

Pharmaceutico - Analytical Study of Hemadri Rasa - A Unique Formulation

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ABSTRACT

Ayurveda is not merely a science of diseases and drugs, where it has every aspect of life in its sphere. *Rasashastra and Bhaishajya kalpana* known as the art of *vedic* alchemy is a fusion between mineral and organic compounds. *Tamaka shwasa* is a dreadful disease mentioned in all Ayurvedic classics as a *Vata Kaphaja* disorder with *sanga* pathology. *Hemadri Rasa* is a unique formulation found in *Rasendra Chinthamani*, having *Shuddha Parada, Shuddha Gandhaka, Shuddha Tamra and Shuddha Manashila* as ingredients. Physical test shows AHR II is Greyish Black in colour with pH 8.67. XRD study compared with 2 θ angle and JCPDF standards and confirms that AHR II is a compound of Metacinnabar in cubic crystal system, Sulfur in trigonal crystal system. Elements present in AHR II as confirmed by the EDS study is Mercury – 2.29%, Sulfur – 13.42%, Copper – 83.92%, Arsenic – 0.97%.

KEYWORDS: Ayurveda, Rasashastra, Hemadri Rasa

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INTRODUCTION

Ayurveda is not merely a science of diseases and drugs, where it has every aspect of life in its sphere. *Rasashastra and Bhaishajya kalpana* known as the art of *vedic* alchemy is a fusion between mineral and organic compounds. *Tamaka shwasa* is a dreadful disease mentioned in all Ayurvedic classics as a *Vata Kaphaja* disorder with *sanga* pathology. The patients suffering from *Tamaka shwasa roga* will be having symptoms like *shwasa kruchrutha, kasa, gurgurutha, asino labhathe soukhyam and urashoola*^[1]. Incidence rates of these diseases have increased multifold vowing to altercations in air qualities in urban areas, modifications of life style and inappropriate cuisine patterns. *Hemadri Rasa* is a unique formulation found in *Rasendra Chinthamani*, having *Shuddha Parada, Shuddha Gandhaka, Shuddha Tamra and Shuddha Manashila* as ingredients^[2]. Even though there are many studies carried out on *Tamaka Shwasa*, very few studies have been carried out with scientific perspective. So it was thought worthwhile to undertake such study.

METHODOLOGY

- Raw materials were collected after authoritative identification through *grahya agrahya lakshanas*.
- Hingulottha Parada was collected form Hingula through *urdwapatana* method^[3].
- Gandhaka shodhana was carried out in *kurmaputa dalana* method with *godugdha* as media^[4].
- Manashila shodhana was carried out in *bhavana* method with *ardraka swarasa* as *bhavana media*^[5].
- Samanya shodhana of Tamra was carried out in *Nirvapa* method in medias like *Taila, Takra, Gomutra, Aranala and Kulattha Kwatha* for 7 times each^[6].
- Vishesa shodhana of Tamra was carried out in *Nirvapa* method in *Kanji media* for 8 times^[7].
- Samaguna Kajjali was prepared by *mardana* method for 140 hours.
- Shoditha Tamra and Shoditha Manashila were mixed well and *bhavana* was done with *nimbu swarasa* as liquid media.

- This mixture was taken in a sharava samputa and kept in valuka yantra and heat was given for 24hrs continuously.
- Later the Manashila marita Tamra and Samguna Kajjali were mixed well and bhavana was done with nimbu swarasa as liquid media.
- This mixture was taken in a sharava samputa and kept in valuka yantra and heat was given for 12hrs continuously.
- Later the outcome product was tested for dadhi pareeksha. After the result came positive, the product was taken for amruthikarana.
- Hemadri rasa and Shuddha Gandhaka were mixed well and bhavana was done with nimbu swarasa and kept inside Surana kanda.
- This whole setup was subjected to gajaputa and after swangashheta collected carefully and sent for analytical tests^[8].

