensions of the beam were limited by a 1 mm-diameter aperture placed in front of the target at a distance of 125 cm. The beam currents were typically in the range of 1-2 nA.

A special Al maiden chamber with a mylar window of thin Al coating was used to make possible the observation of X-ray spectra up to the least energy without collecting the scattered charges. The photons emitted by target X-rays were collected with a Si(Li) detector placed at 90 ° to the incoming beam at a distance of 75 mm from the target. A tantalum diaphragm of 4mm in diameter and 0.5 mm thick placed in front of the beryllium window of the detector determined the solid angle of the X-ray detector and excluded the "border-effect". The energy resolution of the "Ortec" Si(Li) detector was 160 eV at the energy of 5.9 keV. Both X-ray spectra and backscattered ions were registered simultaneously, with a conventional spectrometry set-up.

In order to get the elemental concentration of lead in cosmetic samples knowledge of the absolute sensitivity of the spectroscopic system is required which, in terms of fundamental parameters, can be expressed as [12]

$$\Omega(E) \quad \frac{N_a}{qA}\sigma_K(Z)\,Y_k(Z)\,\delta_{ki}(Z)\,\varepsilon(E) \qquad (3)$$

where σ Z Y_k Z and ($i = \alpha, \beta$) are, respectively, *K*-shell ionization cross-sections, fluorescence yield and line fractions. ε E is the absolute efficiency function of the detector, N_a – the Avogadro number, q – the elemental charge, and A – the atomic mass of the *Z*-element. The sensitivity per unit of charge and per unit of mass surface density was determined by a set of *N*-standard certified samples in the energy region of interest and the fitting function obtained from the *N*-standard samples.

The concentration of the *Z*-element, *C*, defined as the quotient between the elemental mass and the total mass of the sample, was calculated using

$$C \quad \frac{\Phi(E_{Ki})}{mQ\Omega(E_{Ki})} \qquad (4)$$

where $\Phi(E_{ki})$ represents the net number of counts in the Ki peak ($i = \alpha, \beta$), Q is the collected charge at the Faraday cup, and m the mass per unit area.

Table 2. Average activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K (in Bqkg^{-1}) for the investigated cosmetic samples

Material	^{226}Ra	^{232}Th	^{40}K
Khol	160 12	45 12	320 17
Make-up	40 18	35 10	739 19
Hena	33 17	26 12	301 22

RESULTS AND DISCUSSION

Natural radioactivity

The average activity concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in [Bqkg^{-1}] for the investigated samples are presented in tab. 2. Note that no other radionuclides other than those naturally occurring were detected in cosmetic samples under investigation. The average activity values of ^{226}Ra, ^{232}Th, and ^{40}K in khol, make-up and henna types are lower than the corresponding quoted world values. The maximum safe world values of ^{226}Ra, ^{232}Th, and ^{40}K activity concentrations are 50, 50, and 500 Bq/kg, respectively [13, 14].The average activity of ^{226}Ra in khol samples is higher than the world mean value. This is due to the high radioactivity of raw materials. Activity concentrations of ^{232}Th for all samples are lower than the ^{226}R activity concentrations. It can thus be seen that, in comparison to other isotopes, ^{40}K contributes the most to activity. This may be due to the presence of potassium with high concentrations in the route material of the makeup sampled.

Lead element

PIXE techniques were employed for the determination of major, minor and trace elements in the investigated samples. The comparison of lead content in cosmetic samples is given in tab. 3. This technique provides indirect determination of the used samples. In fig. 3, it is clear that most of the lead lines are depicted (*K* and *L* series). Lead is very toxic, especially when eyes are exposed to it. Consequently, it penetrates the brain directly. In fig. 4, make-up samples, most of the elements are light elements such as Zn, Cl, Si… *etc*., but no toxic elements are present. Figure 5. is the spectra of henna. Lead distributions among investigated cosmetic samples are show in fig. 6. Due to the significant difference in lead content between the

Table 3. Comparison of lead content in cosmetic samples

Material	Total sample	No. of samples Pb mg/kg < 0.5	No. of samples 0.5 < Pb mg/kg < 1	No. of samples 1 < Pb mg/kg < 2	No. of samples 2 < Pb mg/kg < 3	No. of samples Pb mg/kg >3	Average (SD) mg/kg
Khol	26	2 (7.69 %)	3 (11.5 %)	4 (15 %)	3 (11.5 %)	14 (53.8 %)	3.80 (0.78)
Make-up	15	15 (100 %)	–	–	–	–	0.15 (0.01)
Hena	15	5 (33.3 %)	2 (13.3 %)	3 (20 %)	4 (26.7 %)	1 (6.76 %)	1.43 (0.38)

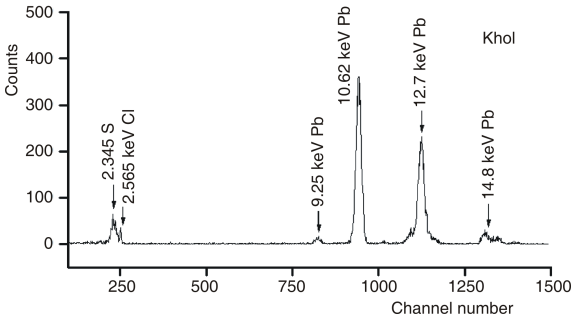

Figure 3. Typical PIXE spectrum of some selected khol samples, using 2.0 MeV protons

