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ICP Characterization of ''Kohl'' Samples in Sudan

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Abstract: *Kohl is a traditional cosmetic, which is almost available in any house in Sudan. This study was conducted to investigate the major elemental constituents of kohl. Inductively coupled plasma (ICP-OES) analysis was carried for eight samples, purchased from Khartoum state markets. The results showed the presence of twenty seven minerals. Na, K, Ca, Mg and P showed relatively high availability in all samples. Significantly high levels of Pb were indicated in five samples. Different concentrations were shown by the trace minerals Mo, Zn, Ni, Co, Mn, Cr, V, Cu and Ti. High Fe content was shown by two samples and one sample have very high Zn. The eight samples showed the availability of As, Sn, Sb, Cd, Ba, Sr and Al in different concentrations.*

Keywords: Kohl, ICP-OES, Cosmetics, lead-based, Trace minerals

1. Introduction

Kohl, the shiny black crystalline stone, is a traditional cosmetic which is used for medicinal and beautification purposes in any Sudanese house. Kohl stones are kept in silver or copper vessels as a part of the local culture (Fig. 1), and it's powder is used as eyeliner for bridegroom during wedding ceremony and for the newly-born infants in their early weeks of life. Today many kohl-based cosmetics are available as commercial products in solid, powder, paste or eyeliner form (Fig .2). Throughout human history, civilizations have used different natural compounds to decorate their bodies, as part of their daily rituals (Draelos, Z. D, 2015, Blanco-Dávila, 2000). Historically kohl preparations were used for the treatment and prophylaxis of various eye diseases (Vaishnav Ragini, 2001, Z A. Mahmood, 2009).

Kohl (Surma), was reported to be antimony based cosmetic (Sb_2S_3), which was used as a medicinal eye drop in ancient Egypt (Gunn, G, 2014, Draelos, Z. D, 2015), where the ancient Egyptian women believed that, blacking of the eyelids and eyebrows would protect children from the glance of the Evil Eye (N Bassal, 2013). The demand for kohl-based eyelids and lipsticks is increased in Europe because of the recent migration of populations from Asia and Africa (Navarro-Tapia, E., 2021).

Fig.1: Different kohl keeping vessels

Fig.2: Some commercial kohl samples available in Sudan

The European legislation prohibits the use of heavy metals in cosmetics due to their harmful effects to pregnant women and children (Navarro-Tapia, E., 2021). Galena (PbS) was reported to be the main component of kohl samples from Qatar and Yemen, in addition to different amounts of, amorphous carbon, Fe_2O_3, FeO(OH), SiO_2, H_3BO_3, ($Mg_3Si_4O_{10}(OH)_2$) and ZnO (Andrew D. H. et al., 2008). According to N. Bassal et al., (2013), the industrial kohl contains calcite ($CaCO_3$), goethite (FeO(OH)) and Talc ($Mg_3Si_4O_{10}(OH)_2$), whereas, the natural kohl and eyeliner contain, Pb , As, U and Th. Chavoshi N. et al., (2022**)**, reported Significantly high Pb and heavy metals in commercial kohl which, may be harmful to women and children. Lead levels greater than 10µg/dl in children blood is abnormal and galena-based kohl may give rise to lead toxicity (Andrew D. Hardy, 2011).

Pb-based cosmetics from Spanish and Germany markets showed significant availability of Pb, As, Cd, Sb, Ni, Co, Cr and Al, which exceeded the established EU and German BVL limits, where the allowed impurities are 5 ppm for make-up powder, rouge, eyeshadow, eyeliner, and kajal, as well as theater and carnival make-up (Navarro-Tapia, E.;, 2021).

The main components of kohl samples from Cairo were found to be, (PbS), amorphous carbon, ($CaCO_3$), (Cu_2O), (FeO(OH)), and ($Mg_3Si_4O_{10}(OH)_2$), (Andrew D. H. et al., 2004). N. Bassal et al., (2013) reported that, the industrial kohl samples were free of lead and radioactive materials and include mainly Ca (92.6%), Fe (80.7%), Si (10.2%), Zn (95.99%), Cu (0.77%), Ni (0.54%), S (4.27%) and Mg (3.06%), whereas, the natural samples showed significantly high Pb (85.37 to 89.39%), and S (9.16 to 13.12 %). O. M. Badeer et al., (2008) found that, eight samples out of sixteen have Pb greater than 70%. Ali AL-Kaff et al., (1993) reported pb as 88% in black stone kohl sample. Andrew D. Hardy (2011), Ragini Vaishnav (2001), Pervez Habib Allah et al., (2010) reported high Pb in some kohl samples as (85%) in Kuwait and (100%) in Nigeria. Pasha, M. A., N. (2016), stated that, some kohl samples are (85.5%) galena. Neda Chavoshi et al., (2022) recommended that, more quality control on commercial kohl is required because of the high levels of toxic elements and their impact on the health of kohl users.

