



Chemical Analysis of Some Cosmetics, Detergent and Pharmaceutical Minerals used in Traditional Medicine of Iran

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In this study, some minerals, which are used in pharmaceutical, detergent and cosmetic products in traditional medicine of Iran, have been analyzed with the aim of identification and determination of their components for toxic element contents. The typical samples with their trademark such as detergent minerals "Gele Sarshoye", cosmetic minerals "Sefidab Roye, Sefidab Ghale, Sefidab Hamam, Kafe Darya and Sorme (Kohl)" and pharmaceutical minerals "Gele Armani, Shangarf, Booreh Armani and Mordar Sang" were collected from traditional drug stores in Iran for sample testing. The qualitative and quantitative analyses were carried out using X-ray diffraction, X-ray fluorescence, inductively coupled plasma optical emission spectroscopy, inductively coupled plasma mass spectroscopy and atomic absorption spectroscopy techniques. Due to lack of control and standardization these minerals have presented positive traces of toxic elements and clear differences when comparing the chemical analysis of similar products.

Key Words: Elemental spectroscopic analysis, Traditional medicine, Toxic elements.

INTRODUCTION

The use of natural minerals and soils as pharmaceutical, detergent and cosmetic products in the traditional medicine of some countries such as China, India, Emirates, Oman, Morocco and Jordan has been typically reported in literature¹⁻¹¹. Iranian ancient medicine also indicated some of these applications. Famous Iranian scientists such as Ave Sina and Razi identified the use of some of these minerals¹²⁻¹⁷.

Although clay is widely known to have a healing efficacy due to its natural chemical properties¹⁸, there are only a few scientific studies carried out on mineral traditional medicine and ancient remedies compared to herbal traditional medicine. Hence these compounds are unknown and their uses are limited to regional traditional medicine.

Since the toxic elements and microbial factors in these compounds are not controlled, sometimes using these natural compounds can be harmful. For example, Sormeh (Kohl) is one of the most popular cosmetic products used as eyeliner for eyes in the Middle East especially for children. This natural mineral is functional as it is believed to improve eyesight, growth of eyelashes and also used for aesthetic purposes. The results of chemically analyzing this material show that the tested samples have different compositions, containing "Pb" as the major constituent in the tested samples^{8,9}.

More people seem to be turning back to nature therapy, however currently natural compounds are often accompanied

by toxic elements. Therefore scientifically, safety validation of these natural products will provide requirements in order to replace synthetic products.

Some elements which can be toxic to human health are As, Cd, Sb, Bi, Pb, Hg, Sn and Al¹⁹. These non essential and mostly toxic elements can enter the human body orally, penetrate through the skin and sweat ducts or inhalation into the lungs²⁰.

In present studies, the presence of toxic elements such as As, Sb, Sn, Cd, Hg, Pb and Bi are studied in the selected natural minerals used in pharmaceutical, detergent and cosmetic products. Since most of collected minerals are exposed to skin and hair, the harmful effect of such exposure must be investigated before marketed.

Some harmful effects to the skin due to the exposure of these toxic elements are reported in literature. For example, arsenic exposure to skin can cause cancer and skin tumors²¹. As an affect of the arsenic toxicity absorbed through the skin's sulfhydryl group, which contain proteins, that cause serious problems²¹. Antimony compounds are irritating to the skin, with lesions in the area surrounding the sweat ducts²¹. Even though Bi exposure can cause some skin diseases such as pityriasis and rosea-like eruption, topical bismuth compounds were used as a treatment for skin lesions, emollient, astringent and disinfectant²¹. This element also has some cosmetic relevance, such as being used in skin lightening creams and as a

pearlescent pigment in makeup products. Toxicity of inorganic lead is extensively studied^{20,21}. It can penetrate through the skin and sweat ducts. Some cosmetics such as Surma or Kohl and hair colouring agents based on lead acetates are some of intentional exposure of skin to this toxic element^{20,21}. In addition mercury is absorbed through the lungs and the skin, it accumulates in body and reacts with protein sulfhydryl groups which can affect the activity of the enzymes and also the structure and function of the membranes²⁰.