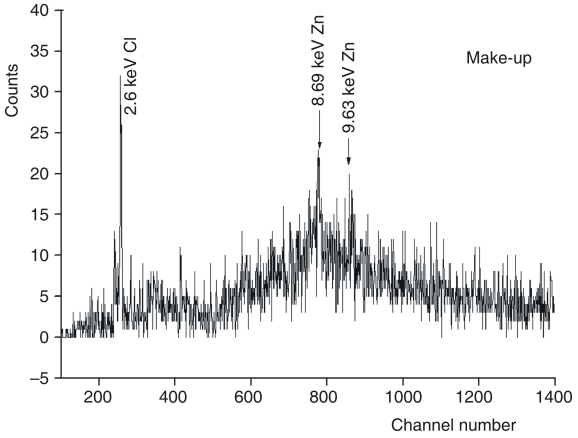

Figure 4. Typical PIXE spectrum of some selected cosmetic face powder samples, using 2.0 MeV protons

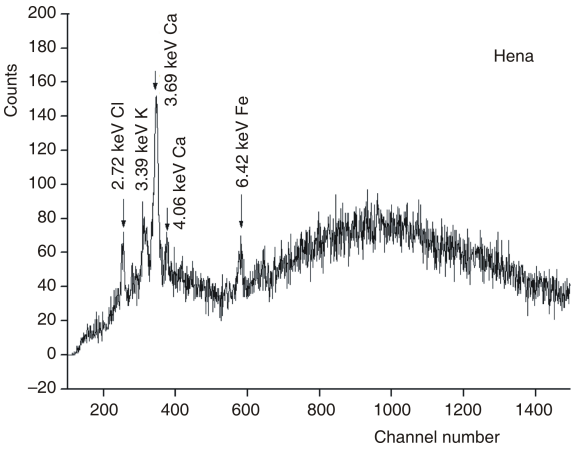

Figure 5. Typical PIXE spectrum of some selected henna samples using 2.0 MeV protons

three categories, the detected lead level range was also separately investigated for cosmetic products. All studied make-up samples contained less than 1 mg/kg of lead. Two samples of henna and three of khol amounted to less than 1 mg/kg of lead. These results show the mean value for lead in khol (3.8 mg/kg 0.78 mg/kg), make-up (0.15 mg/kg 0.01 mg/kg), and henna (1.43 mg/kg 0.38 mg/kg). Our study has

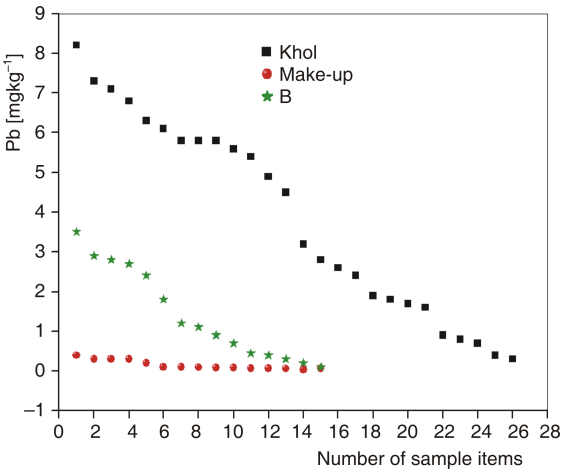

Figure 6. Lead distributions among investigated cosmetic samples

shown that khol has high lead toxicity in comparison to make-up and henna cosmetics. Therefore, the use of khol in cosmetics should be avoided and an acceptable level of lead content defined in order to control associated hazards. At this moment there are not sharp details for permissible levels of hazards in cosmetic products and this why we still research the hazards from many sides.

CONCLUSION

The results of this study clearly show the hazards of the lead detected in cosmetic samples. Higher concentrations of lead in kohl than in make-up and henna samples were reflected in high levels of lead in regular kohl users. Therefore, it is recommended that only lead-free cosmetics should be marketed and used to avoid the hazards of lead toxicity. The prevention of lead poisoning is important and necessitates the promotion of educational programs which enhance local awareness of the hazards of lead-containing traditional cosmetics. The highest radioactivity contribution due to ^{40}K was found in the cosmetic samples.

AUTHOR CONTRIBUTIONS

Experimental analysis of the samples was carried out by M. E. Medhat and figures were prepared by M. E. Medhat. The manuscript was written by M. E. Medhat and V. P. Singh. The authors collectively analyzed and discussed all of the results obtained.

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ПРОЦЕНА ОПАСНОСТИ ОД ОЛОВА И РАДИОАКТИВНОСТИ У КОЗМЕТИЧКИМ ПРОИЗВОДИМА

У раду је приказано испитивање процене опасности од олова и природне радиактивности у козметичким узорцима сакупљеним из различитих земаља. Ови узорци су: пудер за лице, боја за обрве и хена. Присуство олова у козметичким узорцима одређено је применом честицама индуковане емисије Х-зрачења. Максимална концентрација природне радиоактивности ^{226}Ra пронађена је у колу, а ^{40}K у узорцима шминке. Квалитативна анализа козметичких узорака показала је да је олово најтоксичнији елемент пронађен у узорцима боје за обрве.

Кључне речи: традиционална козметика, олово, честицама индукована емисија Х-зрачења, кол