Research Article
Radiological and Toxic Risk Assessment of Nigerian Kohl as Cosmetic Compared with Imported Kohl Cosmetics

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Abstract: A total of 38 different samples of Kohl comprising of 23 indigenous mined products and 15 imported products as control and were analyzed for general elemental composition but with particular interest in those reported to be of relevance (As, Cd, Hg, Ni, Co and Sb) in cosmetics. Energy dispersive X-ray Fluorescence Analysis EDXRA was used for the assay. Only Pb, As, Ni and Cr were detected among the elements of interest. Mean Pb concentrations of 277300 ppm; Ni at 2256 ppm concentration; and As at 810 ppm which are considerably higher than their safety limits (20 ppm $p<0.01$) were obtained in both the indigenous and imported products. The same risk was statistically observed to be involved following the use of both local and imported kohl products. Again Pb concentrations in excess of what was claimed on the labels of the imported kohl products were observed ($p<0.01$), hence the need for scrutiny of imported products by the relevant agency. The high concentration of Cr (7460 ppm, $p<0.05$) in the imported samples signifies its presence as colorant and the need for chromium control for the brands concerned. Also the observed presence of Th in the indigenous (local) samples suggests that Nigerian products may be of radiological effect to health. Measurements were made of gross alpha and beta count of indigenous mined and imported kohl samples The results reveals that all the forms of kohl products assayed, emit both particles but with β's count substantially higher than the α's ($p<0.5$) at a mean β count 4695×10^{-3} cpm and α count as 283×10^{-3} cpm. One of the samples from Zamfara State of Nigeria (known for Pb poisoning due to mining activities) shows an exceptionally high count in both $\alpha = 8998100$ cpm and $\beta = 9315700$ cpm which reveals that products from Zamfara State, need a special attention. Application of this product is therefore very much likely to produce radiation damage to the cornea due to low penetration of α and to the internal tissue of the eye due to the relatively high penetration of β s. However, the non-existence of defined safety limits for these particles in Kohl as cosmetic, suggests the need for further research.

Keywords: EDXRF, eye, kohl, proportional counter, radiation disease, toxic elements

INTRODUCTION

Kohl is a dark powdery substance that has been worn around the eyes for beautification (Kapoor, 2007). It was not until towards the end of the 21st century that the very substance, kohl, that indigenous people (particularly Nigerians) used for centuries as cosmetic, for medicinal and cultural purposes, with so much belief in its benefits was discredited as a source of lead (Pb) poisoning.

Earliest reports Warley *et al*. (1968), Snodgrass *et al*. (1973) and Betts *et al*. (1973) that gave rise to this, is traced to the death of an Asian child and plumbism (lead poisoning) among the Indian and Pakistani children in England to the liberal use of kohl.

Since then series of reports from kohl using countries have been emerging (Parry and Eaton, 1991; Madany and Salim, 1992; Al-Kaff *et al*., 1993; Al-Saleh *et al*., 1993; Al-Hazzaa and Krahn, 1995; Hardy *et al*., 1998, 2002; Al-Ashban *et al*., 2004; Hardy *et al*.,

2006). Worst among these was that from Shaltout *et al*. (1981) that attributed the death incidence of 25% among children in Kuwait with encephalopathy to the liberal use of kohl. All these recognized kohl brands as potential source of lead (Pb) poisoning, except the findings from Tabbara and Burd (1987) when kohl was analyzed for microbial content, The reports on lead as a major constituents of the majority of kohl preparations, serve as the basis for elimination and setting standard for Pb and later other toxic elements (As, Cd, Hg, Ni, Co) found equally as important in kohl preparations (http://en.wikipedia.org/wiki/kohl-cosmetics). All products must therefore strictly adhere to the regulations and must be well labeled for chemical constituents (FDA, 2006).

Despite all these, it had been reported that the use of kohl is still in vogue among the population of Saudi Arabia (Al-Kawajah, 1992). The same can easily be witnessed among different ethnic groups in Nigeria currently.