In this approach a few different types of minerals which are used in traditional medicine of Iran are chosen for analysis. One of them is known and used as detergent mineral named with the trade mark "Gele Sarshoye", seven of them are used as cosmetic mineral named, "Sefidab Roye, Kafe Darya, Sefidab Ghale, Sefidab Hamam, Sormeh and Mordar Sang" and three of them which are known and used as pharmaceutical mineral with trade mark names, "Gele Armani, Shangarf, Boreh Armani", were collected from traditional drug stores in Iran.

As the elements in these minerals exist as major, minor and trace components in different matrices. Therefore a combination of elemental analysis techniques is required for these accurate measurements. Atomic absorption spectroscopy (AAS), inductively coupled plasma optical emission spectroscopy (ICP-OES), inductively coupled plasma mass spectroscopy (ICP-MS) and X-ray fluorescence (XRF) are mostly the proposed elemental analysis techniques^{22,23}. The X-ray diffraction method is also used for qualitative analysis of the minerals²⁴⁻²⁶. Therefore, the qualitative and quantitative analyses of the selected mineral samples were undertaken using these methods. Two digestion techniques were used for AAS sample preparation procedure, (1) boiling acids and (2) complete decomposition by acids.

EXPERIMENTAL

Experiments by X-ray fluorescence were performed on a Philips PW 1480, a wavelength dispersive instrument equipped with a Sc-Mo X-ray tube, 2400 W power generator and using software X40. Measurement by inductively coupled plasma atomic emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectroscopy (ICP-MS) were performed on a Perkin Elmer Optima 530 DV and Perkin Elmer 9000, respectively. The Philips PW 1800 XRD with the APD software, 40 KV, 30 mA current, Cu lamp, Ni filter, 0.05 2 θ S⁻¹ scan rate was used for X-ray diffraction (XRD) experiments. The data of elemental analysis were obtained using Perkin-Elmer 560 atomic absorption spectroscopy. The Buck Scientific 400 A mercury analyzer and the Varian spectra AA220 were used for cold vapour atomic absorption spectroscopy and hydride generation atomic absorption for sample mercury and arsenic content analysis.

Sample collection: Natural mineral samples were collected from traditional drug stores of Iran. Physical appearance and aforementioned ancient remedies for these samples are seen in Table-1.

Samples with trademarks "Gele sarshoye", "Sefidab Roye" and "Sormeh" were prepared from two different traditional drug stores and are abbreviated as GS1, GS2, SR1, SR2, S1 and S2.

TABLE-1
SELECTED SAMPLES FOR CHEMICAL ANALYSIS

Name	Abb.	Physical appearance	Likely remedy
Sefidab Roye 1	SR1	White colour powder	Facial mask and anti acne
Sefidab Roye 2	SR2	White colour powder	Facial mask and anti acne
Sefidab Ghale	SG	White colour powder	Facial mask and anti acne
Sefidab Hamam	SH	White colour balls made by hand according to a traditional process	Facial mask, anti acne and scrubbing agent
Kafe Darya	KD	White colour powder	Facial mask and anti acne
Gele Armani	GA	Brick colour powder	Anti vomiting, anti diarrhea and anti hemorrhagic
Gele Sarshoye 1*	GS1	Beige colour powder	Hair shampoo and hair conditioner
Gele Sarshoye 2*	GS2	Light green colour powder	Hair shampoo and hair conditioner
Mordar Sang	MS	White colour powder	Deodorant
Shangarf	SHG	Red colour powder	Wound healing
Sormeh 1	S1	Black stone	Beauty, improving eyesight and eyelash
Sormeh2	S2	Black powder	Beauty, improving eyesight and eyelash
Boreh Armani	BA	White colour powder	Anti spasm

*GS1 and GS2 are originated from two different cities of Iran (Shiraz and Zanjan)

Reagents standards and samples preparation: Working standards of Fe, Ca, Mg, Na, Zn, Mn were prepared by diluting 1000 $\mu\text{g/mL}$ stock reference solutions to produce proper concentration for each experiments. Deionized water and analytical pure acids were used in the experiments.