RESULTS

Pharmaceutical Results:

Table no 1: Showing results from Hingulotha Parada

Batch	Wt of Hingula taken for urdhwapatana	Wt of Parada obtained	Yield %
Batch I	250gm	140gm	67.39
Batch II	233gm	139gm	

Table no 2: Showing results from Hingulotha Parada Shodhana

Wt of ashoditha Parada taken	Wt of shoditha Parada	Yield %
297g	290g	97.64

Table no 3: Showing results from Gandhaka Shodhana

Wt of Gandhaka taken	Wt of Sh. Gandhaka obtained	Loss	Yield %
500 g	482 g	18gm	73.2
482g	380g	52g	
380g	366g	14g	

Table no 4: Showing results from Manashila Shodhana

No of bhavana	Quantity of Manashila taken	Quantity obtained	Gain	Yield %
1	500g	520g	20g	114.4
2	520g	530g	10g	
3	530g	550g	20g	
4	550g	560g	10g	
5	560g	564g	4g	
6	564g	569g	5g	
7	569g	572g	2g	

Table no 5: Showing results from Tamra Samanya Shodhana

SL No	Name of liquid	Total Qty of liquid	Initial wt in gm	Final wt in gm	Gain/Loss in gms	Yield %
1.	Tila taila	10.5 lt	1000	1500	500g gain	78.7
2.	Takra	10.5 litre	1500	970	530g loss	
3.	Gomutra	10.5 litre	970	938	32g loss	
4.	Kanji	10.5 litre	938	856	82g loss	
5.	Kulattha Kwatha	10.5 litre	856	787	69g loss	

Table no 6: Showing results from Tamra Vishesa Shodhana

Wt of Tamra before Shodhana	Wt of Tamra after Shodhana	Loss	Yield in %
787gm	633 gm	154 gm	73.77%

Table no 7: Showing results from preparation of Kajjali

Wt of Parada	Wt of Gandhaka	Wt of Kajjali obtained	Yield %
250gm	250gm	498gm	99.6

Table no 8: Showing results from 24 hrs valuka yantra paka

Intial weight of chakrikas in gm	Obtained quantity in gm	Loss in gm	Yield %
318gm	254gm	64gm	79.87

Table no 9: Showing results from 12 hrs valuka yantra paka

Initial weight of chakrikas in gm	Obtained quantity in gm	Loss in gm	Yield %
600	456	144	76

Table no 10: Showing results from Amrithikarana of Hemadri Rasa (batch – I)

Quantity taken	Quantity obtained	Loss in gm	Yield %
379gm	71gm	308gm	18.73

Table no 11: Showing results from Amrithikarana of Hemadri Rasa (batch – II)

Quantity taken	Quantity obtained	Loss in gm	Yield %
179gm	140gm	39gm	78.21

Analytical Results**Table no 12: Organoleptic characters of Kajjali, MMT, HR, AHR I and AHR II**

Physical test	Kajjali	MMT	HR	AHR I	AHR II
Colour	Jet black	Brown	Jet black	Brownish black	Greyish black
Odour	Odourless	Odourless	Odourless	Odourless	Odourless
Taste	Astringent	Astringent	Tasteless	Tasteless	Tasteless
Touch	Fine	Fine	Fine	Fine	Fine

Table no 13: DETERMINATION OF P^H VALUE.

Kajjali	MMT	HR	AHR I	AHR II
8.45	8.16	8.72	8.11	8.37

Table no 14: DETERMINATION OF ASH VALUE

Kajjali	MMT	HR	AHR I	AHR II
94.5	88.07	95.85	81.97	94.84

Table no 15: DETERMINATION OF ACID INSOLUBLE ASH

Kajjali	MMT	HR	AHR I	AHR II
72.2	35.07	34.55	40.50	23.47

Table no 16: DETERMINATION OF WATER SOLUBLE ASH

Kajjali	MMT	HR	AHR I	AHR II
6.31	12.2	6.37	11.18	13.78

Table no 17: DETERMINATION OF LOSS ON DRYING AT 110⁰C

Kajjali	MMT	HR	AHR I	AHR II
3.95	2.2	13.35	3.29	6.37

Table no 18: Showing elements and crystal system

Sample	Element	Crystal system
Kajjali	Metacinnabar	Cubic
MMT	Sulphur	Cubic
HR	Metacinnabar	Cubic
AHR I	Copper oxide	Tetragonal
AHR II	Metacinnabar	Cubic

Table no 19: Showing SEM EDS result of Kajjali

Sl no	Element	Mass %
1	O	33.47
2	S	15.66
3	Hg	50.87

Table no 20: Showing SEM EDS result of MMT

Sl no	Element	Mass %
1	Cu	84.32
2	S	12.42
3	O	2.29
4	As	0.37

Table no 21: Showing SEM EDS result of HR

Sl no	Element	Mass %
1	S	23.61
2	Cu	46.11
3	As	1.83
4	Hg	28.15

Table no 22: Showing SEM EDS result of AHR I

Sl no	Element	Mass %
1	S	28.65
2	Cu	56.93
3	As	9.60
4	Hg	3.82

Table no 23: Showing SEM EDS result of AHR II

Sl no	Element	Mass %
1	S	13.42
2	Cu	83.92
3	As	0.37
4	Hg	2.29

Table no 24: Showing Particle Size of *Kajjali*, MMT, HR, AHR I and AHR II

Sample	Mean diameter(nm)
<i>Kajjali</i>	374.7
MMT	850.8
HR	736.1
AHR I	900.6
AHR II	616.7