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Notwithstanding, simple observation of reports on kohl shows that researches are so far limited to products originating from countries of the Far East, Middle East and Asia. Despite the facts that North African and some West African countries, in particular Nigeria, had also been recognized as kohl consumers and producers (Al-Hazzaa and Krahn, 1995), reports on these products are rarely found. Furthermore, since the report from NHMH (2007) that recognized some few brands to carry false claims of Pb concentration, rarely has any effort been made to verify the claims of any labeled product. Moreover, literature review reveals that efforts are almost solely, concentrate on Pb, other elements (As, Cd, Hg, Ni, Cr, Sb, Co) of relevance in cosmetics seem to suffer neglect.

Not only is kohl use for cosmetic purpose, but also for medicinal and traditional reasons (Kapoor, 2007). The use of Kohl is still in vogue in the modern time as kohl products are now available even in the countries of US and Europe (Health Canada, 2006).

Later findings (Hardy *et al*., 2002; Al-Ashban *et al*., 2004; Hardy *et al*., 2006) also confirm the hazardous nature of kohl.

The aim of this study is therefore to analyze the mine kohl products indigenous to Nigeria for general elemental composition, but with particular interest in those of relevance. Imported products shall be analyzed for comparison purpose and verification of claim for the labeled elements.

Unfortunately, all the researches analyzed kohl for chemical composition, except that of Tabbara and Burd (1987), which ascertain the microbial content. The present investigations were therefore, undertaken to in addition characterize the radiological content of the Mined kohl products indigenous to Nigeria. This is necessary as radiation induced diseases (Cember, 1992) are as important as those of chemicals (Berne Convention, 1964). It is hoped that the research will provide vital information for the consumers, manufacturers and the government for economic health and legislative purposes. The analysis would be done through the determination of gross alpha and beta counts. The proportional counter EURYSYS MEASURE IN20 at the Centre for Energy Research and Training, Ahmadu Bello University CERT, ABU Zaria, Nigeria would be employed. CERCA and LEA laboratories in France certified all Measurement.

MATERIALS AND METHODS

The study area: This study covered the major Galena (kohl) deposits along the North East and South east trending belt between latitudes 4°N and 14°N and longitudes 3°E and 15°E (Fig. 1). Minor deposits of the North East extending to the North West were also studied as sources for local consumption. Geological map of Galena deposits in Nigeria is available in Department of Geology Ahmadu Bello University, ABU Zaria.

This research is an analytical and descriptive cross sectional study. Data collection is random and student's t-test with $\alpha = 1$ and 5% were appropriately used throughout for data analyses.

Sample collection: Twenty three kohl samples were collected from different mining ground (both major and minor) across the country Fig. 1. They were immediately wrapped in a three layer of polythene to avoid contamination. In this form the samples were transported to CERT ABU Zaria preparation and analyses.

Fifteen different brands of imported kohl products were purchased as normal consumer products from markets and cosmetic shops. Some of the specimens were in their paste form and others in powdery form. The choice of samples was at random across the six geopolitical zone of the country (Fig. 1).

Sample preparation: Samples were crushed each manually to fine powder using a quartz model No. 3 and mortar model No. 80320 all made by Tyler company, USA. The samples were then homogenized to grain size of less than 125 pm. (0.3-0.5 mg) of the powder samples were each measured using the metler Toledo balance model AE 163 No. 1075 and for the preparation of pellets. The calibration of the weighing balance was done by the Mettler cooperation service unit laboratory, Columbus, OH, USA and certified for stability to about 0.00075 mg before the commencement of this study. However, as recommended by the calibration organization, recalibration of the balance was undertaken with a known weight after every few sets of samples for quality assurance.

The weighted powders were each mixed with 3 drops of organic liquid binder and pressed after wards at 10 tons with hydraulic press (25.011 model), thus samples in powdered and paste form were directly made into pellets.

The pellets were carefully labeled, covered with mila and stored in partitioned samples storage plastic containers ready for both the XRF and the proportional counter (ERISYS MEASURE), α and β counter technique.

