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Study of Heavy Elements and Radioactivity Concentrations in Some Eye Cosmetics Commonly Used in Arabic Regions

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***Abstract*—Thirteen samples of eye cosmetics including five samples of artificial eye cosmetics and eight samples of traditional eyeliner (kohl) were collected from various Arabic markets, and analyzed using inductively coupled plasma-optical emission spectrometer (ICP-OES) to assess concentrations of the most toxic elements (arsenic (As), cadmium (Cd), mercury (Hg) and lead (Pb)), and high purity germanium detector (HPGe) to determine radioactivity concentrations of the natural radionuclides ^{238}U, ^{235}U, ^{226}Ra, ^{232}Th and ^{40}K. The average concentrations of the elements As, Cd, Hg and Pb are a bit high in some samples in a way that they might cause some harm to human health, while the average values of the activity concentrations for ^{238}U, ^{235}U, ^{226}Ra, ^{232}Th and ^{40}K are not that high. Annual absorbed amounts of heavy elements from daily applied kohl were calculated based on roughly assumption that about 50 % of the applied kohl is absorbed into the body. An appropriate simulation has been done for the eye using the MCNP code to estimate the dose rate of the lens of the eye as a result of using contaminated kohl.**

***Index Terms*—Cosmetics, kohl, MCNP code, radioactivity concentrations, heavy elements concentrations.**

I. Introduction

This work represents a part of our study of heavy elements and radioactivity concentrations in 40 samples of cosmetics. In this paper we only present the results of eye cosmetics which include artificial eye cosmetics (eye shadow, mascara and eyeliner) and traditional eyeliner (kohl). Kohl is the most traditional cosmetic used in the Arabic regions. It is often deliberately placed inside the eye, on the conjunctive surface, because of the Arabs thoughts about its benefits: wide eye, purifies it from dust and impurities, and protects it from hot sunshine. Kohl is sold in markets as powders and stones like in Fig. 1.

Heavy elements can harm human health, because after absorbing them, they accumulate in the internal organs of the body such as bone, liver, kidneys, pancreas and lungs, and hence cause damage over time. The most toxic elements are As, Cd, Hg and Pb [1]. The allowable level of lead in cosmetics is 10 ppm as given in Canadian health [1] and 20 ppm in US-FDA [2], while the allowable levels of As, Hg and Cd are 3 ppm in Canadian health [1], and 5 ppm, 1 ppm and 5 ppm respectively in US-FDA [2]. The effect of radiation on the eye is particularly in cataracts, which may happen if the dose exceeds 15 mSv [3].


Fig. 1. Powdered kohl and kohl stone.

II. Experimental Work

A. Samples Collection

The thirteen samples were purchased from various markets in Libya, Egypt and KSA. These samples include one eyeliner, one mascara, three eye shadows, one kohl powder and seven kohl stones.

B. Elemental Analysis

Sample digestion: A 0.15 g of each sample, 7 ml high purity HNO_3 and 2 ml high purity HF are added to a microwave vessel and the mixture is heated to 130 ℃ for more than 15 min. Then, this mixture is held at 130 ℃ for three minutes before the temperature is ramped to 200 ℃ for more than 15 min and held at 200 ℃ for 30 min. After that, 30 ml of 4% high purity H_3BO_3 is added to the vessel for neutralizing the HF, then the mixture is heated again in the microwave to 170 ℃ over 15 min and held for 10 min at 170 ℃. The mixture is then diluted to 50 ml using distilled H_2O.

The samples are analyzed using the Thermo scientific iCap 7000 series ICP-OES spectrometer in Laboratories Compound of Desert Research Center of Egyptian Ministry of Agriculture and Land Reclamation.

C. Radioactivity Measurements

Radioactivity measurements are applied only on samples of kohl stones due to the lack of the suitable standards for other samples. Using a standard sample is necessary to make the efficiency calibration for HPGe detector.

