STUDIES ON THE CHEMICAL COMPOSITION OF KOHL STONE BY X-RAY DIFFRACTOMETER

PERVAIZ HABIB ULLAH[1], ZAFAR ALAM MAHMOOD*[2] MOHAMMAD SUALEH[3] AND SMS ZOHA[2]

[1]22, Davis Road, Lahore, Pakistan
[2]Department of Pharmaceutics, University of Karachi, Karachi, Pakistan
[3]Department of Pharmacognosy, Federal Urdu University of Arts, Science & Technology, Gulshan-e-Iqbal Campus, Karachi, Pakistan

ABSTRACT

Use of Kohl (Surma) creates toxicity or protects eye, is one of the most controversial topic of modern medicines. However, modern researches show that kohl forms a thin film on the eye lens thus avoiding the direct contract of harmful UV radiation and glare of sun with lens. Black and shining particles of galena in kohl shield the eyes from glare and reflection of sun and thus protect them from harmful effect of UV radiation emerging from the sun. Based on these findings and other properties of kohl, it was decided to undertake this study to ascertain it's chemical composition and to correlate these properties scientifically. In the present study, kohl stone obtained from Madina (Saudi Arabia) was analyzed to ascertain it's chemical composition. The chemical analysis and X-ray diffractometer results obtained, showed that the main component of kohl stone is galena (PbS).

Keywords: Kohl, surma, galena (PbS), collyrium, x-ray diffraction, chemical composition of kohl.

INTRODUCTION

A number of scientific studies published during the last three decades show that lead sulphide from kohl is not associated with lead intoxication. Furthermore, these studies also support the view that lead is not absorbed through transcorneal route and thus should not be linked or blame for increased blood lead level and lead poisoning after it's application (Attenburrow *et al*., 1980, Sweha, 1982, Zaheer *et al*., 1991, Khalid *et al*., 1992, 1995, Khan *et al*., 1997, Jaffery, 2001, Monograph of Unani Medicine, 2003). Kohl had been used as an eye preparation, for the treatment and prophylaxis of eye diseases for centuries and also reported as cosmetic for the eyes in several texts of "Old Testament" (Kings II, 9:30; Jeremieh 4:30; Ezekiel 23:40) as well (Narada, 2000; David *et al.*, 2000). Among Muslims, use of Kohl is described as "Sunnah" in Abu Dawud Tib, 14; and Tirmidhi, Tib, 9 (Yursil, 2007). In Islam, kohl has great importance as an eye protector, both for *momin* (muslim men) and *mominat* (muslim women*)* because it's application to eyes is *sunnah,* an act done by Holy Prophet (Peace Be Upon Him) (Habibullah, 2006).

In an earlier review (Mahmood *et al*., 2009), kohl (surma) was defined as an eye preparation in ultra fine form of specially processed "Kohl Stone" (galena) incorporated with some other therapeutically active ingredients from marine, mineral and herbal origin for the protection and treatment of various eye ailments. The other ingredients blended to develop special kohl formulation may include kohl adjuvant, (e.g., zinc oxide, silver leaves, gold leaves), gemstone (e.g., ruby and emerald etc). Marine coelenterates (e.g. coral, coral reef and pearls etc.) and herbs (e.g., neem, saffron, mumeera and fennel extract etc.). The physical characteristics of kohl stone (galena) used in the present study is presented in table 1.

