

COMPARATIVE ANALYTICAL PHARMA-CEUTICAL STUDY OF HARTAL (ORPIMENT) BEFORE AND AFTER SHODHANA (PURIFICATION)

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ABSTRACT

Hartal is one of the uparasa mention in Rasagranthas. Hartala is called orpiment or yellow arsenic with two molecules of arsenic and three molecules of sulphur (AS_2S_3). Patra hartal is shreshtha than pinda hartal. Ashodhit (impure) hartal causes many diseases such as prameha, santapa, vattaprakop and kaphaprakop janya vyadhi, snayu sankoch, sphota. Hence shodhana of hartal is essential. Shodhana is the process of removing chemical, physical impurities and potentiating of drugs. There are different medias are explained in rasagrantha for shodhana of hartal. Such as kushmanda swarasa triphala kwatha, gomutra, kanji. According to shodhana process there will be chemically and physically change in shodhit (purified) hartala. According to media of purification quality and physicochemical

properties of hartal will vary than ashodhit hartal. Present study includes shodhana of patra hartal as per classical reference of Rasatarangini. Where shodhana of patra hartal is done by kushmanda (*Benincasa hispida*) swarasa and triphala kwatha. The analytical study reveals that there will be some changes in properties of shuddha hartal than ashuddha hartal. The differences in the parameters reveals that the importance of purification and also the properties of media used.

KEYWORDS: vattaprakop and kaphaprakop janya vyadhi, snayu sankoch, sphota.

INTRODUCTION

Ayurveda is not only branch of medical science but also it is science of life. which is practiced in south Asia since vedic period. Ayurveda has given vital importance to metals and

minerals based treatment, includes use of drugs originates mainly from metals and minerals after going through systemic procedure of shodhana (purification) and marana (incineration). Hartal means yellow arsenic or orpiment which is one of the uperasha mentioned in Rasagrantha. It is chemically made from two molecules of arsenic and three molecules of sulphur (As_2S_3). It can be used in various pathologies such as skin disorders, respiratory disorders, infections etc. We can't use hartala alone because it is poisonous also it is mentioned in kalpasthana of Sushruta Samhita under category of visha. Consumption of impure hartala may lead to vomiting, abdominal pain, tingling sensation of extremities, muscle cramping, death. According to Ayurveda consumption of ashodhita hartala causes many diseases such as prameha, santapa, snayu sankoch, vataj and kaphaj vyadhi, sphota etc. Therefore shodhana of hartala or shodhana of any other metal or minerals gains lots of importance in Ayurveda.

Letral meaning of shodhana is purification of drug. According to Ayurveda shodhana is a samskara, which works as gunantaradhana. When any metal or drug goes under shodhana process its physio-chemical properties change. Media used for shodhana not only remove harmful chemicals from drug but also increases its effects, which is more beneficial for treatment. It helps to overcome the effects of poison like tikshnatva, vikasi, vyavayi, ushna. Hartal is used in two forms shuddha hartal and hartal bhasma. Which is used in many kalpas. Which are useful in kushtha vyadhi, vicharchika, vatarakta, visarpa, vishamjwara, vrana, nadvirana etc.

AIM OF THE STUDY

A study of hartal shodhana according to Rasatarangini and its physio-chemical analysis.

OBJECTIVE

- To study the concept of shodhana.
- Authentication of patra hartal.
- To perform shodhana of hartal by kushmanda swarasa and trifala kwatha.
- Analytical analysis of hartal before and after shodhana procedure.
- Physicochemical analysis of hartal before and after of shodhana.

Practical study is comprised of.

- Preparation of Kushmanda Swarasa, Practical 1.
- Hartala Shodhana by Kushmanda Swarasa Practical 2.

- Preparation of trifala kwatha.- practical 3
- Haratala Shodhana by trifala kwatha - Practical 4.

Preparation of Kushmanda Swarasa (Practical 1)

Ref.: sharangdhar Sanmhita madhyamkhanda 2/1

Date of Completion: 1st Day.

Material Required: Stainless steel vessels, Knife, Mixer Grinder, Weighing Balance, Clean cotton cloth, Measuring jar, Spoons.

Ingredients - Kushmanda Phala - 15 kg.

Procedure - Kushmanda Phala was washed in water and cleaned externally, With a clean knife the outer covering was removed. The pulp was cut in to small pieces, and then put in mixer grinder Kalka was prepared. Kalka was squeezed with a clean cloth and juice was extracted. It was filtered with clean cotton cloth and filtered liquid was collected as Kushmanda Swarasa.