Sample preparation: Kohl stone is crushed to a powder form which is then collected through a 0.85 mm mesh sieve. After that, the sample is placed in an oven at about 90 ℃ until constant weight is achieved. Due to the high density of kohl samples (~ 4 g/cm^3) we use pure silica powder (SiO_2, 2.46

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g/cm^3) to get samples with densities nearly equal the density of reference material. Silica has an appropriate mass attenuation coefficient for gamma rays as shown in Fig. 2. Values of the mass attenuation coefficient (μ/ρ) of SiO_2 are obtained according to the simple summation [4].

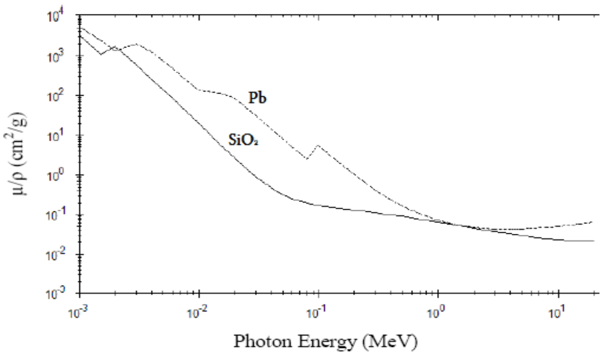

Fig. 2. Mass attenuation coefficient of SiO_2 and Pb as a function of gamma-ray energy.

$$\mu/\rho = \sum_i w_i (\mu/\rho)_i ,$$

where w_i is the fraction by weight of the ith atomic constituent, and the $(\mu/\rho)_i$ values are taken from [4]. In order to confirm that the use of silica does not affect the rate of self-absorption of the emitted gamma-rays, we used two masses of kohl samples (90 and180 g), and then we added the appropriate amount of silica for each mass to fill 240 ml plastic beakers. Silica and kohl are mixed well to get a homogenous sample which is then sealed for more than 28 days to reach the secular equilibrium between ^{226}Ra and its short lived products.

The radioactivity concentrations are measured using HPGe detector in the Egyptian Nuclear Authority. The same geometry and size are used for both measured and reference material samples. The measurements are collected for 20 to 24 hours [5].

TABLE I: HEAVY ELEMENTS CONCENTRATIONS IN PPM (MEAN ± RSD%)

Sample name	Sample code	Country of origin	As	Cd	Hg	Pb
Eyeliner	SEL18	unknown	3.38±0.89	<0.0003	Nil	5.33±1.74
Mascara	SMM14	UK	3.62±2.72	<0.0003	0.09±0.50	3.37±1.67
Eye shadow	SESR9.1	China	<0.008	<0.0003	Nil	35.18±1.20
	SESY9.3	China	<0.008	<0.0003	0.04±2.4	13912.47±0.33
	SEB31	Unknown	<0.008	<0.0003	0.12±0.06	29.12±1.91
Kohl powder	SKA17	India	<0.008	<0.0003	0.08±1.10	2771.38±0.34
Kohl stone	SKK20	KSA	6.23±1.02	8.00±0.27	Nil	50666.67±0.71
	SKP22	Pakistan	13.55±0.55	39.87±0.34	0.02±0.83	547896.44±1.08
	SKI23	India	4.54±4.51	19.25±0.03	Nil	564369.31±0.38
	SKK24	KSA	11.23±1.05	7.56±0.25	0.06±0.21	527565.89±1.06
	SKA1	KSA	7.1±2.8	7.86±0.53	68.85±0.00	707033.84±1.05
	SKR2	KSA	106.12±0.48	6.39±0.04	67.9±0.12	669993.35±0.66
	SKL3	Iran	4.5±2.62	15.6±0.07	152.55±0.01	748344.54±1.40