The samples were grounded and sieved through a 200 μm screen. 1 g of each sample was packed into the sample container for XRD analysis. The samples for XRF analysis were prepared by adding 3.5 g of each mineral to 0.7 g adhesive and 3 g boric acid and then pressed by 20 ton/in² mechanical press.

Two techniques of digestion were used for sample preparation prior to measurement by AAS for silicate base samples such as GS1, GS2 and GA. One technique used was digestion by using boiling acids such as HCl and HNO₃ and the other is complete digestion by drying the sample with HF and then dissolving in HNO₃.

Digestion by boiling acids is time saving compared to the complete digestion. However, this method is an incomplete digestion, due to some insoluble components such as metal silicates, therefore it could not result in total components measurement.

RESULTS AND DISCUSSION

The results of XRD analysis for the interested samples are shown in Table-2. The primary studies on these samples as natural compounds, show some discrepancies in expected known structure of the collected samples. For instance the results illustrated in Table-2, show that SR1 and SR2 which were

Abb.	Major Constituent	Minor constituent	Trace constituent
SR1	Zincite ZnO	–	–
SR2	Calcite CaCO ₃	Quartz SiO ₂ Dolomite CaMg(CO ₃) ₂	–
SG	Barite BaSO ₄ Sphalerite ZnS	Sweetite Zn(OH) ₂	–
SH	Calcite CaCO ₃	Dolomite CaMg(CO ₃) ₂	Quartz SiO ₂
KD	Halite NaCl aragonite CaCO ₃	Calcite CaCO ₃	–
GA	Quartz SiO ₂ Hematite Fe ₂ O ₃ Gypsum CaSO ₄ ·2H ₂ O	Muscovite KAl ₂ Si ₃ AlO ₁₀ (OH) ₂ Kaolinite Al ₂ Si ₂ O ₅ (OH) ₄ Calcite CaCO ₃ Albite NaAlSi ₃ O ₈	–
GS1	Montmorillonite Na _{0.3} (Al,Mg) ₂ Si ₄ O ₁₀ (OH)·xH ₂ O	Muscovite KAl ₂ Si ₃ AlO ₁₀ (OH) ₂ Quartz SiO ₂ Dolomite CaMg(CO ₃) ₂	Calcite CaCO ₃
GS2	Montmorillonite Na _{0.3} (Al,Mg) ₂ Si ₄ O ₁₀ (OH)·xH ₂ O	Albite NaAlSi ₃ O ₈ Calcite CaCO ₃ Quartz SiO ₂ Clinoptilolite KN ₂ a ₂ C ₂ (Si ₂ 9Al ₇)O ₇	–
MS	Massicot PbO Litharge PbO	Portlandite Ca(OH) ₂	–
SHG	Cinnabar HgS	–	–
S1	Galena PbS	–	–
S2	Zincite ZnO	–	–
BA	Hydroboracite CaMg(B ₃ O ₄ (OH) ₃) ₂ ·3H ₂ O Priceite Ca ₄ B ₁₀ O ₁₉ ·7H ₂ O	Gypsum CaSO ₄ ·2H ₂ O	–

sold under the same trademark (Sefidab Roye) contain different major and minor constituents. Zincite is the major component in SR1, while calcite is the major constituent in SR2.