In an earlier review (Mahmood *et al*., 2009), the historical of eyeliner was reported. The record shows use of eyeliner in ancient Near East and Egypt (Keville and Green, 1995; Cohen, 1999). Further, kohl also been reported as a symbol of status in the lives of Egyptians. Based on this, kohl was reported to be an essential commodity in the lives of Egyptians and even applied before mummification. This indicates that the Egyptian hygiene was based on sound medicinal, therapeutic and spiritual reasons (Pauline, 2007). Accordingly recipes for Kohl were passed from one generation to other down through centuries, i.e., Old Kingdom (Height of Classical Egyptian Culture "The Age of Pyramids," 2900-2240 BC) to the encaustic portraits of the Roman Occupation (Susan, 2003; Devine, 2006). During Egyptian rule, galena (lead sulphide) was familiar under the name of "Mestem" or "Stim", while this word was identical to Greek word, "Stimmi" or "Stibi" and to Latin word "Stibium", meaning Antimony (Fischer, 1894). Gelena is reported to be found near the "Red Sea", "Aswan", and in "Eastern Desert" at Gebel-el-Zeit, while malachite is found in "Sinai" and the "Eastern Desert" (Pauline, 2007). These were carried across the trade routes into Egypt (North Africa) and Middle East (Catherine, 2005).

**Corresponding author*: e-mail: zamahmood@hotmail.com

Table 1: Physical Characteristics of Kohl stone identified as galena

Color	Lead to silver gray sometimes with a bluish tint
Luster	Metallic to dull in weathered faces.
Transparency	Crystals are opaque
Crystal system	Isometric; 4/m bar 3 2/m
Crystal habits	Cube, octahedron and combinations of the two. Spinal twinning is possible forming flattened crystals. Also massive and granular.
Cleavage	Perfect in four directions forming cubes
Fracture	Uneven and rarely seen because of the perfect cleavage.
Hardness	2.5+
Specific gravity	7.5 (heavy even for metallic minerals)
Streak	Lead gray
Associated minerals	Calcite, dolomite, sphalerite pyrite and other sulfide minerals also lead oxidation minerals such as cerussite and anglesite
Other characteristics	Brighter metallic luster on cleavage surfaces than on crystal faces
Notable occurrences	Texas-Oklahoma-Missouri, USA, Germany, Peru, Mexico, Isfahan (Iran), Morroco, Zambia, and England.

The traditional Ophthalmologists have argued that applying kohl at the time while going to bed (also a sunnah) promotes vision (Habibullah, 2006). The powder remains in pores of eyelids for long time and being germicidal, kills germs & removes sludge which collects on the sides of eyes during constant blinking of eyelids, while in the day time kohl forms a fine but porous layer on eye lens and protects it from the UV radiation and other harmful radiation to come in direct contact with lens, which are otherwise highly detrimental. Similarly some harmful radiation is absorbed by particles of kohl and those affected particles are removed during blinking. Modern researches show that kohl forms a thin film on the eye lens thus avoiding the direct contract of harmful UV radiation and glare of sun with lens. Black and shining particles of galena in kohl shield the eyes from glare and reflection of sun and thus protect them from harmful effect of UV radiation emerging from the sun, reflected dust of desert and snow of the mountains. Further, some experiment show PbS thin films have higher absorption, lower transmittance in UV light band. Other ingredients present in the kohl or added, such as zinc oxide, have an excellent natural sun block property which enhances protective capacity of kohl against glare of sun (Mitchnick *et al.*, 1999).

Ophthalmology also received its share of encouragement from the Holy Quran, which stimulated research in this field and consequently, many Muslim scientists contributed in finding and establishing remedies for many illnesses of the eyes and improving eyesight. This inspiration produced great ophthalmologists in Islamic civilization, such as Abu Ruh Muhammad al-Jurani called, Zarridnast (The Golden Hand), Hunayn Ibn Ishaq and Ali Ibn Isa (Habibullah, 2006).

The objectives of the present study was to analyze and report the chemical composition of kohl stone and correlate the findings with it's established properties and action. The kohl stone was analyzed using X-ray diffractometer.

MATERIALS AND METHODS

Chemical analysis

Chemical analysis of kohl stone (Galena) was done by the method described in Vogel's - textbook of quantitative inorganic analysis (Bassett *et al*., 1985).

X-Ray Diffractometer

The sample of kohl stone was ground and studied by X-Ray Diffractometer BRUKER D8 Discover – Germany. This diffractometer has several accessories that allow it to perform different types of analysis: textures, residual stress, X-ray reflectometry, etc. (fig. 1).