III. RESULTS AND DISCUSSIONS

A. Elemental Analysis

Elemental analysis has been applied on the 13 samples using ICP-OES spectrometer. The mean values of heavy elements concentrations are shown in Table I. According to this table the heavy elements concentrations in artificial eyeliner and mascara samples are lower than the allowable levels [1], [2] except As which has some increases (3.38, 3.62 ppm, respectively) more than the allowable level (3 ppm) [1]. The concentrations of As, Cd and Hg are lower than the allowable levels in eye shadow and powdered kohl samples, while the concentrations of Pb in these samples are higher than the allowable levels. However, these concentrations of Pb are so low compared with those in kohl stone samples which have concentrations of the four elements higher than the allowable levels (see Table I). R. M. Al-Ashban *et al.* [6] show that the lead concentrations in imported samples available in KSA range between 0.004 to 53% (40 to 530000 ppm). Also R. M. Al-Ashban *et al.* [6] and other earlier studies [7], [8] illustrate the reduction of hemoglobin and the increase of lead level in blood for individuals using kohl compared with those who do not use kohl. Another study [9] indicates the high level of lead in cataract lenses in comparison with clear lenses. R. M. Al-Ashban *et al.* [6] provide information showing that Kohl mentioned previously in the Arabic and Islamic history is quite different from the currently circulated kohl in Arabic markets by providing considerable evidence to support the suggestion that earlier types of kohl mainly contained antimony sulphide. As antimony sulphide became scarce, it was replaced by lead sulphide and lead oxide [6].

Most Arabic women use kohl at a rate of one to two times daily, with approximately 1 g each time. Since we cannot estimate the exact amount absorbed into the body from the used kohl, ingested or entered through the tear duct, we roughly assume that about 50% of the used kohl is absorbed into the body and then calculate the amount of As, Cd, Hg and Pb absorbed per year by using kohl two times a day. The results are shown in Table II. According to this table the values of maximum annual absorbed amount of As, Cd, Hg are 38.73, 14.55 and 55.68 mg respectively, while the maximum value for Pb is 273145.76 mg and so lead is a main reason to classify kohl as a toxic material [10]. The US-FDA [2] warned not to use the present Kohl as a color additive in any of the products and did not allow the entry of these products to the USA because of kohl contamination by lead. There is no regulation permitting its use in a cosmetic or in any other FDA-regulated product [10].

TABLE II: ANNUAL ABSORPTION OF HEAVY ELEMENTS FROM KOHL AND EYELINER

Sample Code	The amount of heavy elements absorbed annually (mg) As	Cd	Pb	Hg
SEL18	1.23	Nil	1.95	Nil
SKA17	Nil	Nil	1011.55	0.03
SKK20	2.27	2.92	18493.33	Nil
SKP22	4.95	14.55	199982.20	0.01
SKI23	1.66	7.03	205994.80	Nil
SKK24	4.10	2.76	192561.55	0.02
SKA1	2.59	2.87	258067.35	25.13
SKR2	38.73	2.33	244547.57	24.78
SKL3	1.64	5.69	273145.76	55.68

B. Radioactivity Measurements

The objective of radioactivity measurements is to determine the concentrations of natural radionuclides (^{238}U, ^{235}U, ^{226}Ra, ^{232}Th, and ^{40}K) in kohl stones and to assess the risk from their usage. The IAEA Safety Guide RS-G-1.7 [11] suggests that radiation protection control is not necessary if the radioactivity concentration of naturally occurring radionuclides in a material is below the IAEA Criteria (10 Bq/Kg for ^{40}K and 1 Bq/Kg for all other radionuclides of natural origin).

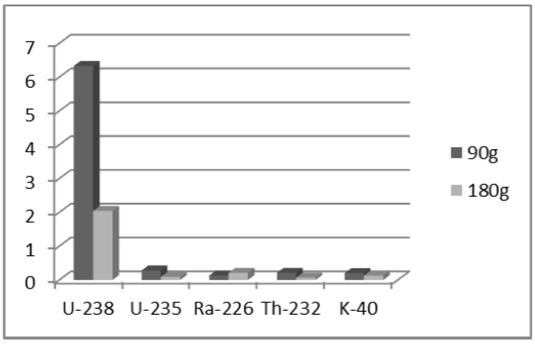

Fig. 3. Activity concentrations (Bq/Kg) of radionuclides for the two different masses of (SKA1) kohl sample.

