



## PHARMACEUTICAL STANDARDIZATION OF *SHILA SINDOORA*: AN AYURVEDIC HERBO- MINERAL FORMULATION

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### ABSTRACT

**Background:** *Kupipakwa rasayana* is the most popular and advance preparation in Ayurveda containing mercury, sulphur and arsenic compounds. In this process, *Parada* is heated along with *Gandhaka* and other metals and minerals resulting in a very intimate bondage which may help to exhibit superior qualities compared to other formulations. *Shila Sindoor* is indicated in all types of skin disorders (*Sarva Kusthahara*), skin problems associated with itching (*Kandu*), *Rakta dosha hara* (blood born diseases) and other diseases of infectious origin like fever (*Jwara*, *Sannipataja jwara*), cough (*kasa*), *shwasa*, abscess (*vidradhi*) and gonorrhoea (*upadamsha*). **Aims And Objectives:** The aim of this study is to establish the standard manufacturing process for *Shila Sindoor* and analyze its organoleptic and physicochemical properties. **Design:** Pharmaceutical standardization. **Material And Methods:** *Samaguna Kajjali* was prepared by adding equal amount of *Hingulotha Parada* and *Shuddha Gandhaka*. Fine powder of *Shuddha Manahshila* was added to the *Kajjali*, triturated till the blend becomes a homogenous mass. This blend was levigated with *Ghritakumari Swarasa* for 8 hrs till it gets dry. The dried powder was filled in *Kupi* and processed in an electrical muffle furnace for 25 h. On cooling, the product formed at the neck of the *Kupi* was collected. Organoleptic and physicochemical parameters of *Shila Sindoor* were analyzed and tabulated. **Results And Conclusions:** *Shila Sindoor* is a *Galastha Kupipakwa Rasayana*. It requires shortening duration of *Mrudu Agni* for 4 hrs. (<250 °C), *Madhyama Agni* for 13 hrs. (250-550 °C) and *Teevragni* for 8 hrs. (550-700°C) for an average yield of 45.60%. There is presence of HgS and As<sub>2</sub>S<sub>3</sub> and 21.80% of Mercury, 6.23% of Sulphur and 14.34% of Arsenic was found. Average size of particles found to be 767.1 nm and distribution of particles are in between 652.9 to 941.2 nm.

**KEYWORDS :** Ayurveda, *Shila Sindoor*, Arsenic compound, *Kupipakwa rasayana*, Standardization.

### INTRODUCTION:

*Rasa Shastra* can be defined as the science chiefly dealing with pharmaceutical process of *Rasa* (Mercury) and various types of minerals, metals, herbal poisons and aquatic origin substances etc. *Rasa Chikitsa* is the best therapy among others due to quicker recovery from disease and effective in even very small dose, easy palatable and administration<sup>1</sup>.

The mercurial formulation which is prepared in glass bottle by specific type of heat treatment is known as *Kupipakwa Rasayana*<sup>2</sup>. *Rasa sindoor*, *Makaradhawa*, *Sameerapannaga rasa*, *Swarana vanga* and *Shila Sindoor* are few therapeutically potent and widely used formulation prepared by this method. *Shila Sindoor* is prepared by the combination of *Hingulotha Parada* (mercury), *Shodhita Gandhaka* (Sulphur) and *Shodhita Manashila* (Arsenic disulphide) in equal quantity triturated with *Kumari Swarasa* and processing done by *Kupipakwa* method in electrical muffle furnace (EMF)<sup>3</sup>. It is indicated in all types of skin disorders (*Sarva Kusthahara*), skin problems associated with itching (*Kandu*), *Rakta dosha hara* and other diseases of infectious origin like fever (*Jwara*, *Sannipataja jwara*), abscess (*vidradhi*) and gonorrhoea (*upadamsha*)<sup>4</sup>.

Ayurvedic medicine is prepared using many steps and with variety of plant, animal and mineral drugs. The entire composition makes it more difficult to standardize and then manage the final product's quality. Therefore, it is essential to standardize and document the product on organoleptic as well as physico-chemical parameters to determine their chemical and biological configurations. Some work regarding pharmaceutical standardization, Toxicity and efficacy studies of *Shila Sindoor* has been done but only a few of them are published. Although no data is available for

SMP of *Shila Sindoor* along with its physico- chemical standards.