Precaution: To avoid contamination both pestle and mortar were washed with detergent and sponge after which they were rinsed thoroughly with tap water, dried with an absorbent (towel) and then cleaned with acetone (E/65/457-1) using tissue paper. This was done before each sample was prepared.
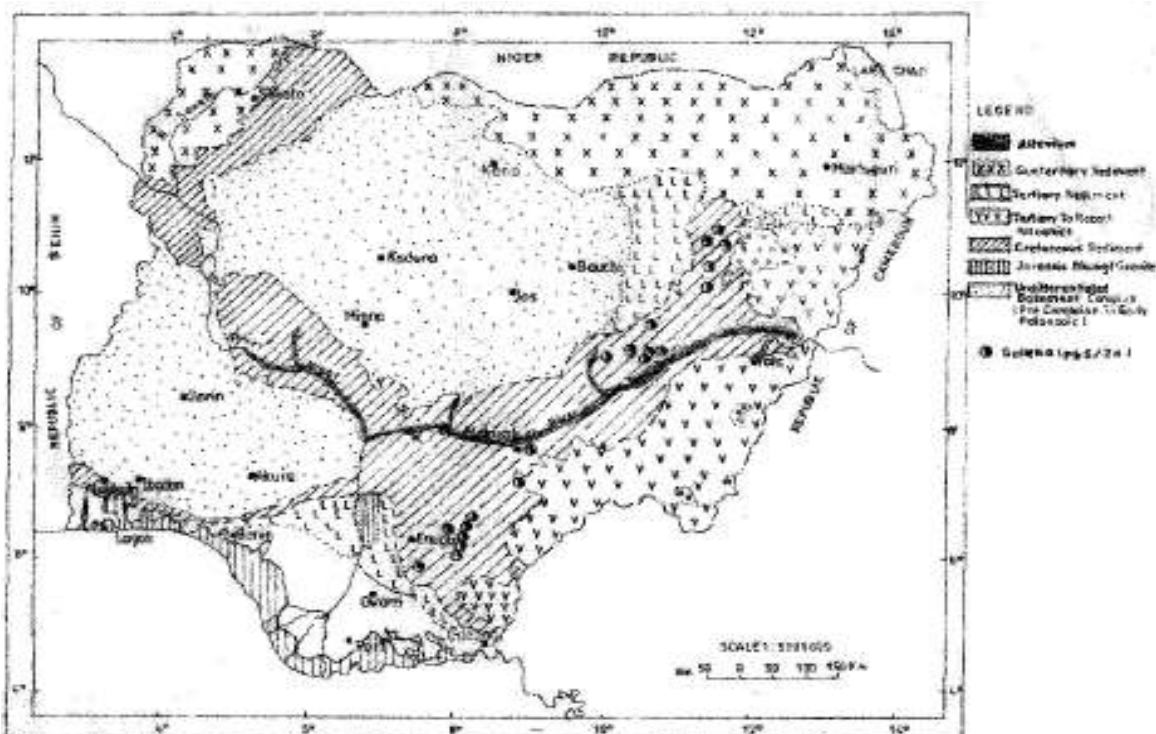
Fig. 1: Map of major galena deposit in Nigeria (Geology Department, ABU Zaria, Nigeria)

RESULTS AND DISCUSSION

Among the elements of interest only Pb, was largely detected but with some few traces of as and Ni detected in the locally (Nigerian) mined samples Table 1.

Only one sample (NIG/Hdjia3) is Pb free, so that 22 out of the 23 (95.6%) natural samples analyzed contain Pb in the concentration range of 0-43% with a mean concentration 27.23±16.70%. Six out of the samples (26%) have less than 1% Pb concentration. The entire 8 sample areas (S/N 8, 15, 16, 17, 18, 20, 21 and 22) observed with high Pb concentration ranging from 39-43% are known for mining activities in Nigeria, but none of the samples carries Pb up to and above 50% as reported by other investigators (Al Hazzaa and Krahn, 1995; Hardy *et al.*, 2006).