The D8 Discover Diffractometer uses a small X-ray beam (typically 50-500 μm), allowing point analyses of a selected area in the sample of a few tens of micrometer in diameter. Among other benefits, it improves limit detections of minor mineral phases scattered within the sample (Carolina, 2009).

RESULTS

Chemical analysis

Results of chemical analysis are given in table 1. The main constituents estimated are Lead (85.51%), Sulphur (11.43%) and antimony (2.06%). While Carbon is also detected in small quantity (0.689%). Since, lead and antimony are found in nature in combination with sulphur, therefore, lead detected in the test sample in the form of PbS as major and antimony as SbS as minor component, supports the earlier studies that kohl stone by nature is galena. Further, the physico-chemical analysis presented in tables 1 and 2 respectively, also strengthens

this view that the main mineral present in kohl stone is galena.

Table 2: Results of the Chemical Analysis of Kohl stone from Madina (Saudi Arabia) and Surma sold on the street

Element		Kohl stone	Surma from sold on the street under brand name
Lead	(Pb)	85.51%	5.974%
Sulphur	(S)	11.43	0.054
Antimony	(Sb)	2.06	ND
Carbon	(C)	0.689	0.152
Iron	(Fe)	0.02	0.094
Chromium	(Cr)	0.002	ND
Copper	(Cu)	ND	ND
Nickel	(Ni)	ND	ND
Zinc	(Zn)	ND	ND
Magnesium	(Mg)	ND	0.01
Calcium	(Ca)	ND	0.02
Sodium	(Na)	ND	ND
Potassium	(K)	ND	ND

ND = Not detected
Chemical analysis: Performed at Mineral Processing Research Centre, Pakistan Council of Scientific & Industrial Research, Lahore, Pakistan.

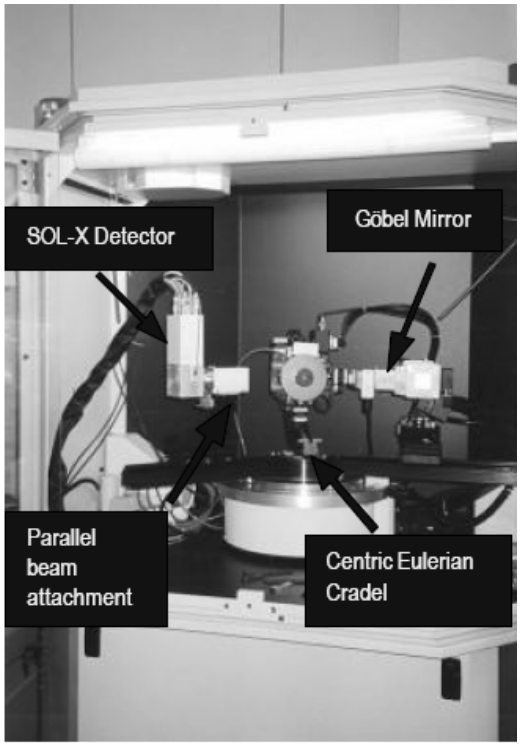

Fig. 1: X-ray Diffractometer Bruker D8 Discover
Parameters:
Scan speed – 3 degree / min, Increment – 0.1 degree
Temperature – 25°C Scan range – 8 -80
Tube voltage – 40 KV Tube current – 40 mA
Source – Cu Kα = 1.6 A°

For comparison, a sample of surma powder sold on the street, was also analyzed by same method. The results are given in table 1. As per chemical analysis, it contains very little amount of lead (5.974%) as compared to the amount of lead (85.51%) present in the kohl stone. Similarly S, Fe and C are also found in very little amount as compared to that present in kohl stone sample. It indicates that surma powder analyzed in the present study is made by mixing very little kohl stone powder with other materials. These are volatile materials as observed during chemical analysis.