Observations

- After removing the greenish outer covering, white pulp was observed.
- Pulp was cut in to small pieces of 0.5 inch size.
- During the grinding little frothing was observed. It took approximately 2 hrs to extract the juice. The colour of extracted juice was light creamish white.

Precautions

- Utensils, vessels and filtering cloth should be clean.
- Outer covering of kushmanda was very hard. so it was carefully separated.
- Pulp was made into small piece procedure. Squeezing should be done properly to extract maximum juice.

RESULT

- Final quantity of Kushmanda Swarasa obtained is: 6.5 ltr.
- Colour: Light creamish white.
- Taste: Alpa Madhura Rasa
- Odour – kushmanda Gandhi
- Texture – creamy liquid with some froth.

Haratala Shodhana by Kushmanda Swarasa (Practical 2)

Ref: Rasatarangini 19/11.

Practical time: 1 day.

Material Required: Stainless Steel Vessel, Gas Stove, Spatula, Weighing Balance, Measuring Jar, Clean Strong, Cotton Cloth, and Mercury Thermometer etc.

Ingredients

- Ashuddha Patra Haratala: 1 kg.
- Kushmanda Swarasa: 6.5 lit.
- Sanskara Adopted: Swedana Sanskara.

Procedure

- Physical impurities like stone, sand etc. were manually cleaned.
- Ashuddha Patra Haratala was taken in a clean Khalwa Yantra and made in to small pieces.
- The pieces were spread on a clean strong cotton cloth and Pottali was prepared.
- This Pottali was tied to a clean and thick wooden stick and the Pottali was suspended in a clean stainless steel vessel.
- Then the Swarasa was added in such a quantity that the Pottali got completely immersed. (approx. 4 liter.) It was kept on gas stove and fire was ignited (Gas knob was set on sim). This arrangement resembles the Dola Yantra.
- The apparatus was heated for 3 hours. After that the Pottali was washed with warm water and the Haratala pieces were collected carefully.
- Haratala pieces were washed with warm water and dried for 6 hours.
- After complete drying the Shuddha Haratala was collected.

OBSERVATIONS

- The color of Ashuddha Haratala was yellowish, brownish black tinge with little shining and having peculiar odor.
- During boiling the colour of the Swarasa changed to Orange dark color.
- During heating little aromatic smell of Kushmanda was found. As the process continued smell of hartala was found.
- As the process continued little quantity of Swaras was added as the Swarasa evaporated.
- Bright yellowish shining pieces of sbuddha hartal was collected after proper drying.

Temperature and duration

Day	Heating device	Duration	Temp $^{\circ}\text{C}$
1 st	Gas stow	3 hrs	74 ⁰ -98 ⁰ C

RESULTS

Asahuddha patra hartala	1 kg
Kushmanda swarasa used	5 lit.
Shuddha hartala obtained after shodhana.	992 gm.
Total duration for the process	1 day. (approx.)

Precautions

- Utensils and vessels should be clean and disinfected.
- Ashuddha Patra Haratala should be made in to very small pieces before subjecting to the process.
- Pottali should be prepared from a strong cotton cloth.
- Pottali should completely get dipped in Swarasa and it should not touch the bottom of the vessel.
- Heating should be controlled and temperature should be maintained about 74-98 $^{\circ}\text{C}$ inside the vessel.
- Temperature should be checked time to time with the help of mercuric thermometer.
- Continuous adding of Swarasa should be done as it gets evaporated.
- After proper Shodhana the pieces were carefully washed with warm water and collected carefully and dried.

Preparation of trifala kwath (Practical 3)

Ref.: sharangadhar Samhita madhyamkhanda 2/2

Practical Time – 2 day.

Material Required: Stainless steel vessels, Weighing Balance, Clean cotton cloth, measuring jar, Spoons.

Ingredients: bharad churna of amalaki, bibhitaka, haritaki.

1. Bharad Churna -1000gm (each 333.33 gm)

2. Water (Portable) – 16 lit.

Procedure

- Bharad churna of trifala was taken in clean utensil and soaked overnight in 3 lit. of water.

- Next day 13 lit. water added in same container and placed on gas stove.
- Kwath is prepared by evaporating water upto $\frac{1}{4}$ part is remaining.
- Kwath is strained in clean container by clean cotton cloth.