More SR samples were collected and analyzed by FAA spectrometry for determination of major elements. The results of analysis show that, the structure of two of the ten collected samples are similar to SR1 and those of the other eight samples are the same as SR2. It is expected that zinc be the major

component in "Sefidab Roye" (SR) as "zinc" is translated to "Roye" in Persian. Therefore, it is assumed that the two samples containing zincite, are the proper natural mineral in comparison to the other eight samples. The extent of the application of zincite (ZnO) in cosmetic and hygienic products is well known²², therefore, it is concluded that zinc oxide can be the active major component in the SR sample, which is used as facial masks and anti acne agents in traditional Iranian medicine.

The samples which are sold under the same trademark name of "Sormeh or Kohl" such as S1 and S2 have basically different components. According to the results shown in Table-2, S1 contains PbS as the major component, but that of S2 sample is ZnO. Discrepancy in results for Sormeh or Kohl analysis was also observed in the collected samples, which were reported in other countries such as Oman and United Arab Emirates^{8,9}. The extent of application of this natural mineral used as cosmetic material in Middle East countries make it a necessity to control the products which are sold under this trademark.

Elemental analyses of the typical samples have been performed by ICP-MS, ICP-OES, XRF and AAS techniques. The results of quantitative analysis of the selected samples for toxic elements such as As, Sb, Bi, Pb, Cd, Hg, Al and Sn are shown in Table-3. All the elements are determined by ICP-MS method except for Al which is measured by ICP-OES. The results of these elements determined by XRF and AAS, also confirmed the results which are shown in Table-3.

Unfortunately, there is no certified reference standard for these natural minerals in current literature or when market. When consumers are exposed to the toxic elements of GA and BA, due to hair and skin exposure or orally consumed, this results in body fluid contamination. The exposure of the toxic elements GA and BA stems from using the following products: SR1, SR2, SG, SH, KD, GS1, GS2, MS, SHG, S1 and S2. Hence, the written threshold standards for these elements in literature should be considered for control of using these minerals.

Typical arsenic concentration in normal soils range from 1-40 µg/g. No quantitative studies have been performed on the dermal absorption of inorganic arsenic in human after exposure. Arsenic concentration in hair and skin is reported as 0.02-8.17 and 0.009-0.590 µg/g, respectively, based on examination of 1250 people without normal daily exposure to high levels of this element²¹. Therefore, GA and SHG samples,

Sample	As (µg/g)	Sb (µg/g)	Bi (µg/g)	Pb (µg/g)	Hg (µg/g)	Sn (µg/g)	Cd (µg/g)	Al (µg/g)
D.L.	0.5	0.1	0.1	0.2	0.05	0.2	0.1	10
SR1	21.4	4.4	<D.L.	522	0.4	10.7	8.3	291
SR2	4.1	<D.L.	1.5	1.6	<D.L.	<D.L.	0.3	252
SG	8.1	4.3	0.2	4	<D.L.	0.3	620	610
SH	14.6	0.5	<D.L.	5.1	<D.L.	<D.L.	0.4	1880
KD	20	0.7	<D.L.	3.6	1580	0.2	0.6	1590
GA	2640	68.7	0.2	746	5.2	2.6	0.5	65700
GS1	10.1	1.6	0.2	11.6	<D.L.	1.9	0.2	77100
GS2	2.5	0.6	<D.L.	9	<D.L.	2.2	0.4	71300
MS	24	1900	153	66600	0.08	388	3.9	1250
SHG	49.1	3.5	<D.L.	65.1	78200	<D.L.	<D.L.	135
S1	1	299	<D.L.	69100	0.09	<D.L.	3	60
S2	1.5	1.4	<D.L.	21.2	0.07	<D.L.	11.4	33
BA	5.4	2.8	<D.L.	564	0.09	0.7	0.9	9173

which contain 2640.0 and 49.1 $\mu\text{g/g}$ of As, respectively, show high levels of this element in comparison to the normal soils. The maximum permissible arsenic level in drinking water in the United States is set at 0.05 $\mu\text{g/g}^{20}$. Thus, an orally consumed GA sample is over the threshold permitted for this toxic element.