X-ray Diffractometer

Results of the X-ray diffraction analysis are shown in fig. 2. The results showed the presence of lead and sulphur in large quantity, carbon and iron in minor quantity, tin in traces, antimony is either absent or in traces while copper is not detected. The lead, the form of PbS confirms that "galena is the main mineral present in kohl stone". Results of x-ray diffraction are in accordance with the results of chemical analysis.

Interpretation 2 theta – scale Lin counts curve

X-ray diffractometer works on Braggs law

$$n\lambda = 2d \sin\theta$$

where

n = 1
λ - wavelength
d = atomic spacing
θ = angle

2θ - linear count curve of apparatus shows that most of the peaks appearing on the graph are identical with PbS peaks. It indicates that PbS is the main constituent present in the sample, carbon and iron are found minor quantity, tin in traces while antimony is absent. In caption of fig. 2 on the left side are lib files which are consulted for comparison and confirmation of the particulars of elements present in the sample. The particulars of each file are mentioned in the front of each file.

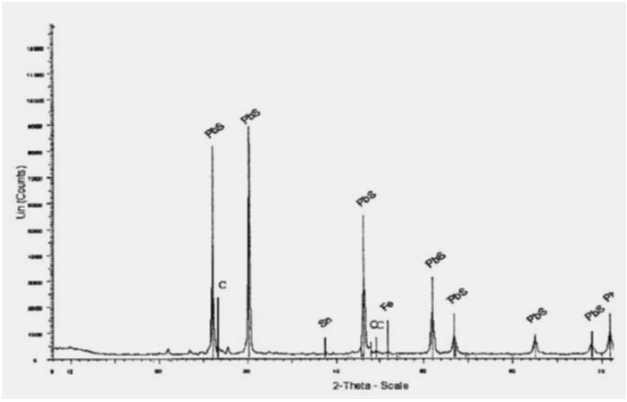

Fig. 2: X-ray diffractometer analysis.

DISCUSSION

In past half century, number of articles have appeared on the retrospect and prospect of use of kohl/surma as eye liner. Some researchers and authors reports have estimated high quantity of "galena" in kohl and have proposed that use of kohl/surma as eye cosmetic or for the treatment of eye disease, particularly in children, may be injurious because it increases blood lead level. Contrarily work of other scientists set aside any such idea of interlink and inter dependency of application of surma and increase in blood lead level. They argue, almost every human civilizations used it to keep the eyes cool and clean and for the prevention and treatment of eye diseases such as, blepharitis, trachoma and cataracts. Further, kohl is also reported for improvement of vision, strengthening and keeping the eyes healthier (Awan, 1956; Levey and Al-Khaledy, 1967; Zaheer *et al*., 1981; Khan *et al*., 1997 and Monographs of Unani Medicine, 2003).

A number of research studies published earlier (Aslam *et al*., 1980 and Healy *et al*., 1982) indicated that transcorneal route is not the primary route for lead absorption from kohl (surma). However, these authors also indicated the possibility of some of the material being washed into the naso-lachrymal duct on tear formation after application of kohl should not be excluded in children. It was further elaborated by these authors that the principal route for ingestion in man appears to be orally, via the fingers. The authors have the opinion that when kohl is applied to children, it may transfer from their fingers to mouth and finally been absorbed through ingestion as children usually rub or wipe their eyes with their fingers which provides a way for the lead present in the product to ultimately reach to stomach where absorption takes place, but this is very unlikely among adults. However, according to others (Zaheer *et al*., 1981; Khalid *et al*., 1992, 1995 and Mahmood *et al*., 2009) such a possibility has been suggested but has not been conclusively established.