Observations

- Colour of kwath is dark brown.
- 4000 ml kwath prepared.

Precautions

- Stirring should be done after every 15 min, so that kwath may not be burnt.
- Utensils, vessels and filtering cloth should be clean. Filtering should be done properly.

RESULT

- Final quantity of trifala kwath – 4000ml.
- Colour: dark brown.
- Taste: tikta rasatmak. Bitter.

Haratala Shodhana by trifala kwath (Practical 4)

Ref.: Rasatarangini 19/11.

Practical Time – 1 day.

Material Required: Stainless Steel Vessel, Gas Stove, Spatula, Weighing Balance, Measuring Jar, Clean Strong Cotton Cloth, Mercury Thermometer etc.

Ingredients

1. Ashuddha Patra Haratala: 992 gm

2. trifala kwath – 4000 ml

Sanskara Adopted: Swedana Sanskara.

Procedure

- Physical impurities like stone, sand etc. were manually cleaned.
- Ashuddha Patra Haratala was taken in a clean Khalwa Yantra and made into small pieces.
- The pieces were spread on a clean strong cotton cloth and Pottali was prepared.
- This Pottali was tied to a clean iron rod and the Pottali was suspended in a clean stainless steel vessel.

- Then trifala kwath was added in such a quantity that the Pottali got completely immersed. It was kept on gas stove and fire was ignited (Gas knob was set on sim). This arrangement resembles the Dola Yantra.
- The apparatus was heated for 3 hours. After that the Pottali was washed with warm water and the Haratala pieces were collected carefully.
- Hartala pieces were washed with warm water and dried for 6 hours.
- After complete drying the Shuddha Haratala was collected.

OBSERVATIONS

- The color of Ashuddha Haratala was yellowish brownish black tinge with little shining and having peculiar odor.
- During boiling the color of the Trifala kwatha changed to dark color
- During heating a peculiar odor was observed.
- As the process continued little quantity of trifala kwath was added as the kwath evaporated.
- Yellowish dull small pieces of Shuddha Haratala were collected after proper drying.

Temperature and duration.

Day	Heating device	Duration	Temp. ⁰ C
1 st	Gas stove	3 hours	62 ⁰ - 95 ⁰ C

RESULT

Patra hatala shodbit in kushmand swarasa	992 gm
Trifala kwatha	4 lit.
Suddha hartala obtained	985 gm
Total duration for shodhan process	1 day

Precautions

- Utensils and vessels should be clean and disinfected.
- Patra Haratala shodit in kushmanda swarasa should be made into small pieces before subjecting to the process.
- Pottali should be prepared from a strong cotton cloth.
- Pottali should completely get dipped in trifala kwatha and it should not touch the bottom of the vessel.
- Heating should be controlled and temperature should be maintained about 62-95⁰C inside the vessel.

- Temperature should be checked time to time with the help of mercuric thermometer.
- Continuous adding of trifala kwatha should be done as it gets evaporated.
- After proper Shodhana the pieces were collected.

Analytical Study

Various analytical studies have been performed of medias used for Shodhana, also an analytical study of before and after Shodhana of Haratala has been carried out. Organoleptic characters various samples of Haratala described in Table 2. Physicochemical parameters of ashuddha hartala and different Shodhana media which has been use Triphala Kwatha, kushmanda swarasa have been described in Table 3. Physicochemical parameters of samples Of ashodhit hartala and Shodhita Haratala have been described in Table 4. XRF graf shown in tabe no 2.

Table no.1: Organoleptic character of various samples of Hartala.

Character	Ashuddha hartala	Kushmand swaras shodhit hartala	Trifala kwath shodhit hartala.
Colour	yellowish orange	Shine decreases, bright yellow	Shine decreases. bright yellow brownish (due to kwath)
Odour	Characteristic smell of Arsenic	Characteristic smell of Arsenic with kushmand swaras	Characteristic smell of Arsenic with triphala swarasa.
Consistency	Crystalline	Crystallinity decrease, loss in luster	Crystallinity decreases than before, loss in luster
Touch	Thin separable pieces	Thin separable pieces	Hardness decreases.

Table no. 2: Average results obtained during shodhana of hartala.

