

# Chemical and toxicological studies on different brands of Asmad (Antimony sulphide) available in Pakistan and Saudi Arabia

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**Abstract:** Eye is the most beautiful, important and sensitive organ of human body. It is not only linked with visionary complex optical system also has the ability to differentiate among the millions of colors. The apparent human personality is also associated with it. Asmad/Antimony Sulfide/Kohl/Surma powder is one of the eye preparation has been used since ancient time. There are several aesthetic and ophthalmic preparations available for human eye and they have closed association between the aesthetic and medicinal significance such as cleansing, soothing, strengthening and anti-infectious actions along with beautifying purpose of eye. The main objective of present research is to provide scientific findings regarding beneficial and toxic effects of Asmad products available in market for the frequent users. The chemical and toxicological investigations on ten selected famous brands of Pakistan samples (PHS1, PHS2, PLS, PMS and PSS) and Saudi Arabia samples (SBS, SAS, SHS, SMS and STS) were carried out through advanced and sophisticated technique Scanning Electron Microscope (SEM) linked with Energy Dispersive X-ray Spectroscopy (EDS) which is used to determine the presence different percentages of organic and inorganic elements in all the brands of Pakistani and Saudi Arabian samples. The safety and toxicity depends on the Na, Mg, Ca, K, Al, Cu, Zn, Fe, Bi, Si, O, C, S and Pb percentages respectively of the Asmad products.

**Keywords:** Asmad/antimony sulfide, toxicity, SEM, EDS, organic and inorganic elements.

## INTRODUCTION

Eye preparations are available in different dosage forms including Eye drops, lotions, eye shadow, eye liner, mascara, cleansers and powders cake etc. Eye cosmetics are part of everyday life around many parts of the world. In western society, women and men judge eye cosmetic use as a factor in facial attractiveness (Mulhern *et al.*, 2003). Asmad is one of the eye preparation well documented in Islamic and other literatures. Asmad/Kohl is a traditional powder-like mixture, such as powdered antimony sulfide, used as cosmetic eyeliner and to treat eye diseases in many Middle and Far East countries (Al-Hawi, 1986).

Asmad is an eye formulation of ultra-fine and homogenized powder contains mixture of minerals or elements. It is the most popular eye product reported in almost every human civilizations used to keep the eyes cool and clean and for the prevention and treatment of eye diseases such as, blepharitis, trachoma, chalazion, pterygium, cataract, conjunctivitis, ectropion, as well as for the prevention of recurrence of trichiasis (Sweha, 1982). Antimony (III) Sulfide,  $Sb_2S_3$ , was recognized in predynastic Egypt as an eye cosmetic (kohl) as early as about 3100 BC, when the cosmetic palette was invented (Shortland, 2006).

There are several scientific debates between two schools of thoughts for the Lead (Pb) toxic and beneficial effects. First thought believes that Lead either organic or inorganic both are harmful and toxic substance hence it should not be the part of ophthalmic preparation while other believes that only organic lead are responsible for toxicity while inorganic lead are not toxic and has been using since long back because of its biomedical importance.

Asmad benefits from Islamic prospects are well documented, Abdullah Ibn Umar narrates that the Prophet (P.B.U.H) said, "You should use Kohl for it improves the eyesight and makes the eyelashes grow" (Hasan, 3495). Ibnul Qaiyum also narrated that Prophet (P.B.U.H) said, "Ithmid is the best type of Kohl used for the eye, especially for old people whose eyesight has weakened". (Eng trans. Medicine of the Prophet by Imam Ibnul Qaiyum, p.251). Asmad has also been used in Asian, African and Middle East countries as a cosmetic for a long time. In addition, mothers would apply kohl to their infants' eyes soon after birth. Some did this to "strengthen the child's eyes", and others believed it could prevent the child from being cursed by the evil eye (Hardy *et al.*, 2004).

Asmad has been used for long time because of several reasons including eye cleansing, strengthening, brightening and for the resistance to possible cause of infections. Asmad several studies (Zaheer *et al.*, 1991;

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Khan *et al.*, 1997; Awan, 1956; Levey and Al-Khaledy, 1967) show that it improves the vision, strength and keeps the eye healthier. Some Asmad preparations contains galena or lead sulphide as major constituents produce beneficial effect related to eye protection by providing shield to eye through reflection of sun light and thus protects eyes from harmful effect of UV rays emerging from the sun and dust of the desert (Cohen, 1999; Heather, 1981; Kathy, 2001).