A total of 15 other trace elements: Cu, Fe, Mn, Ni, V, Ti, Th, Nb, Ca, Zr, Br, Sr, As, Zn and Rb were also detected together with Pb in all the samples as depicted by Fig. 1 and 2. The observed higher Pb concentration compared with any other element present in each local sample was also seen in the imported kohl samples analyzed. This conforms to the earlier reports (Al-Hazzaa and Krahn, 1995; Kapoor, 2007) that identified majority of kohl preparations to be dominant with Pb and other elements at variable concentrations.

The unique presence of V, Nb, Zr, Br and Rb as depicted by the Fig. 1 for the indigenous kohl samples
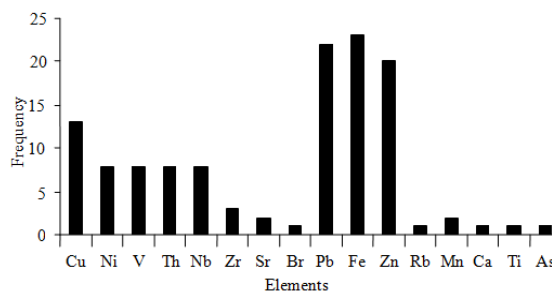

Fig. 2: Histogram of elemental frequency in indigenous samples

have never been reported as constituent of kohl and particular the presence of Th further suggests that Nigerian products may be of radiological risk as well.

In terms of conformity to Pb standard, Table 2 declares majority of the available kohl cosmetic products both local and imported in this region as unsafe because the recorded mean Pb value of 27.73% is significantly higher than the German standard (20 ppm) which is the highest established safe limit (p<0.01) (Health Canada, 2009).

Other elements with atomic number less than 11 reported as constituent of kohl from other countries may be equally present in the samples, but not detected in the samples. This may be due to the inherit limitation of EDXRF technique. Antimony however can be concluded to be absent as it is among the elements in favor of the excitation source Viz Cd.

Table 1: Elemental analysis result for local kohl samples from Nigeria

S/N	Sample code/location	Elemental concentration (%)		
		Pb	As	Ni
1	NIG/Hdjia1	0.12±0.00	0.081±0.00	ND
2	NIG/Hdjia2	0.18±0.00	ND	ND
3	NIG/Hdjia3	ND	ND	ND
4	NIG/BGwari1	25.90±0.27	ND	ND
5	NIG/BGwari2	0.02±0.00	ND	ND
6	NIG/Jos 1	28.50±0.28	ND	ND
7	NIG/Jos 2	27.50±0.28	ND	ND
8	NIG/Jos 3	39.00±0.50	ND	0.26±0.00
9	NIG/NsRwa 1	28.40±0.34	ND	ND
10	NIG/NsRwa 2	32.80±0.34	ND	ND
11	NIG/ZmFara	0.12±0.00	ND	0.02±0.00
12	NIG/Mkurdi	32.60±0.35	ND	ND
13	NIG/BCH 1	27.50±0.28	ND	ND
14	NIG/BCH 2	0.65±0.00	ND	ND
15	NIG/AbKLk 1	42.20±0.50	ND	0.20±0.00
16	NIG/AbKLk 2	42.60±0.50	ND	0.20±0.00
17	NIG/AbKLk 3	43.40±0.51	ND	0.23±0.00
18	NIG/Maru	42.30±0.50	ND	0.27±0.00
19	NIG/MRdun	34.30±0.35	ND	ND
20	NIG/Admwa	40.90±0.50	ND	ND
21	NIG/Eygba	39.50±0.01	ND	ND
22	NIG/Ameri	39.50±0.50	ND	0.22±0.00
23	NIG/Ameka	27.00±0.27	ND	ND
Std. deviation (%)		16.70	4.12×10^{-4}	8.95×10^{-4}
Mean		27.23	3.52×10^{-3}	0.23

ND: Not detected

Table 2: Data of XRF analysis for Pb in indigenous (Nigerian) Kohl and imported kohl compared with standard values ($\alpha = 1\%$, one tailed)