Samples	Before shodhana colour of hartala	Initial Ph of media	Final Ph of media	After shodhana colour of hartala	Shodhita hartala (g)	Waight loss during process (g)
Kushmanda swarasa	Yellowish orange	3.7	4.2	Bright yellow	992 gm.	8 gm.
Trifala kwatha	Yellowish orange	3.5	4.7	Brownish yellow	985 gm.	7 gm.

Hartala shodhana



Ashuddha Hartala



Kushmand Swarasa



Swedan by Dolayantra



Shuddha Hartala

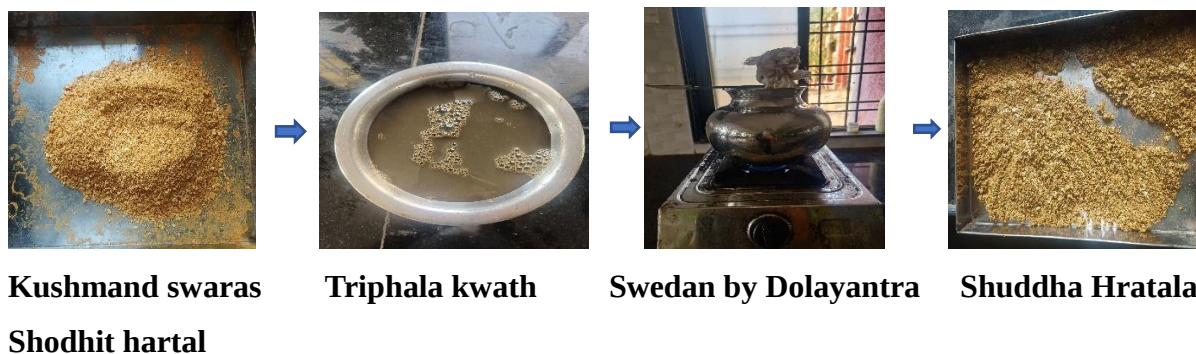


Table no. 3: X- Ray Fluorescence Study of Ashuddha Hartala.

NO.	COMPONENT	RESULT
1	As ₂ O ₃	54.3 mass %
2	SO ₃	44.4 mass %
3	SiO ₂	0.660 mass %
4	Sb ₂ O ₃	0.392 mass %
5	CaO	0.152 mass %
6	HgO	0.0702 mass %
7	PbO	0.0118 mass %
8	Fe ₂ O ₃	0.0087 mass %

Table No. 4: X-Ray Fluorescence Study Of Shodhit Hartala.

NO.	COMPONENT	RESULT
1	AS ₂ O ₃	51.9 mass %
2	SO ₃	46.5 mass %
3	SiO ₂	0.988 mass %
4	Sb ₂ O ₃	0.342 mass %
5	CaO	0.341 mass %
6	Fe ₂ O ₃	0.0207 mass %

DISCUSSION

After Shodhana of Haratala in different Shodhana media, as shown in Table 1, there was shift of pH of media toward alkalinity or reduction in acidity. pH of a sample reflects H ion concentration. Hence, reduction in acidity reflects reduction in H⁺. Highly toxic fumes of sulphur and arsenic are emitted when in contact with acid or acid fumes. Produced sulphur gas may form H₂S which is soluble in aqueous media. As₂S₃ reacts with water, steam, or even moist air to produce hydrogen sulphide gas. Utilization H ions from solution might have been responsible for increase of pH of both media after Shodhana.

Analysis was carried, Table 2 reveals that sample 1, i.e. Ashuddha Patra Haratala, is having yellowish orange, peculiar strong typical arsenic odour with crystalline smooth surface with small thin separable pieces. Sample 2, i.e. Shuddha Haratala (kushmanda swarasa Shodhita

Haratala), was bright yellow, decreased shine, dull colour, weak arsenic odour, crystalline smooth with small separable pieces. Sample 3 i.e. shuddha hartala (triphala swarasa shodhit hartala) was yellow brownish decreased shine, loss in luster, decreased crystalline nature, weak arsenic odour, with small separable pieces. During shodhana of hartala total 1000gm of asuddha hartala was taken and after shodhana we got 985 gm of shuddha hartala and total loss was 15 gm.

In XRF study, percentage of As_2S_3 in ashuddha hartala was 54.31% and besides that it also contain some percentage of lead monoxide, mercuric oxide which are poisonous. Along with that calcium oxide, iron oxide are also present, after shodhana of hartala percentage of arsenic seen reduced which is 51.9%.and percentage of lead monoxide, mercuric oxide was absent and percentage of calcium and iron was increased.