One of the benefit of applying kohl, apart from it's therapeutic effect is to block and counter act against the UVB radiation coming out the sun. The UVB have the right amount of energy to break the bonds of amino acids in the proteins of the eye lens. The lens of the eye is very sensitive to these radiations. The galena based kohl forms very thin film on the surface which diffracts the harmful UV radiations and protect it from degeneration. This idea was practically demonstrated by a number of researchers (Nair *et al*., 1992 and Pop *et al*., 1997). This provides reasonable justification to conclude that the black and shiny particles of galena or lead sulphide shields the eyes from the glare and reflection of sun and thus protects the eyes from the harmful effect of UV rays emerging from the sun and dust of the desert.

This concept was further elaborated and demonstrated by a group of workers in China through a comprehensive study (Li-Yun *et al*., 2008). For demonstration, the authors used a thin film of lead sulphide prepared on "Indium Tin Oxide" (ITO) and reported the ultraviolet (UV) absorption spectra of this film. The spectra showed that lead sulphide thin films had higher absorption and lower transmittance in UV light band which further increases with the increased deposition voltage. Lead sulphide is an important direct narrow-gap semiconductor material with an energy band gap of -0.4 eV at 300K and a relatively large excitation Bohr radius of 18nm. If we analyze all these data and findings then it give some good scientific basis and reasonable justification to conclude that kohl formulation prepared from galena does have a natural protective effect against glare of the sun when applied in the eyes and thus support the earlier claims and uses as reported else where. The scientific correlation relating to addition of other ingredients of kohl was also investigated. It was observed that zinc oxide, probably sued in kohl because of its powerful natural sun block property (Mitchnick *et al*., 1999) which may possibly enhance the protective capacity of galena against the glare of the sun. While Naeem (*Azadirachta indica*) may be added because of its well known astringent and antibacterial properties (Almas, 1999 and Linda, 2001). Similarly, silver leaf, *neem* also possesses anti-viral activity as well (Badam *et al*., 1999).

Findings of the present paper and data provide some good and reasonable scientific basis and justification to conclude that kohl containing PbS as major ingredient has natural protective capacity against the glare of the sun. It protect eye from many diseases such as cataract. Among Muslim, staining eyes with kohl is described as sunnah. Even in 21st century, the modern findings make it evident that an act of Holy Prophet (Peace be upon Him) is always for the betterment and blessing of human being.

ACKNOWLEDGEMENTS

Authors are grateful to Mrs. Sumra Naeem CSO and Mrs. Uzma Zafar, SSO, MPRC, PCSIR Labs. Complex Lahore, for chemical analysis and Mr. Farooq Bashir, Equipment Maintenance Engineer of Central Research Lab, Lahore College for Women University, Lahore, for X-ray diffraction of kohl. Special thanks are for Geologist, Ch. Rahseed Ahmad, Director Geological Survey of Pakistan, Lahore for valuable discussion on galena and Principal, College of Pharmacy, Punjab University.

REFERENCES

Almas K (1999). The antimicrobial effects of extract of *Azadirachta indica* (neem) and *Salvadora persica* (arak) chewing sticks. *Indian J. Dent. Res.,* **10**(1): 23-26.

Aslam M, Healy MA, Davis SS and Ali AR (1980). Surma and blood lead in children. *The Lancet,* **22**; **1**(8169): 658-659.

Attenburrow AA, Campbell S, Logan RW and Goel KM (1980). Surma and blood lead levels in Asian children in Glasgow. *The Lancet,* **9**; **1**(8163): 323.

Awan MH (1956). Kitab al-Mufradat, 2nd edition, Sheikh Ghulam Ali & Sons, Lahore, p.552.

Badam L, Joshi SP and Bedekar SS (1999). *In vitro* antiviral activity of neem (Azadirachta indica A. Juss) leaf extract against group B coxsackieviruses. *J Commun Dis.,* **31**(2): 79-90.

Carolina C, Isabel G, Julia RP, Giuseppe C, and Alejandro RN. (2009). Innovative analytical methodology combining micro-x-ray diffraction, scanning electron microscopy-based mineral maps, and diffuse reflectance infrared fourier transform spectroscopy to characterize archeological artifacts. *Analytical Chemistry,* **81**(2): 604-611.