2. Methodology

Eight kohl samples were purchased from Khartoum local markets (Table. 1)

0.2 g of each kohl sample was used for (ICP-OES) analysis. All chemicals used were of standard analytical grade.

Table (1): Color and origin of the samples

Samples (No)	Colour	Origin
1	Black	Saudi Arabia (Medina)
2	Dark grey	Saudi Arabia
3	Black	Saudi Arabia
4	Black	India
5	Black	Sudan
6	Dark grey	India
7	Shine grey	Nigeria
8	Shine grey	Saudi Arabia

3. Results and discussion

The macro minerals, Ca, Mg, K, and P showed significantly high concentrations in Samples (No.3, 4 and 6), and moderate concentrations in samples (No.1 and 5), compared with relatively low availability in samples (No.7and 8).

Relatively high concentrations of Ca, Mg, K, Na, and P, were shown by samples (No.1 and 5). In the eight samples Ca is the most available mineral (table. 2).

Andrew D. Hardy (2011), reported the presence of Ca, and Na in kohl samples as calcite, and halite ($CaCO_3$, NaCl). Ca-based kohl samples were identified by Andrew D. H. et al., (2004) and N. Bassal et al., (2013).

Table.2: Macro minerals content of kohl samples (mg/l)

Sample No.	Ca	Mg	K	Na	P

1	2276	735.3	651.7	586.9	643.5
2	2955	161	818	408.1	131.7
3	112000	554.1	2221	501	1301.3
4	28593	5369	4268	443	634.6
5	2051	661.9	554.1	341.8	634.1
6	65647	35373	774	337	172.3
7	792	63.07	676.7	313.7	79.27
8	595.2	47.53	644.9	318.2	81.13

Different concentrations of micro and trace minerals were shown by the eight samples (table. 3). B, Li and Se concentrations were generally low except in sample (No.7) where Se availability was (16.13 mg/l). Sample (No.1) showed the lowest amount of Pb (131.4mg/l), compared with, high concentrations of Mo (266.4mg/l), Cu (1678 mg/l), Zn (1065mg/l), Ni (321.5 mg/l), Co (30.93mg/l), Mn (5140mg/l), Ti (322.4mg/l) and significantly high Fe content (453,067mg/l). This may indicate that, sample (No.1) is a natural Fe- based rock sample. Trace mineral contents were generally low in sample (No.2) except Zn (7780 mg/l), Cu (520.27 mg/l) and Fe (906.7 mg/l). Low trace minerals content was also shown by sample (No.3) except, Fe (992.7 mg/l), Zn (33.0 mg/l) and Cu (24.07mg/l). The highest availability of Ni (571.0 mg/l), V (867.3mg/l), and Li (2.733mg/l) was shown by Sample (No.4), in addition to relatively high Fe (13,227 mg/l) and Mn (325.2 mg/l). Unexpected availability of Cr (1671 mg/l), Cu (1578 mg/l), Mo (251.07 mg/l) and very high Fe (445,800 mg/l), was shown by sample (No. 5). Samples No.1 and 5 showed almost similar elemental constituents (table .3). The highest trace mineral in sample (No. 6) was, Zn (97,733 mg/l) followed by Fe (6860 mg/l), Cu (254.7 ppm), Ti (95.00 mg/l), V (88.53 mg/l) and Mn (72.2 mg/l). All the trace minerals showed very low and sometimes similar concentrations in sample (No. 7 and 8). The highest Se was shown by sample (No. 7).

Table 3. Trace minerals content of kohl samples (mg/L)

Sample No.	1	2	3	4	5	6	7	8
B	<0.00188	<0.00188	<0.0019	<0.0019	<0.00188	<0.0019	<0.0019	<0.0019
Se	<0.00345	6.333	2.600	2.733	<0.00345	2.733	16.13	4.133
Mo	266.4	4.533	4.067	8.400	251.07	4.067	2.933	3.267
Zn	1065	7780	33.00	66.20	876.0	97733	78.27	55.07
Ni	321.5	3.667	4.467	571.0	339.9	11.07	14.60	6.133
Co	30.93	2.93	2.33	33.67	30.60	15.47	2.133	2.333
Mn	5140	19.00	16.87	325.2	5310.0	72.20	2.267	2.400
Cr	1276.0	4.333	6.467	46.07	1671	13.07	2.867	2.73
V	46.33	4.267	3.267	867.3	46.80	88.53	2.200	1.533
Li	<0.00039	<0.00039	<0.00039	2.733	<0.00039	0.2667	<0.0004	<0.0004
Cu	1678	520.27	24.07	35.80	1578	254.7	7.400	336.1
Fe	453067	906.7	992.7	13227	445800	6860	72.00	72.53
Ti	322.4	9.733	6.667	518.6	314.1	95.00	3.933	4.667