## **MATERIALS AND METHODS**

Asmad (Antimony Sulfide) 10 different brands samples were collected from local market of Pakistan and Saudi Arab regions. These ten samples were named as PHS1, PHS2, PLS, PMS, PSS, SBS, SAS, SHS, SMS and STS. Five samples PHS1, PHS2, PLS, PMS and PSS picked from Karachi, Pakistan while other five samples SBS, SAS, SHS, SMS and STS picked from Jeddah, Saudi Arabia. The sample coding abbreviation, first word stands for country name, second word represents brand name and third word represents surma (Asmad common name in Pakistan and other Asian countries). Analysis of all these samples was performed in the Centralized Science Laboratories, University of Karachi, Pakistan. An analytical protocol, qualitative and quantitative investigation was carried on Scanning Electron Microscope (SEM) with Energy Dispersive X-ray Spectroscopy. These samples were coated with gold up to 300°A using quick auto coater model # JFC-1500 from Jeol, Japan. The samples were then placed in Scanning Electron Microscope model # JSM 6380A from Jeol, Japan. Accelerating voltage were kept 20kV, spot size 40 and working distance from 20um for each sample to determine the presence of elements. The Scanning Electron Microscope technique uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure. The technique determines sample Qualitative and Quantitative details.

## **RESULTS**

The Qualitative analysis revealed external morphology of subjected research samples. The displayed scanning images of all samples found different from each other which indicating that each sample have entirely different physical appearance with respect to the morphology/ texture and crystalline structure. However, Quantitative analysis confirmed the presence of different elements concentration in all sample brands.

## **DISCUSSION**

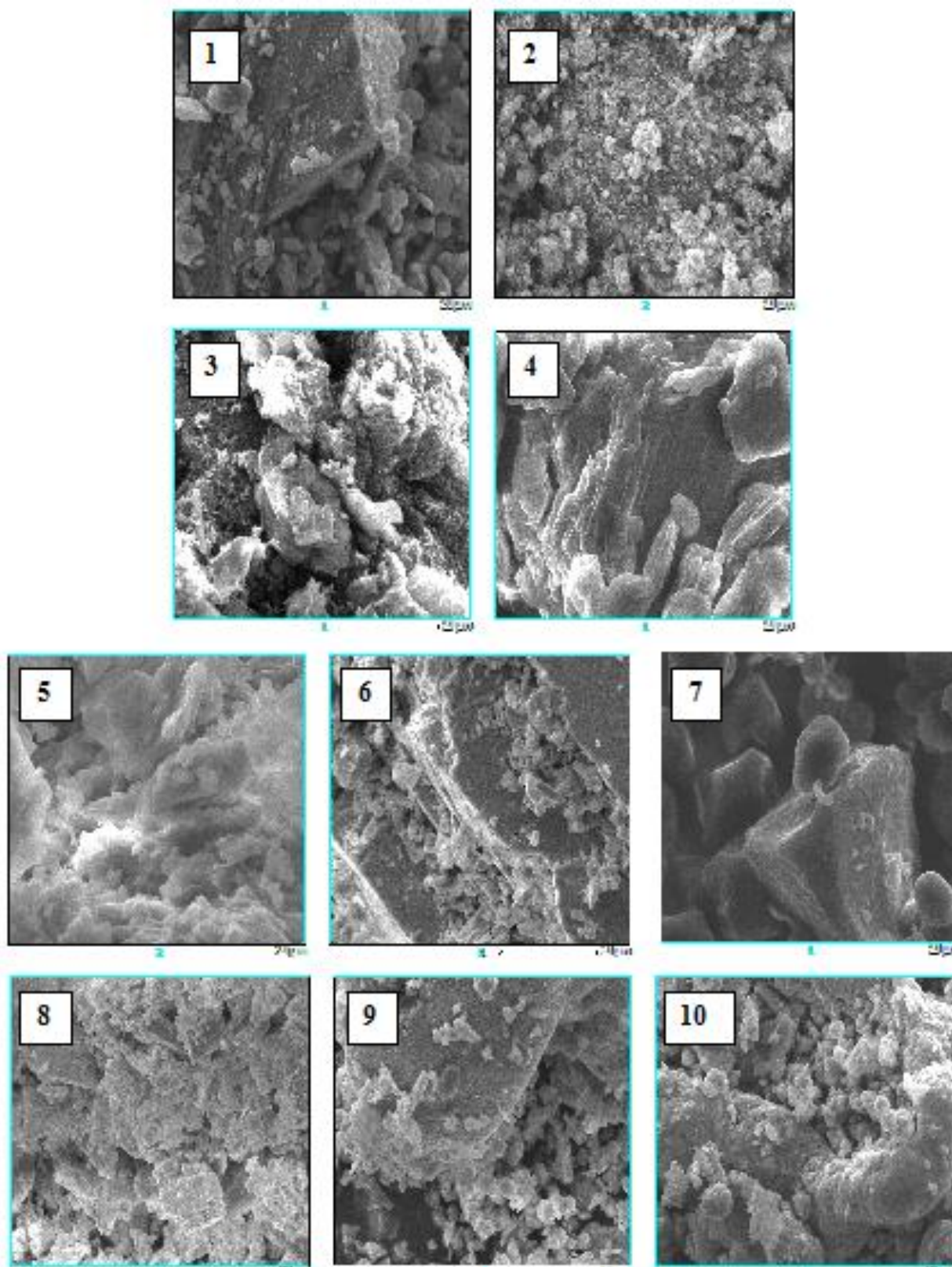
The eye is sensitive and precious part of human body. The human eye consist of rods and cones, rods provides