Table no 25: Showing FTIR Peaks of *Kajjali*

Sample peaks Cm^{-1}	Bond	Functional groups
3439	O-H (free)	phenols
668,714,733,757,828, 859,902,921,953	C-H (out- of- plane bend)	Alkenes
	C-H (out- of- plane bend)	Aromatics
549,511,486,478,455, 448,440	C-X	Bromide, Iodide
757,733,714,668,549	C-X	Chloride
	C-H (out- of- plane bend)	Aromatics
1269,1214, 1213,1012	C-O (strong) stretch	Alcohols, Ethers, Carboxylic acids, Esters, Anhydrides.
	C-N (medium)stretch	Amines
1981, 1962, 1884, 1811,1763	C-H (weak)- fingerprint region	Phenyl Ring Substitution Overtones.

Table no 26: Showing FTIR Peaks of MMT

Sample peaks Cm^{-1}	Bond	Functional groups
2912	C-H (variable)scissoring and bending	Alkenes
982,918,878,831, 781,703, 674	C-H (out- of- plane bend)	Alkenes
	C-H (out- of- plane bend)	Aromatics
617	C-X	Bromide, Iodide
781, 703,674,617,536	C-X	Chloride
	C-H (out- of- plane bend)	Aromatics
1228, 1109	C-O (strong) stretch	Alcohols, Ethers, Carboxylic acids, Esters, Anhydrides.
	C-N (medium)stretch	Amines
1987, 1943, 1930 1920,1849, 1819	C-H (weak)- fingerprint region	Phenyl Ring Substitution Overtones.
2904, 2836	C-H (stretch)	Alkenes.
	O-H (broad) stretch	Carboxylic acids
3482,3441,3417 3410, 3395	N-H (stretch)	Primary and secondary amines and amides.

Table no 27: Showing FTIR Peaks of HR

Sample peaks Cm^{-1}	Bond	Functional groups
1632	C-H (variable)scissoring and bending	Alkenes
790,847,873	C-H (out- of- plane bend)	Alkenes
	C-H (out- of- plane bend)	Aromatics
613,594,549	C-X	Bromide, Iodide
712,781	C-X	Chloride
	C-H (out- of- plane bend)	Aromatics
1269,1122, 1156,	C-O (strong) stretch	Alcohols, Ethers, Carboxylic acids, Esters, Anhydrides.
	C-N (medium)stretch	Amines
913,873,847 790	C-H (out- of- plane bend)	Alkenes
1618,1733, 1798	C-H (weak)- fingerprint region	Phenyl Ring Substitution Overtones.
3407	C-H (stretch)	Alkanes.
	O-H (broad) stretch	Carboxylic acids
3537,3530	N-H (stretch)	Primary and secondary amines and amides.

Table no 28: Showing FTIR Peaks of AHR I

Sample peaks Cm^{-1}	Bond	Functional groups
1384	C-H (variable)scissoring and bending	Alkenes
657,696,797,806, 836,848,863,872, 986	C-H (out- of- plane bend)	Alkenes
	C-H (out- of- plane bend)	Aromatics
657,615,541,503, 472,461	C-X	Bromide, Iodide
872,863,848,836, 806,797,696	C-X	Chloride
	C-H (out- of- plane bend)	Aromatics
1171,1325	C-O (strong) stretch	Alcohols, Ethers, Carboxylic acids, Esters, Anhydrides.
	C-N (medium)stretch	Amines
657,696,797,806, 836,848,863,872, 986	C-H (out- of- plane bend)	Alkenes
1724,1628	C-H (weak)- fingerprint region	Phenyl Ring Substitution Overtones.
2881,3063,3363	C-H (stretch)	Alkanes.
	O-H (broad) stretch	Carboxylic acids
3363	N-H (stretch)	Primary and secondary amines and amides.