The present study is carried out in an attempt to develop Standard Manufacturing Procedure (SMP) of *Shila Sindoor* preparation and to develop its organoleptic and physicochemical standards.

### MATERIALS AND METHODS:

#### Procurement Of Raw Materials:

*Ashuddha hingula* (HgS), *Ashuddha Gandhaka*(S) *Ashuddha Manahshila* ( As<sub>2</sub>S<sub>3</sub>) were procured from Shree Ram Herbals, Jaipur. *Goghrita* and *Godugdha* were purchased from local market of Jodhpur. Fresh *Ghritakumari* (*Aloe barbadensis miller*) and *Nimbu* were procured locally.

#### Materials:

*Khalva yantra* (Length-12-inch, Width-7.9-inch, Depth-3.6-inch, Thickness-1 inch), *Nada Yantra* (Upper circumference - 88 cm, Middle circumference-130 cm, Depth- 29 cm), *Kupi* (Seven-layer mud smeared glass bottle, capacity-750 ml), EMF-inner hearth (length: 10.2 cm, breadth: 10.2 cm, depth: 25.3 cm, maximum temperature capacity: 850 °C) were used as per requirement.

#### Methods:

A part from the main procedure, the following procedures also have been carried out in the laboratory. *Hingula Shodhana* has been carried out by trituration in *Nimbu Swarasa* for seven times<sup>5</sup>. *Hingulotha Parada* has been obtained from *Hingula* by *Nada Yantra*<sup>6</sup>. *Gandhaka Shodhana* has been carried out by *Dhalana* in *Godugdha*<sup>7</sup>. *Manahshila Shodhana* has been carried out by trituration in *Nimbu Swarasa* for seven times<sup>8</sup>. The preparation of *Shila Sindoor* was divided into three

stages, namely, *Purva Karma* (Pre heating phase), *Pradhan Karma* (Heating phase) and *Pashchat Karma* (Post heating phase) stages. *Shila Sindoor* was subjected to various organoleptic and physicochemical analyses such as texture, colour, taste, odour, pH, Loss on drying, Total ash, Acid insoluble ash, Alcohol-soluble extractive value, Water-soluble Extractive value, determination of crystallinity of a compound (by XRD), Particle size analysis and percentages of Mercury, Sulphur and Arsenic (By ICP-MS).

#### **Purva Karma (Pre heating phase):**

*Samaguna Kajjali* was prepared by adding equal amount of *Hingulottha Parada* and *Shuddha Gandhaka*. It took 32 hours of time to get the *Siddhi lakshanas* of *Kajjali* [Fine, black and luster free]. Fine powder of *Shuddha Manahshila* was added to the *Kajjali*, triturated till the blend becomes a homogenous mass. This blend was levigated with *Ghritkumari Swarasa* for 8 hours till it gets dry [Table No.1]. The dried powder was filled in *Kupi* and *kupi* was placed in EMF [figure 1].

Ingredient	Batch - I	Batch - II	Batch -III
<i>Hingulottha Parada</i> (gm)	100	100	100
<i>Shuddha Gandhaka</i> (gm)	100	100	100
<i>Shuddha Manahshila</i> (gm)	100	100	100
<i>Ghritkumari Swarasa</i> (ml)	100	100	100

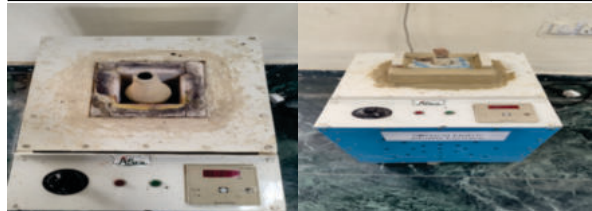


Figure-1

#### **Pradhan Karma (Heating phase):**

Preparation of *Shila Sindoor* was carried out in EMF by providing controlled intermittent and gradually increasing temperature that is, *Mrudu Agni* for 4 hours (<250 °C), *Madhyama Agni* for 13 hours (250-550 °C) and *Teevragni* for 8 hours (550-700°C). In between, the hot iron rod was regularly inserted to clean the neck of the bottle and to avoid blockage by deposition of sublimated *Gandhaka*. After observation of the confirmative tests like, complete cessation of *Gandhaka* and *Arsenic* fumes, copper coin and *sheet shalaka* test were positive, the mouth of the *Kupi* was corked and the temperature was increased to around 40 °C and was maintained for 4 hours to facilitate complete formation of the compound. After cooling, the bottle was removed and thus *Shila Sindoor* was prepared in three batches of 288 gm of *Kajjali* in each.