scotopic vision which useful in low light and cones provide photopic vision which useful in bright light. It is estimated that our photopic vision can distinguish about 10 million colours (Judd and Wyszecki, 1975). There are different human eyes preparations available having cosmetic and therapeutic values. Asmad/ Antimony sulphide is one of the famous product available in Asian and Middle East countries and being used since long ago for eye cleansing, strengthening, brightening and improve the vision.

In Pakistan and Saudi Arabia, the use of Asmad is frequent in healthy eyes because of Islamic and historical importance. Pilgrims going to Saudi Arabia from Pakistan and other countries for performing Hajj or Umrah, while returning they are bringing goods along with Asmad (Surma) as Tabarrukat or gift. The Asmad manufactured by Saudi Arabia are very famous and well known from the spiritual and Islamic heritage aspects.

The current research topic was selected because Asmad formulation contains different elements in ultra-fine powder form and applying directly on the human eye which may cause harmful effects. The aim of this study is to give valuable information or knowledge to Asmad frequent users related to toxic and beneficial effects through detail scientific investigation findings followed by chemical and toxicological studies.

The chemical composition investigation revealed that Pakistan and Saudi Arabia samples contain multiple elements which are essential for human bodies and play key role for different physiological system. The sample belonging to Pakistan contains C, O and Ca as major elements. In addition Na, Cu, Zn, Pb, Mg, Si, Bi, S and Al observed in minor quantities. In contrast, the samples of Saudi Arab contains C, O, S, Pb and Fe are as major elements, however, Zn, Cu, Al and Si also detected in minor quantities through EDS analytical technique. The detected few of these elements like Fe, Zn and Cu play vital role in ophthalmic system. The intraocular fluid (aqueous and vitreous humour) and lens concentration of Fe increased significantly after ocular inflammation (Mc Gahan, 1992). Copper is responsible to increase the sharpness of vision through reducing thin layer of skin in cataract (Siddiqui *et al.*, 2003). However Zn plays an important role in the metabolism of the retina and the lens of the eye (Karcioglu, 1982). Although, samples of both countries contain essential elements for eye functioning including strengthening, brightening and soothing effects. The toxicological investigation was focused on Lead (Pb) amount or percentage present in the samples of both countries. The study findings confirmed that three Saudi samples (SHS, SBS and SMS) contain Pb in high amount. In contrast only one sample of Pakistan i.e. PHS2 had Pb in less amounts.



**Fig. 1:** SEM images displaying for Pakistan and Saudi Arabia Asmad samples. (1) represents sample PHS1, (2) sample PHS2, (3) sample PLS, (4) sample PMS, (5) sample PSS, (6) sample SBS, (7) sample SAS, (8) sample SHS, (9) sample SMS and (10) sample STS.

**Table 1:** The quantitative elemental compositions of Pakistan and Saudi Arab samples. Quantitative analysis provides detail and accurate information about the distribution of elements in each sample. These elements are essential for human

Sample ID	Elements Percentage (%age) in samples													
	Al	Bi	C	Ca	Cu	Fe	K	Mg	Na	O	Pb	S	Si	Zn
PHS1	1.91	-	17.71	25.02	-	-	-	1.08	2.44	47.93	-	0.52	3.41	-
PHS2	0.25	3.39	51.26	-	-	-	-	-	-	4.34	33.22	6.21	-	1.33
PLS	-	-	66.04	-	-	-	-	-	-	32.96	-	-	-	0.99
PMS	0.18	-	28.13	-	-	-	-	-	0.38	71.32	-	-	-	-
PSS	-	-	-	2.68	-	-	0.92	-	1.29	95.12	-	-	-	-
SBS	1.33	-	20.57	-	2.26	-	-	-	-	3.20	60.08	10.02	-	2.54
SAS	1.46	-	55.89	-	-	-	-	-	-	40.44	-	2.22	-	-
SHS	0.72	-	11.49	-	-	-	-	-	-	9.60	67.70	10.49	-	-
SMS	0.34	-	12.26	-	1.90	45.35	-	-	-	20.61	16.48	2.24	0.82	-
STS	-	-	15.09	-	-	58.23	-	-	-	25.63	-	-	1.06	-