Mean values of measured activity concentrations of natural occurring radionuclides in kohl stone samples are listed in Table III. According to this table, the radioactivity concentrations of ^{235}U, ^{232}Th and ^{40}K in kohl samples are lower than the IAEA critical values, while the activity concentrations of ^{238}U and ^{226}Ra have some increases higher than critical values [11]. It is known that the activity concentration is independent on the mass of sample, but during our measurements of activity concentrations in kohl samples, we notice that the nps value (number of counts per second which is directly proportional to activity concentration) in 90 g kohl/sample is larger than its value in 180 g kohl/sample of the same kohl type. This is attributed to the high concentration of Pb in kohl (see Table I). The amount of Pb in 180 g kohl/sample is larger than in 90 g kohl/sample which increases the rate of self-absorption of gamma rays before reaching the detector. As a result, some of the gamma emitted from the kohl used to decorate the eye can be absorbed in kohl itself before reaching the eye. For explanation, we show in Fig. 3 and Fig. 4 the activity concentrations in 90 g and 180 g of SKA1 and SKR2 samples respectively.

TABLE III: RADIOACTIVITY CONCENTRATIONS (BQ/KG) IN KOHL STONE SAMPLES

Sample code	^{238}U	^{235}U	^{226}Ra	^{232}Th	^{40}K
SKK20	6.87±1.35	0.29±0.03	1.31±0.04	0.28±0.03	4.35±0.18
SKP22	3.87±0.60	0.14±0.02	1.34±0.04	0.06±0.01	3.35±0.12
SKI23	2.49±0.39	0.11±0.02	0.16±0.01	0.60±0.07	0.85±0.04
SKK24	4.12±0.59	0.20±0.02	1.01±0.03	0.31±0.02	3.18±0.13
SKA1	6.33±0.27	0.28±0.03	0.13±0.01	0.21±0.02	0.20±0.01
SKR2	6.49±1.05	0.29±0.08	2.61±0.05	0.25±0.03	2.15±0.10
SKL3	1.09±0.14	0.05±0.01	0.28±0.01	0.16±0.01	0.45±0.02

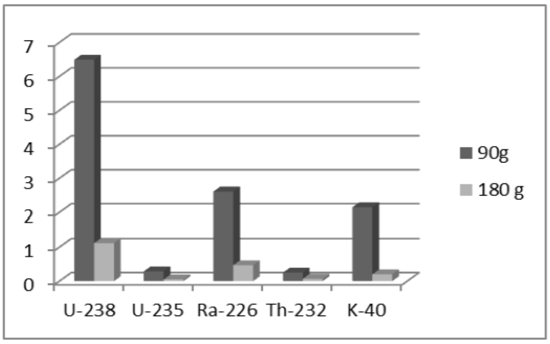

Fig. 4. Activity concentrations (Bq/Kg) of radionuclides for the two different masses of (SKR2) kohl sample.

IV. THEORETICAL MODEL

From the previous sections we see that the radioactivity concentrations for the natural radionuclides in the kohl samples are low, which can give the indication that the radiation dose that may affect the eye will be small. However, in Arabic areas some women use kohl two or three times a day, and we think this may lead to an appreciable annual dose affecting the eye, and therefore in this section we try to make a simple model using the MCNP code [12] to estimate how much the annual dose could be.

In our simple model we depict the eye as a sphere with radius 1.25 cm, with the medium inside having the structure of the eye [13]. We then put the radioactive source on the surface of the sphere and calculate the flux through the surface of the lens of the eye. This surface is the intersection of the plane with the sphere shown in Fig. 5. We do these calculations for the natural radionuclides ^{238}U, ^{235}U, ^{226}Ra, ^{232}Th and ^{40}K for seven kohl samples assuming 2g of kohl. The results are shown in Table IV in units of μSv/yr, where the last column shows the total of all the nuclei. In this table, we don't show the relative errors in those numbers because they are very small. As shown in the table, in spite of assuming frequent use of kohl, the dose rates are still small and insignificant. Also from the table we can notice that the largest contribution is from ^{40}K and then ^{238}U.