#### **Pashchat Karma (Post heating phase):**

After Self-cooling, *Kupi* was taken out from the EMF. The layers of mud smeared cloth were scrapped. A thread soaked in kerosene was tied around the *kupi*, one inch below from the level of the sublimed product and then ignited. On complete burning, a wet cloth was wrapped around the burning thread. A cracking sound was produced and bottle broke into two parts. Final product was collected from the neck of *Kupi* and residue collected from the bottom of the *Kupi*. It was weighed and packed.

#### **OBSERVATION AND RESULTS:**

Different stages during the process like *Gandhaka* and *Arsenic* fuming, melting of *Kajjali*, flaming, confirmative test for completion of product formation such as flame disappearance, copper coin test positive (Positive copper coin test revealed particles of free *parada* on surface of copper.), *Sheeta Shalaka* test positive (*Sheeta Shalaka* was inserted into the *kupi*, a thin layer along with shiny light black coating was formed on it, suggesting compound formation), etc., were observed and recorded [Table No. 2].

Table No. 2 Temp. Pattern & Observations During Preparation Of *Shila Sindoor*

Time (hrs.)	Temperature (°C)			Observation
	Batch- I	Batch-II	Batch-III	
0	29	45	48	Furnace switched on
01	72	96	98	No changes were seen
02	124	137	144	Mild smell of SO <sub>2</sub>
03	193	202	201	White fumes coming out with characteristic smell.
04	266	264	257	Dense yellow fumes of SO <sub>2</sub> were observed.
05	294	297	298	Yellowish fumes of <i>Gandhaka</i> gradually became dense.
06	327	330	324	Semi-solid state of <i>Kajjali</i> was felt at the base of bottle with <i>sheeta shalaka</i> .
07	372	376	373	Mild Yellow flames appeared on the neck of <i>kupi</i> when red hot <i>shalaka</i> inserted in the <i>kupi</i> .
08	398	401	396	<i>Kajjali</i> was found in molten state as observed. Bubbling sound was heard during <i>Kajjali</i> melting.
09	437	433	432	Mild SO <sub>2</sub> fumes were still evolving. orange flames appeared on the neck of <i>kupi</i> when red hot <i>shalaka</i> inserted in the <i>kupi</i> .
10	483	488	481	Light blue flames appeared on the neck of <i>kupi</i> when red hot <i>shalaka</i> inserted in the <i>kupi</i> .
12	502	500	498	Maroon red appearance seen in the bottom of the <i>kupi</i> .
13	508	503	504	White fumes and blue flames were still coming.
14	534	532	534	Light Blue flames appeared on the neck of <i>kupi</i> without <i>shalaka sanchalana</i> .
16	586	584	581	Blue-Orange flames appeared on the neck of <i>kupi</i> when red hot <i>shalaka</i> inserted in the <i>kupi</i> .
17	588	590	586	Bright orange flames were produced when red hot <i>shalaka</i> inserted.
18	618	618	611	Copper coin test was performed after every 5 mins. and was found with the deposition of black soot over its surface.
19	648	647	643	White Yellow fumes coming out when red hot <i>shalaka</i> inserted.
20	659	654	657	No flames were produced when hot <i>shalaka</i> was inserted in the mouth of <i>kupi</i> . Copper coin test was found negative.

21	663	667	662	The examination of bottle's interior with the help of torch revealed maroon red colour in the bottom of the <i>kupi</i> . Positive copper coin test. Corking of the <i>kupi</i> was done with brick cork and mud smeared cloth was tightly wrapped around it.
22	685	686	681	Intense heat given for 4 hours.
25	720	713	702	EMF Switched off.

*Shila Sindoor* was collected from the neck of *Kupi* from all the batches were weighed and calculated for the percentage of absolute and relative yield [Table No.3]. *Shila Sindoor* was subjected to various organoleptic and physicochemical analysis result obtained is depicted in Tables No. 4, 5, 6,7 and 8.