Antimony exists in the earth's crust at a concentration of about 0.2-0.5 $\mu\text{g/g}$ dry weight. A Japanese autopsy study examined the level of antimony in tissues in unexposed humans. The mean body burden was 0.7 mg, with the highest level of antimony found in skin and hair. The Japanese autopsy study has showed that skin contains 0.1 $\mu\text{g/g}$ wet weight²¹. Hence, GA, MS and S1 samples, which contain 68.7, 1900 and 299 $\mu\text{g/g}$ of Sb, respectively, present high levels of this element.

Bismuth level in the normal soil is approximately 0.001 $\mu\text{g/g}$ and the total daily intake in food is approximately 5-20 μg^{21} . Furthermore the investigation indicates the significant skin absorption rates for this metal or, accumulation in tissues over an extended period of exposure. No quantitative information on skin penetration of Bi compounds is available at present²⁰. Bismuth concentration in the MS sample is 153 $\mu\text{g/g}$ which is over the allowable level in normal soil.

Inorganic lead can penetrate through the skin. The tolerable weekly intake of lead through food and drinking water is 0.025 $\mu\text{g/g}$ body weight reported by Joint FAD/WHO expert committee on food additives^{20,21}. The allowable concentration of lead occurring in adult human hair is 2-20 $\mu\text{g/g}^{20}$. The skin exposure may be due to the use of cosmetics (Koh or Surma). According to Iran's National Organization, the threshold for Pb toxic element in skin powder is 20 $\mu\text{g/g}$ for adults²⁷. Therefore, SR1, GA, MS, SHG, S1 and BA show high levels of this toxic element. The measured concentrations of Pb in these samples are 522.0, 746.0, 66600.0, 65.1, 69100.0 and 564.0 $\mu\text{g/g}$, respectively.

The cadmium concentration in normal soil is usually less than 1 $\mu\text{g/g}^{21}$. Penetration through dermal absorption is not a significant way of entry into the human body for cadmium compounds²⁰. Concentration range of Cd occurring in adult human hair is 0.4-1.0 $\mu\text{g/g}^{20}$. After a lifetime of exposure from food at an average intake of approximately 200 $\mu\text{g/day}$, renal effects have been observed at age 50²⁰. Therefore, there is no threat of Cd exposure by skin and orally consumption of these samples.

All forms of mercury are absorbed through biological membranes including mucosa and skin. The mercury concentration in adult human hair is 0.5-2.0 $\mu\text{g/g}$ and the lethal dose is approximately 1 g of mercuric salt²⁰. So according to the results shown in Table-3, KD and SHG samples, which contain 1580 and 78200 $\mu\text{g/g}$, respectively, can be harmful due to the high levels of mercury. It should be noted that Cinnabar, which is used as traditional remedy in Oman for Vitiligo (a dermal disease)²⁴, is the major constituent of SHG according to the results shown in Table-2. This sample is used as wound healing agent in traditional Iranian medicine. Exposure of this mineral with an open wound for example can be extremely harmful as all forms of mercury are absorbed through the skin.

The average natural concentration of tin in hair is ca. 0.05-0.40 $\mu\text{g/g}^{20}$. No quantitative data is available currently on the rate of skin absorption of any tin compounds in human, but oral consumption of 45 $\mu\text{g/g}$ of stannous chloride can cause

Vomiting and Diarrhea in Cats. In addition oral LD₅₀ of 775 $\mu\text{g/g}$ body weight for tin oxide in deer mice is reported²⁰. No harmful effects have been reported from skin contact with tin or inorganic salts of tin²⁰, however, therapeutic organotin compounds can penetrate through the skin and cause irritation and systematic effects²⁰. Hence, there is no harmful effect due to the presence of Sn in these selected minerals.