Catherine CJ (2005). Kohl as traditional women's adornment in North Africa and Middle East, *Introduction to Harquus: Part 2: Kohl,* pp.1-9.

Cohen M (1999). Cosmetics and perfumes, Egypt, 10,000 BCE.

Devine D (2006). Kohl: Drawing the line. *Habbibi-Middleeastern Music & Dance Journal,* **21**(2): 1-6.

Fischer X (1892). The Ancient Egyptian Eye Preparation, *Arch Pham,* **230**: 9.

Habibullah P (2006): The Sacred Paraphernalia, belongings of Holyphrophet (Peace Be Upon Him), Educational Press, Pakistan Chowk, Karachi, pp.191-194.

Healy MA, Harrison PG, Aslam M, Davis SS and Wilson CG (1982). Lead Sulphide and traditional preparation: Routes for ingestion, and solubility and reaction in gastric fluid. *J. Clin. Hosp. Pharm.,* **7**: 169-173.

Jaffery FN (2001). Current status of lead in India. Report released on World Environment Day, UNEP, pp.1-42.

Keville K and Green M (1995). *A History of fragrance*. The Crossing Press, pp.1-156.

Khalid Q, Ismat M, Sultana L and Qadeeruddin M (1995). Studies on the blood lead levels after application of surma to eyes in children and adults. *Pak. J. Pharmacol.,* **12**(2): 37-41.

Khalid Q, Maryam M, Qadeeruddin M, Rahman Z, Qureshi IH and Rizvi SSH (1992). Scientific investigation on surma. *Pak. J. Sci. Ind. Res.,* **35**(1-2): 30-31.

Khan AH, Khan A, Ghani F and Khurshid M (2001). Low-level lead exposure and blood lead levels in children: a cross-sectional survey. *Arch. Environ. Health,* **56**(6): 501-505.

Levey M and Al-Khaledy N (1967). The Medical Formulary of Al-Samarquandi. Published by University of Pennsylvania Press, Pennsylvania, p.136.

Linda SR (2001). Mosby's Handbook of Herbs & Natural Supplements, Mosbey, pp.616-618.

Li-Yun C, Wen H, Jian-Feng H and Jian-Peng W (2008). Influence of deposition voltage on properties of lead sulfide thin film. *American Ceramic Society Bulletin,* **87**(6): 9101-9104.

Mahmood ZA, Zoha SMS, Usmanghani K, Hasan MM, Ali O, Jhan S, Saeed A, Zahid R and Zubair M (2009). Kohl (Surma): Retrospect and Prospect. *Pak. J. Pharm. Sci*., **22**(1): 107-122.

Mitchnick MA, Fairhurst D and Pinnell SR (1999). Microfine zinc oxide (Z-Cote) as a photostable UVA/UVB sunblock agent. *J. American Academy of Dermatology,* **40**: 85-90.

Monographs of Unani Medicine (2003). Surma. Hamdard Foundation Pakistan and DC & TMD, National Institute of Health, Islamabad, Pakistan, pp.1-664.

Nair PK, Gomezdaza O and Nair MTS (1992). Metal sulphide thin film photography with lead sulphide thin film. *Adv. Mater. Opt. Electron.,* **1**: 139.

Narada T (2000). Ancient cosmetics and fragrance. Egypt, Greece and Rome. Cyonic Nemeton, pp.1-6.

Pauline WT (2007). Ancient Egyptian costume history, Part 6- Ancient Egyptian make up and cosmetics. www.fashion-era.com.

Pop I, Nascu C and Lonescu V (1997). Structural and optical properties of PbS thin films obtained by chemical deposition. *Thin Solid Films,* **307**: 240-244.

Susan JH (2003). Ancient African Civilizations To ca. 1500 – Text supplement and study guide for history/PAS 393, revised edition, pp.1-63.

Sweha F (1982). Kohl along history in medicine and cosmetics. *Hist. Sci. Med.,* **17**(2): 182-183.