Sample/element	Conc. (ppm)	S.D. (ppm)	Min. standard values (ppm)	t-value	Frequency	Decision
Indigenous	277300	1608	20	16.51	22	Significant
Imported (Pb)	180900	1973	20	1.24		Significant
Indigenous	2256	120	49	15.31	08	Significant
Imported (Ni)	1140	100	49	3.50		Significant
Indigenous	810	412	5	16.51	01	Significant
Imported (As)	1630	-	5	-		Significant
Indigenous	-	-	-	-	-	-
Imported (Cr)	7460	350	5	12.30		Significant

Arsenic is detected in only one of the sample (NIG/Hdjia1) at a concentration of 0.081% (810 ppm) with a mean of 35.22 ppm and S.D. of 4.12 ppm. This value is much higher than the recommend limit for As (5 ppm) in cosmetics according to the German standard (Table 2). The value is equally higher than the safe limit of 3 ppm by Canada and US, respectively. Because this product also contains Pb, the total risk involved in the use of this product is then 96% (92% Pb+ 4% As).

Ni is present in 7 of the local samples (S/N 6, 13, 14, 15, 16, 19 and 22, respectively) at concentrations ranging from 1970 to 2690 ppm and a mean of 2256.25±8.95 ppm. Nickel is among the toxic elements whose safe limit in cosmetics has not been established. However Lilisa Saino *et al.* (2001) demonstrated that a level of 49 ppm of Ni in cosmetic is high enough to cause skin allergic symptoms. Based on this, it is concluded that Ni concentration in the samples is higher that the 49 ppm value at 2256.25±8.95 ppm (Table 2). The minimum Ni concentration level (1970 ppm) detected in this study is a clear indication that none of the products from these region is safe for use as per Ni content. And for the products in general the possibility
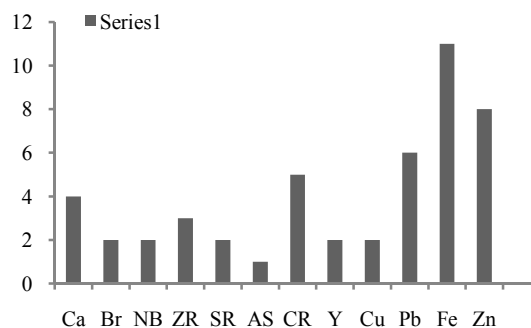

Fig. 3: Histogram elemental concentration in imported kohl cosmetic samples

of Ni poisoning is 7/23≈1/3 = 23%. Because all the 7 samples also contains Pb (39.5≤Pb≤43.4%), the total risk involved in the use of these products is then 26% (8/31) (due to Ni) +71% (22/31) (due to) Pb, to a total = 97% toxic.

Six out of the 15 imported kohl cosmetic samples are analyzed as Pb free. The remaining 9 has Pb concentrations ranging from 0.16-49% (Fig. 3). There are 6/9 of them that contain higher Pb concentration

Table 3: Radiological data for the comparison of α and β within indigenous (Nigerian) and imported kohl samples

Products	α (cpm) x10^{-3}	β (cpm) x10^{-3}	t-cal	t-critical	Decision α = 0.5%
Indigenous x̄	283	5277	2.83	2.76	Significant
S.D.	189	4695			
Imported x̄	283	3070	3.60	2.76	Significant
S.D.	268	2883			