Conclusion

Consumers tend to use natural products as opposed to synthetic materials. Therefore, the identification of the constituent of these compounds and assessments for safety levels are necessary. In conclusion, the lack of systematic control and the lack of standardization on traditional Iranian drugs caused discrepancies in the drugs with the same trademark. Differing in the amount of active agents or inadequate amount present, as shown in present experiments using the tested minerals. The presence of toxic elements in these natural drugs should be investigated, else their usage could be more harmful than using synthetic compounds. The threshold level of toxic elements, the rate of absorption in human body, their distribution and their excretion should be further researched to ensure their use in traditional cosmetic and pharmaceutical minerals meet the efficacy as well as safety levels.

REFERENCES

1. L. Efraim and A. Zohar, *J. Ethnopharmacol.*, **82**, 131 (2002).
2. E. Lev and Y. Peri, *Harefuha*, **140**, 1109 (2001).
3. A. Pieroni, C.L. Quave and R.F. Santoro, *J. Ethnopharmacol.*, **95**, 373 (2004).
4. A. Pieroni, *J. Ethnopharmacol.*, **91**, 331 (2004).
5. X. Feng and Y. Wuming, *Pub. Med.*, **14**, 331 (1989).
6. H. Xu, K. Huang, Q. Gao and X. Han, *Pub. Med. Pharmacol. Res.*, **44**, 1 (2001).
7. N. Lekouch, A. Sedki and A. Nejmeddine, *Sci. Total Environ.*, **280**, 39 (2001).
8. A.D. Hardy, H. Sutherland and R. Vaishnav, *J. Ethnopharmacol.*, **80**, 137 (2002).
9. A.D. Hardy, R. Vaishnav and S.S.Z. Al Kharusi, *J. Ethnopharmacol.*, **60**, 223 (2002).
10. J.J. Chuu, S.H. Lui and S.Y. Lin Shiau, *Pub. Med. Proc. Nat. Sci. Council. Repub. Chin.*, **25**, 128 (2001).
11. S.C. Foo, C.H. Ngim, W.O. Phoon and J. Lee, *Sci. Total Environ.*, **72**, 113 (1988).
12. Translated by A. Sharafkandi, Ghanoon Dar Teb, Soroosh Press, Ave Sina, (In Persian), Iran (1987).
13. R. Jodieh, The Association of National Remnants, (In Persian), Iran (1951).
14. M.Z. Razi, Alhavi, Alhavi Pharmacy Institute, (In Persian), Iran (1990).
15. Khaje Nasir Adin Toosi, Pedigree of Ilkhani, (In Persian), Iran (1984).
16. Movafagh Adin Abomansoor, Alabnieh An Haghaeghe Aladviye, Tehran University, (In Persian), Iran (1967).
17. Nafisi Ali Akabar, Nafisi Dictionary, Khayam, (In Persian), Iran (1964).
18. F. Rouessac and A. Rouessac, Chemical Analysis Modern Instrumental Methods and Techniques, John Wiley (2001).
19. I.S. Krull, Trace Metal Analysis and Speciation, Elsevier, Amsterdam (1992).
20. R.H. Guy, J. Hostynek, R. Hinz and C. Lorence, Metals and the Skin Topical Effects and Systemic Absorption, Mercel Dekker (1999).
21. G.F. Nordberg, B. Fowler, M. Nordberg and L. Friberg, Hand Book of the Toxicology of Metals, AP (2005).
22. M. Vimaladevi, Text Book of Cosmetics, CBS (2005).
23. P.M. Steven and J.M. Nocerino, *Environ. Sci. Tech.*, **30**, 204 (1996).
24. C. Kilbride, J. Poole and T.I.R. Hutchings, *Environ. Poll.*, **143**, 16 (2006).
25. M.H. Ramsey, P.J. Potts, P.C. Webb, P. Watkins, J.S. Watson and B.J. Coles, *Chem. Geol.*, **124**, 1 (1995).
26. A.D. Hardy, H. Sutherland and R. Vaishnav, *J. Ethnopharmacol.*, **49**, 17 (1995).
27. Iran's National Standard, Characteristics of Adults Skin Powders, No. 1204.