Table no 29: Showing FTIR Peaks of AHR II

Sample peaks Cm^{-1}	Bond	Functional groups
742	C-X	Chloride
2929.76	O-H stretch	Carboxylic acids
	C-H stretch	Alkanes
2355.36	C-H stretching	Alkane
1605.23	C=N stretching	Imine/oxime
843.67	=C-H bend	Alkenes
	N-H wag	1 ⁰ , 2 ⁰ amines

Table no 30: Showing TLC results with Rf values

Sl no	Sample	Rf value
1	Kajjali	0.85
2	MMT	0.82
3	HR	0.99
4	AHR I	0.89
5	AHR II	0.95

Table no 31: Showing results for ICP – MS for Kajjali, MMT, HR, AHR I, AHR II in ppb

Sample	Hg	S	Cu	As	Fe	Ca	Na	Mg	Zn
Kajjali	10638.6	1077.7	1058.3	244.9	810.1	4430.5	16765.9	30842	303.6
MMT	38.5	10477.6	135836.3	324937.2	16232.4	9171.1	30588.1	19134.5	36182.6
HR	1287.6	10803.7	135836.3	445867.6	20040.4	9405.2	28461.8	27102.2	42613.3
AHR I	136.7	73430.1	135836.3	44970.4	22773.5	9929.9	21698.6	13893.2	19979.4
AHR II	1762.2	9433.4	135836.3	343694.2	14542.3	8081.9	24518.9	29150.5	33259.7

Table no 32: Showing Observations during NPST

Sample	I phase(0-5min)	II Phase(5-20min)	III Phase(20 min-1hrs)
AHR II	Brownish red central spot.	Central brown colour with thin bluish margin	Chocolate brown colour in the center with bluish green periphery

DISCUSSION

- Manashila has lekhana, tikshna and ushna properties which may help in reduction of particle size of Tamra
- Nimbu swarasa being a bhavana dravya, has tikshna quality which also aids in reduction of particle size
- During bhavana, the mixture might contain a mix of molecules like arsenic sulphide, copper sulphide, copper sulphate, copper oxide and other organic acids.
- The boiling point of Manashila or realgar is between 500°C to 560°C. the temperature attained was 502°C which may have facilitated boiling of Arsenic di sulphide and convert into arsenic oxide and sulphuric oxide
- The time duration was 24 hrs which may have also assisted in sublimation process thereby reducing the particle size.
- The output product was brown which indicates greater percentage of Copper.
- The upper sharava had a coat of shiny white layer which indicates formation of Sulphuric acid
- The use of valuka yantra instead of conventional puta helps in gradual increase and decrease of heat in an uniform pattern.
- Pressure will be uniform throughout the valukayantra and sharava samputa which facilitates in faster transmission of heat.
- While powdering the output product it was noticed that the texture of product wasn't soft indicating the incomplete process of bhasmikarana.
- Bhavana of kajjali with Manashila marita Tamra was given again with nimbu swarasa for 3 hrs which aided in reducing particle size.
- Chakrikas were prepared with the thickness keeping the mind that neither it breaks into powder nor be so thick that it hampers the rate of temperature flow.
- The temperature given was for about 12 hrs but room temperature was attained at 18 hrs.
- The maximum temperature attained was 402°C.
- After opening sharava samputa, the upper sharava had whitish particles adhered to it probably indicating Sulphur particles.