Where Al=Aluminium, Bi=Bismuth, C=Carbon, Ca=Calcium, Cu=Copper, Fe= Iron, K=Potassium, Mg=Magnesium, Na=Sodium, O=Oxygen, Pb=Lead, S=Sulphur, Si=Silicon, Zn=Zinc.

**Table 2:** Shows the presence of Lead (Pb) concentration (mass percentage) in samples. The study revealed that only one Pakistani sample i.e. PHS2 observed with Lead (Pb), in comparison, three brands of Saudi Arabia i.e. SBS, SHS and SMS noted with Lead (Pb) in higher level.

Sample No.	Sample Name	Samples Pb Concentration in Percentage (%age)
Sample No.1	PHS1	-
Sample No.2	PHS2	33.22 %
Sample No.3	PLS	-
Sample No.4	PMS	-
Sample No.5	PSS	-
Sample No.6	SBS	60.08 %
Sample No.7	SAS	-
Sample No.8	SHS	67.70 %
Sample No.9	SMS	16.48 %
Sample No.10	STS	-

Over the last 20 years, kohl has gained a bad reputation, due to its high content of lead (Warley *et al.*, 1968; Ali *et al.*, 1978). But the later studies confirmed that Lead toxicity is associated while it administered orally. The study (Healy *et al.*, 1982; Aslam *et al.*, 1980) confirmed that the primary route for lead absorption is not trans-corneal transport while applied on human eyes. So the Lead absorbed through semi-external rout could not be responsible to reach Lead in blood stream because the probability of absorption from trans-corneal or semi-external rout is rare and negligible.

The previous chemical composition study also confirmed that many Asmad products of modern period contain Pb in huge amount i.e. above the recommended limit set by the Regulatory Authorities. Pb toxicity and poisonous effects are well documented in many literatures. The study (Mahmood *et al.*, 2009) has claimed that the use of

Kohl/ Asmad is safe because galena or Lead sulphide is not reported to cause toxic injury. The Food and Drug Administration (FDA) has recommended safe daily diet Pb (Lead) intakes 75 micrograms (mcg) for adult, 25 mcg for pregnant women, 15 mcg for children age 7 or up and 6 mcg for children under age of 6 years. FDA estimated safety level of Pb amount known to cause health problem is 750 micrograms (mcg) for adult, 250 mcg for pregnant women, 150 mcg for children above 7 years and 60 mcg for children under 6 years. (Food and Drug Administration, 2010). For cosmetic products FDA recommends Pb limit 10ppm or less (FDA Guidance, 2016).

The precaution of Asmad include that it should be used only by the health eyes and not by the infectious and injured eyes which could cause the harmful effect. The eye liner stick use for the application on eyes must be handled properly to avoid any contamination. However, sample special container with narrow neck bottle gives protection to the sample by avoiding the exposure from external environment.

## CONCLUSION

Asmad (Antimony Sulfide) samples contain multiple elements in the composition which are essential for human body and play important role in different physiological system. The subjected samples after detail chemical and toxicological investigation assume that Pakistani samples can be considered safer as compared to Saudi Arabian samples because most of the Saudi sample brands noted with Lead as compare to Pakistani samples. Moreover, the Pb level identified in Saudi samples almost double as compare to Pakistani samples. Lead amount below the recommended limit is safe and not harmful to the human eyes. The past study also confirmed that Asmad application through eye is not the cause for toxicity because the trans-corneal transport is not the

primary route for the absorption of lead which indicates that Asmad is not responsible for increase concentration of lead in blood stream. Hence the absorbance of Pb through semi external or trans-corneal transport is almost negligible and there is rare possibility for producing any harmful effect. In addition, the manufacturers should also follow the incorporation of Pb concentration in Asmad formulation according to defined regulatory limit to minimize the toxic effects associated with Lead. Prior to apply as cosmetic or medical purpose sample should be analysed properly according to the standard protocol (ultra-fine particle size, homogenized and free from contaminants) for the safeguard. The research findings prove the chemical composition and safe use of Asmad as cosmetic and therapeutic agent for healthy human eyes without causing any serious consequences.

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