Sample No. (1 and 5) showed the lowest Pb content as (131.4 and 297.4 mg/l) and almost typical concentrations of Sn, As, Sb, Cd, Ba, Be and Sr (table. 4). Since, the two samples were from different origins (Table. 1), their similarity may be due to geochemical formation background.

The highest Pb concentrations were shown by samples (No .2, 8, 7, 6 and 3) as (971,333mg/l), (826,667 mg/l), (718,667 mg/l), (260,000 mg/l) and (21,707mg/l) respectively. These five samples may be classified mainly as lead-based kohl. Habibullah P. et al., (2010), reported that, the main component of kohl stone is galena (PbS), with total mineral concentrations as Pb (85.51%), S (11.43%), Sb (2.06%), C (0.689%), Fe (0.03%) and Cr (0.002%). High Cd (120.0mg/l) and Sb (261.2 mg/l) were shown by sample (No.2). The concentrations of Sb in samples (No.4, 7 and 8), were (0.4667, 587.5 and 351.3mg/l) respectively. The levels recommended by European Union for kohl-based cosmetics are, Pb < 20 ppm, As < 5 ppm, Cd < 5 ppm, Sb < 100 ppm, and Ni < 200 ppm, whereas in Germany, the levels are, Pb < 2 ppm, As < 0.5 ppm, Cd < 0.1 ppm, Sb < 0.5 ppm, and Ni < 10 ppm (Butschke, A, 2010, Goverment of Germany, 2020, Navarro-Tapia, E., 2021). Sample No.4 showed the highest concentrations for Ba (34,466.7mg/l), Sr (433.3mg/l) and Al (10,833mg/l).

Table 4. The hazardous minerals content of kohl samples (mg/l)

Samples. No	Sn	As	Sb	Cd	Ba	Pb	Sr	Be	Al
1	70.33	27.87	63.87	2.467	222	131.4	11.4	1.600	961.3
2	6.33	7.467	261.2	120.0	97.53	971333	242.3	1.533	519.4
3	7.333	2.800	7.933	2.40	181.60	21707	78.33	1.533	120.7
4	2.00	1.333	0.4667	2.07	34466.7	716.7	433.3	1.867	10833

5	70.13	26.67	68.07	2.133	231.4	297.4	9.467	1.600	623.7
6	4.533	4.667	56.20	5.933	142.7	260000	42.67	1.600	2437
7	8.933	2.267	587.5	5.800	3.867	718667	1.800	1.533	68.40
8	9.267	4.400	351.3	11.20	1467	826667	17.80	1.533	63.93

As shown by (table. 5) the samples (1 and 5) were mainly Fe-based compounds. On the other hand samples (2, 6, 7 and 8) may be classified as Pb- based and samples (3 and 4) as Ca-based compounds. Sample (No 6) showed considerable content of many minerals, Pb (55.39%), Zn (20.82%), Ca (13.896%), and Mg (7.54%). The results obtained by this study may strongly enhance the findings reported by, Ali AL-Kaff et al (1993), Ragini Vaishnav (2001), O. M. Badeer et al., (2008), Pervez Habib Allah et al ;(2010), Andrew D. Hardy (2011), Pasha, M.A., Nallusamy (2016), Navarro-Tapia, E. et al., (2021), and Neda Chavoshi et al., (2022).

Table 5. The most available minerals in each sample (%)

Sample. No	Fe %	Pb %	Mg %	Ca %
1	96.47	0.027	0.157	0.485
2	0.092	98.5	0.016	0.299
3	0.71	15.53	0.39	80.12
4	13.00	0.70	5.3	28.1
5	96.5	0.064	0.001	0.44
6	1.46	55.39	7.54	13.896
7	0.0099	99.6	0.0088	0.1
8	0.0087	99.68	0.0057	0.0717

4. Conclusions

The kohl samples obtained from Khartoum state markets showed different elemental composition. All the samples showed considerable Na, K, Mg, Ca and P content. Two samples showed almost identical chemical composition, with lowest Pb and highest Fe content. Three samples showed high Pb content as if they were pure metallic lead. Antimony which is expected to be the major constituent of kohl showed very low concentrations in all samples.

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