that ranges from 27.8 to 49%. The mean (±S.D.%) concentration value of the samples was found to be 10.34±17.20% which is significantly higher than the (0.002%) established safe limit for Pb (Student's t-test, p<0.01). Even the minimum detected value (0.16%) is also found to carry Pb in excess of the safe limit. It is therefore, concluded that only the Pb free products 6/14 (43%) are considered safe for use in this regard, but again the observed presence of As, Cr and Ni beyond the safety limits in these Pb free sample is a problem. Arsenic is present in a Pb free imported sample at a concentration of 1630>>5 ppm the German safe limit and consequently very much was also found in the other five Pb free imported kohl samples at concentrations ranging from 3450-9270 ppm with a mean of 7460 ppm (Fig. 2). This is much significantly higher than the 5 ppm recognized by Kang in 2002 and 2005 to cause skin allergies (p = 0.005, α = 0.01). Thus the products are unsafe due to the presence of Cr only. The non detection of Cr in natural samples signifies its presences in artificial samples as a colorant. Again less regard is paid to the Cr control. Finally, Nickel was also observed in one of the samples with an observed Cr poison. The measured Ni is valued at a concentration of 1140 ppm which is also higher than the recognized (49 ppm) to cause allergic symptoms (Lilisa Saino *et al.*, 2001). Therefore, effect due to Ni intoxication is very much likely for the regular consumers of that product in addition to the Cr poison.

When the Pb concentrations of these imported samples are compared with those of the local samples, statistical analysis showed that there is no difference between the products (p<0.01) but for the additional radiological effect of the local samples and the toxic effects from Cr most pronounced in the imported Pb free samples.

Verification of claims: Out of the fifteen samples, nine were unlabeled. Two-thirds of these (1-6 inclusive) were Pb free. The remaining 1/3 carry Pb far in excess of the safety margin (20 ppm). None of the labeled products carried Pb in conformity with the level carried by its label. While they were labeled to contain Pb below the safety level, it is found that their Pb content is far beyond the recommended limit of the 20 ppm (with a mean of 178366 ppm; and standard deviation of 947 ppm).

Table 3 depict the statistical information on the α and β emission from both local and imported products. It is clear from table that β emission in the two products is considerably higher than the α s (p<0.05). Thus suggesting that the great majority of the elements comprising the products are β emitters of which majority are low Z elements. A sample from Zamfara state shows an exceptionally high count in both α (8998100 cpm) and β (9315700 cpm). Products from this region therefore need a special attention this observation is consistent with the higher Pb concentrations obtained in kohl samples from that state Table 1 (S/N 18 and 19). Application of kohl from such sources is therefore very much likely to produce radiation damage to the cornea due to low penetration of the α-particles. The internal tissue of the eyes are equally at risk as a result of the penetration of the β-particle of the relatively higher energy. Uptake of kohl via licking the lips, feeding and the direct ingestion from the younger ones, could therefore greatly increase α-particle damages, due to direct contact with the tissues. It was also realized that there is no difference between the proportion of α to β in both imported and local products (Table 3) and the same risk of radiation induced diseases should be expected following their usage. However, the non-existence of defined safety limits for these particles (α and β) in Kohl, suggests the need for further research.

CONCLUSION

In conclusion, our findings reinforce the growing body of evidences that the majority of kohl preparation, irrespective of the formulae used in their preparation, carry substantial amount of Pb together with smaller quantities of other elements. Pb and Ni concentrations are quite comparable in the indigenous and imported products. It follows that the same risk of Pb and Ni induced diseases should be expected following their usage. The high concentration of Cr in some of the imported brands (p<0.05) signifies the risk to which the patronage's of the brands concerned are exposed. The non-detection of Cr in local (Nigerian) samples indicates its presence as colorant in the imported samples and attention must be paid to Cr control. Finally, the particular presence of Th indicates that Nigerian products may be radiological hazard to health.

Again, this study, which to the best of our knowledge, was the first to describe the radioactive properties of Kohl, illustrated that, all forms of Kohl products are α and β emitters with β s' count rate substantially higher then α s'. Thus suggesting that majority of elements could be characterized as good beta emitters, composing of low z elements but for one of the samples from Zamfara State with an exceptionally high count in both α and β. It follows that

Kohl products from Zamfara State require a special attention or better avoided as a cosmetic due to its likelihood to cause radiation damage. Uptake of kohl via licking the lips, feeding and the direct ingestion from the younger ones, could also greatly increase α-particles damages, due to direct contact with the tissues. It was also realized that same risk of radiation induced diseases should be expected following their usage of both imported and local products. However, the non-existence of defined safety limits for these particles in Kohl, suggests the need for further research.

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