- The output product was then subjected to both dadhi pareeksha and amla pareeksha.
- Dadhi pareeksha was positive at 72 hrs and amla pareeksha was positive at 12 hrs indicating complete formation of Bhasma
- The pH value of Kajjali, MMT, HR, AHR I and AHR II were 8.45, 8.56, 8.72, 8.11 and 8.37 respectively. The pH around 8 implies that drug solubility isn't affected by hyperacidity or alkalinity in GI system.
- Kajjali, MMT, HR, AHR I and AHR II were evaluated for ash value and it was found to be 94.5%, 88.07%, 95.875%, 81.97% and 94.48% respectively which indicates the presence of inorganic materials etc.
- Acid insoluble ash of the Kajjali, MMT, HR, AHR I and AHR II were 72.72, 35.07, 34.55, 40.50 and 23.47 respectively. It signifies that a considerable amount of drug is soluble in the acidic media of stomach.
- The water soluble ash of Kajjali, MMT, HR, AHR I and AHR II were 6.31, 12.2, 6.37, 11.18 and 13.78 respectively. As the values are least and indicates that water is not soluble media for it
- In the present study Kajjali, MMT, HR, AHR I and AHR II are having 3.95, 2.2, 13.35, 3.29 and 6.37 respectively loss on drying at 110°C. Hence it can be stated that all have very less amount of moisture content and very rare chance of bacterial and fungal growth.
- Kajjali was in cubic system with elemental formula HgS
- MMT was in cubic system with element detected Sulphur
- HR was in cubic system with Metacinnabar elemnt
- AHR I was in tetragonal crystal system with Copper oxide
- AHR II was in cubic system with Metacinnabar
- Elements found in kajjali are Hg, S, O in the percentage of 50.87 15.66 and 33.47 respectively. This shows that mercury is in greater proportion and the elements may be in the form of oxides.
- Elements found in Manashila Marita Tamra are Cu, S, AS and O in the percentage of 84.92, 12.42, 0.37 and 2.29 respectively. Here copper is the major element and probably be in the form of oxide and sulphide.
- Elements found in Hemadri Rasa are S, Cu, As and Hg in the percentage of 23.61, 46.11, 1.83, 28.15 respectively. Decrease in the percentage of mercury and copper might be due to puta samskara.
- Elements found in Amrithikritha Hemadri Rasa I are S, Cu, As and Hg in the percentage of 28.65, 56.93, 9.6 and 3.82 respectively. Significant increase in Arsenic might be due to increase in the threshold of detectable levels after puta samskara.
- Elements found in Amrithikritha Hemadri Rasa II are S, Cu, As and Hg in the percentage of 13.42, 83.92, 0.37 and 2.29 respectively. Since this sample contains copper in major percentage along with Mercury and Sulphur, the probable mode of action can be expected along the lines of Tamra bhasma and kajjali.
- The LD₅₀ of Tamra bhasma is 2500mg/kg body weight, by computing the percentage of Copper for 125mg, it can be noted that it well below lethal dose.
- Copper element remains the same all throughout the samples except kajjali indicating that there is no loss of Tamra during the entire procedure.
- Arsenic quantity has increased in AHR II compared to AHR I while Sulphur quantity has slightly decreased
- After analyzing the elements and their quantity, we can hypothesize that the end product maybe mixture of HgS and CuS.
- N.P.S.T is a modification of circular paper chromatography. N.P.S test gives a clear differentiation of individual products in a group and also product can be identified by its classical name not by the chemical name.
- The continual chemical reactions taking place gradually between 2 chemical substances on static media at fraction of second and also after certain interval of time are easily detected by their distinct colour changes and the pattern of spot.
- Formation of cetral chocolate brown spot indicates the precence of Copper in the solouction, which is due to formation of Cupric ferrocyanide.

$$\text{Cu}^{2+} + \text{K}_4\text{Fe}(\text{CN})_6 \longrightarrow \text{Cu}_2[\text{Fe}(\text{CN})_6]$$
- Intermediate and peripheral rings showed light and dark blueish colour, that may be due to formation of Hydrated ion of Copper – [Cu(H₂O)₄]

CONCLUSION

- *Hemadri rasa* is a formulation containing ingredients which are *tridosahara* in the treatment of *Tamaka Shwasa*, hence selected for study.
- *Hemadri Rasa* is an unique formulation found in *Rasendra Chinthamani*, having *Shuddha Parada*, *Shuddha Gandhaka*, *Shuddha Tamra* and *Shuddha Manashila* as ingredients
- Physical test shows AHR II is Greyish Black in colour with pH 8.67.
- XRD study compared with 2θ angle and JCPDF standards and confirms that AHR II is a compound of Metacinnabar in cubic crystal system, Sulfur in trigonal crystal system.
- Elements present in AHR II as confirmed by the EDS study is Mercury – 2.29%, Sulfur – 13.42%, Copper – 83.92%, Arsenic – 0.97%.
- FTIR analysis of AHR II shows it contains organic functional group like Amine, Amide, Alkene, Aromatics, Acid, Alcohol, Alkane, Carbonyl, Alkyl halide, Ester, Nitro, and Ether. Alcohol, Acid, Amide, Alkane, Carbonyl, Aldehyde, Ester, Ketone, Aromatic, Nitro, Amine, Alkyl halide, Alkene.
- Mean particle size of AHR II is 616.7 nm.
- Further detailed study is required to bring out many more characteristics of this unique formulation.



Chakrikas placed in Sharava



Sharava samputa at center of Valuka yantra

FIGURES



Mixing of Manashila and Shuddha Tamra churna



After completion of Bhavana



24hrs valuka yantra paka



Opening of sharava samputa



Mixing of MMT and Kajjali



Opening of sharava samputa



Pouring of nimbu swarasa



Kept for Dadhi pareeksha



Chakrikas placed in Sharava



Dadhi pareeksha positive after 72hrs



12hrs valuka yantra paka



Bhavana for amruthikarana





Gajaputa for Amruthikarana



NPST at 20 min



NPST at 5 min



NPST after 72hrs

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