**Table No. 3 Comparative Results Of *Shila Sindoor* Preparation All Batches**

Batch	Initial weight of the material (kajjali)	Time (hrs.)	Max Temp.	Status of Kupi	Weight of product	%Yield
1 <sup>st</sup> batch	288 gm	25	736°C	Blast	98.80 gm	34.30%
2 <sup>nd</sup> batch	288 gm	25	713°C	Blast	152.90 gm	53.09%
3 <sup>rd</sup> batch	288 gm	25	703°C	Intact	142.30 gm	49.40%

**Table No. 4 Results Of Organoleptic Tests**

Colour	Colour (After trituration)	Taste	Odour	Texture
Maroon red	Brick red	Tasteless	Odourless	Compect red

**Table No. 5 Results Of Physico-chemical Tests<sup>9</sup>**

Batch	pH (10% Aq. Solution)	Loss on Drying	Total Ash	Acid-insoluble Ash	Alcohol-soluble Extractive	Water-soluble Extractive
I	6.84	0.03 %w/w	0.09 %w/w	BLQ	0.25 %w/w	0.45 %w/w
II	6.95	0.09 %w/w	0.08 %w/w	BLQ	0.11 %w/w	0.28 %w/w
III	6.92	0.07 %w/w	0.76 %w/w	BLQ	0.19 %w/w	0.36 %w/w

Abbreviation: BLQ – Below limit of Quantification, LOQ – Limit of Quantification (LOQ:0.1)

**Table No. 6 Results Of ICP-MS Analysis Of *Shila Sindoor***

Sr. No.	Test Parameter	Unit	Results
1.	Mercury (Hg)	%	21.802
2.	Arsenic (As)	%	14.345
3.	Sulphur	%	6.23

**Table No. 7 Results Of XRD Of *Shila Sindoor***

Sample Name	Obs. Max	d (Obs. Max)	Net Height	Net Area	Intensity
	2-Theta °	Angstrom	Cps	Cps x 2-Theta °	%
HgS	26.6814	3.34114	439.58	0.2362	100.00
As <sub>2</sub> S <sub>2</sub>	28.3645	3.14659	104.85	0.2362	23.85
As <sub>2</sub> S <sub>2</sub>	31.3696	2.85167	420.18	0.2066	95.59

Sharp peaks observed that major compounds as Mercuric Sulphide of majorly at 100% intensity on 26.6814, 2-theta value with amorphous shape and structure.

**Table No. 8 Result of Particle Size Analysis of *Shila Sindoor***

**(EMF-II batch)**

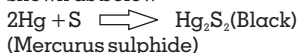
Sr. No.	Sample name	Average Particle Size (nm)	Poly Dispersity index %
1.	Shila Sindoor-1	707.2	9.1
2.	Shila Sindoor-2	652.9	16.5
3.	Shila Sindoor-3	941.2	26.3
	Average	767.1	

Particle size distribution of *Shila Sindoor* Means Average size of particles found 767.1 nm and distribution of particles are in between 652.9 to 941.2 nm.

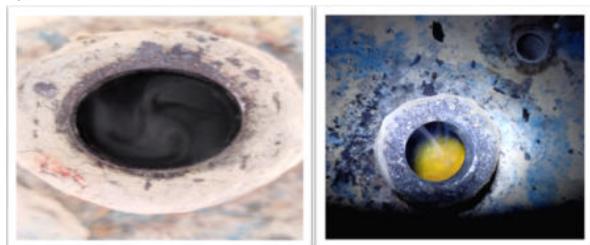
**DISCUSSION:**

*Shila Sindoor* is a *Kantastha* (final product accumulates at neck of bottle) *Kupipakwa Rasayana*. Present reference used for preparation describes the preparation of *Shila Sindoor* in 48 hours, but slight modification in time duration that is, 25 hours duration was preferred in previous studies for proper formation of compound. *Hingulotha Parada* and *Shuddha Gandhaka* were taken in equal parts in *Khalva Yantra* and *Mardana* was done for 32 hrs. *Mardana* was done till the *Kajjali* became very fine, soft, *Nischandra* and attain black in colour thereby fulfilling all the examinations of *Kajjali*. Due to greasiness of *Gandhaka*, *mardana* became difficult in the beginning. Fine powder of *Shuddha Manahshila* was added to the *Kajjali*, triturated till the blend becomes a homogenous mass. When *Shuddha Manahshila* was added, the mixture turned greenish black (dark *mehandi*). Total weight loss was around 2.9%. It was due to mixture spillage during *mardana*, some particles of *Kajjali* adhere to *Khalva* which is difficult to collect and some *Kajjali* was lost while the confirmatory test was being performed on the product. This mixture (*Manahshila* + *Kajjali*) was levigated with *Ghririkumari Swarasa* for 8 hrs. Total 100 ml *Ghririkumari Swarasa* is required for *Bhavana* of mixture (*Manahshila* + *Kajjali*) and weight gain was observed to be 2.38%. Weight gain in mixture (*Manahshila* + *Kajjali*) occurs due to the incorporation of solid components from the liquid media.