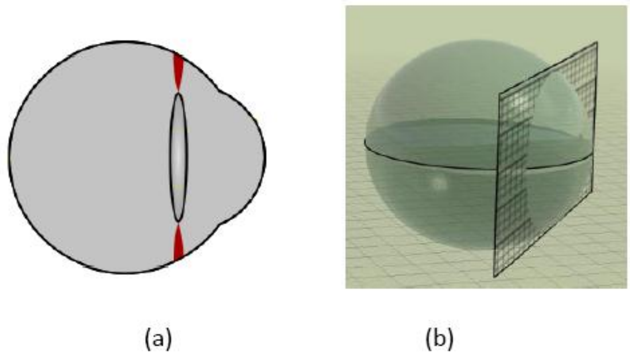

Fig. 5. The eye lens geometry, (a) real eye lens shape, (b) eye lens shape as we assumed in MCNP simulation.

TABLE IV: ANNUAL DOSE OF THE LENS OF THE EYE FOR NATURAL RADIONUCLIDES DUE TO APPLIED KOHL (μSV/YR) (ANSI/ANS)

Sample code	^{238}U	^{235}U	^{226}Ra	^{232}Th	^{40}K	Total
SKK20	0.064	0.002	0.024	0.011	0.197	0.298
SKP22	0.036	0.001	0.024	0.002	0.152	0.215
SKI23	0.023	0.001	0.003	0.024	0.039	0.090
SKK24	0.038	0.002	0.018	0.012	0.144	0.214
SKA1	0.059	0.002	0.002	0.008	0.009	0.080
SKR2	0.060	0.002	0.048	0.010	0.097	0.217
SKL3	0.010	0.0004	0.005	0.006	0.020	0.0414
SKL3(ICRP)	0.007	0.0003	0.004	0.006	0.019	0.0363

To convert from the calculated particle flux to human biological dose equivalent rate, we use ANSI/ANS-6.1.1-1977 conversion factors (American National Standards Institute, and American Nuclear Society) [14]. This gives the results shown in Table IV. However, it’s known that conversion factor sets are subject to changes based on the actions of various national and international organizations due to the reevaluation of existing data and calculations or the availability of new information, and so, for comparison, we use another set of conversion factors, the ICRP-21 (International Commission on Radiological Protection) [14]. We apply it only on the kohl sample SKL3, the results of which are shown in the last line in Table IV but with no significant differences from ANSI/ANS.

V. CONCLUSION

After analyzing thirteen samples of eye cosmetics circulating in Arabic markets, we found that some of them are not really safe to use. Some eye shadows contain various concentrations of Pb which are higher than the allowable levels. The radioactivity concentrations in kohl samples are very low, and so they don’t have radiation risk on the eye, as was confirmed by the simple simulation model. However, these kohl samples are contaminated by significant concentrations of heavy elements As, Cd, Hg and Pb. Depending on our assumption that 50% of the applied amount of kohl is absorbed, the maximum values of the annually absorbed amount of As, Cd, Hg and Pb from daily applied kohl (2g a day) are 38.73, 14.55, 55.68 and 273145.76 mg, respectively. Therefore appreciable amounts of these elements can be absorbed through skin or drop to the mouth and finally move into the blood, kidneys and other organs of the body where they accumulate and cause damage to these organs. It is worth to mention that most of Arabic women prefer to use kohl more than eyeliner to decorate their eyes because of cultural heritage, but according to our results here, we see that it's safer for them to use eyeliner because the heavy elements concentrations in the eyeliner sample are lower than the allowable levels.

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