The probable reaction in *Kajjali* during Trituration could be shown as below<sup>18</sup>-



After 3 hours, when the temperature was recorded 260-270°C, the *Kajjali* started to slowly melt and emit mild sulphur fumes (White & Yellow fumes). At this point, we needed to regularly clean the neck of *kupi* because *Gandhaka* particles began to adhere to it, requiring cleaning with a hot *Shalaka* [Figures-3,4].

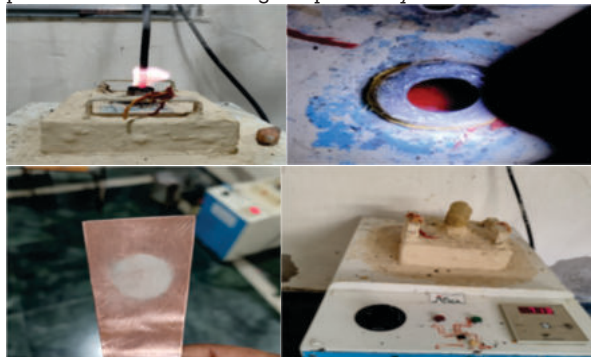


After 8 hours, when the muffle furnace reached a temperature of 410-430°C, flames started to appear at the mouth of the *kupi*, likely to indicate the ignition temperature of Sulphur. This caused Sulphur to catch fire and produce a flame [Figure-5].

After 20 hours of heating at a temperature of 660-670°C, the bottom of the *kupi* turned maroon red in colour [Figure-6]. During this stage, when *Sheeta Shalaka* was inserted into the *kupi*, a thin layer along with shiny light black coating was formed on it, suggesting compound formation. At this stage flames completely disappeared. Additionally, the copper coin test yielded positive results, as placing a copper coin over the *kupi*'s mouth resulted in a silver-white mercurial coating,

indicating the evaporation of *Parada*. Corking was crucial at this stage to prevent product loss. If a black coating was observed on the copper coin, it meant that the compound still contained Sulphur, which needed to be burned off before corking. When Sulphur is completely burnt and copper coin test becomes positive then proper corking of *Kupi* should be done [Figures-7,8].

Corking of the *kupi* was accomplished using a piece of brick and then secured it with *Kapadamitti*. Proper *Kapadamitti* application was essential to maximize the final product yield. After corking, the temperature was gradually raised to 700°C in duration of 4 hrs. and maintained for an additional hour. This stage allowed the compound to evaporate and sublimate on the neck of the *kupi*. Increasing the temperature after corking is necessary because it facilitates the evaporation process and ensures the highest possible yield.



*Kupi* should be broken [Figure- 9] after cooling naturally as it plays an important role for proper crystallization of the final product [Figure- 10].



Breaking of kupi

Final product

#### CONCLUSION:

*Shila Sindoorā* is a *Kantastha Kupipakwa Rasayana*. The maximum temperature to prepare *Shila Sindoorā* is to be given around 690- 700°C to obtain good quality of product. 25 hours duration was preferred for proper formation of compound. Analytical study showed that elemental composition of *Shila Sindoorā* is HgS along with Micro level of  $As_2S_3$  and 21.80% of Mercury, 6.23% of Sulphur and 14.34% of Arsenic was found. Particle size of *Shila Sindoorā* is found in between 652.9 to 941.2 nm.

#### ACKNOWLEDGMENT:

The author would like to thank *Hon. Vice Chancellor Prof. (Vd.) Pradeep Kumar Prajapati, DSRRAU, Jodhpur*, for their valuable guidance and support.

#### Footnotes:

##### Source of support:

PG. Department of RS & BK, PGIA, Jodhpur

**Conflict Of Interest:** None declared

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