Arsenic trisulfide reacts with water or steam to produce toxic and flammable vapors, it can react vigorously oxidizing materials. As a resultant of produced arsine gas, the concentration of arsenic in sample might have been reduced after Shodhana.

Upon analysis of data of Arsenic content in samples of Ashuddha and Shuddha Haratala, it is observed that, arsenic percentage after Shodhana has been significantly reduced [Table 4] which is probably due to leaching of arsenic in aqueous media as it is well known fact that arsenic partially leaches in water upon heating, may release arsine gas, even humidity also helps the phenomenon. It is known that solubility of arsenic trisulfide increases in sulphide solutions and more in alkaline sulphide solutions. Released arsine gas may form several organo-arsenic compounds with liquid media (kushmanda swarasa, Triphala Kwatha.), thus reducing arsenic content. Arsenic dissolution increases in sulphide solutions and due to the formation of H_2S gas while heating, sulphide solution of several trace elements, sulfurous acid in traces may get formed thus facilitating further leaching of arsenic in to the liquid media for Swedana. Similar reduction has been observed in XRF study of samples of Shodhit Haratala as that of Ashodhit Haratala which is evident from reduction of intensities of the same respective major percentage as arsenic trisulfide.

Ayurvediya rasa shastra is a very vast branch, standardization, and validation of pharmaceutical processes and developing their analytical profile for understanding the chemistry behind the role of different principles and processes is major point of concern with

calibration of instrumental techniques for reproducible results and collecting a standard database for future research works.

CONCLUSION

Shodhana of Haratala reveals that the importance of Shodhana media.both Shodhita and Ashodhita Haratala shows different physical and chemical properties. Organoleptic characteristics of samples of Haratala possess different colors, touch, and odor, also pharmaceutically and analytically difference has been found before and after Shodhana. Thus it can be concluded that sample of shodhita Haratala can be used for further processing of formulation due to the reduction arsenic percentage of Haratala and also diminish of other harmful contents lik PbO, HgO and increase of iron and calcium in sample after Shodhana process.

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REFERENCES

1. Sri Sadananda Sharma, Rasa Tarangini, Hindi Vyakhya By Kashinath Shastri, Motilal Banarasidas, Varanasi, Reprint, 2004; 11/16-25 page 247.
2. Sri Vagbhatacharya, Rasa Ratna Samucchaya, Hindi Vyakhya By Pandit Dharmananda Sharma, Motilal Banarasidas, Varanasi, Second Edition, 1999; 3/1, 38pp.
3. Sri Vagbhatacharya, Rasa Ratna Samucchaya, Hindi Vyakhya By Pandit Dharmananda Sharma, Motilal Banarasidas, Varanasi, Second Edition, 1999; 3/73, 48pp.
4. Sri Vagbhatacharya, Rasa Ratna Samucchaya, Hindi Vyakhya By Pandit Dharmananda Sharma, Motilal Banarasidas, Varanasi, Second Edition, 1999; 3/75, 49pp.
5. Ayurvedic Formulary of India, Part 2, Part B, Published by G. O. I., Ministry of Health and Family Welfare, 2003, 31pp.
6. Ayurvedic Formulary of India, Part 2, Part B, Published by G. O. I., Ministry of Health and Family Welfare, 2003; 7pp.
7. The Ayurvedic Pharmacopoeia of India (Ministry of health & family welfare Gov. of India), Part 1, Vol. I, 1st Edition-1999, Published by The, controller of publication Delhi-54, Appendix-2, Pg. 214(2.2.9).

8. The Ayurvedic Pharmacopoeia of India (Ministry of health & family welfare Gov. of India), Part 1, Vol. I, 1st Edition-1999, Published by The, controller of publication Delhi-54, Appendix-2, Pg. 213(2.2.3).
9. The Ayurvedic Pharmacopoeia of India (Ministry of health & family welfare Gov. of India), Part 1, Vol. I, 1st Edition-1999, Published by The, controller of publication Delhi-54, Appendix-2, Pg. 213(2.2.4).
10. The Ayurvedic Pharmacopoeia of India (Ministry of health & family welfare Gov. of India), Part 1, Vol. I, 1st Edition-1999, Published by The, controller of publication Delhi-54, Appendix-2, Pg. 213(2.2.5).
11. The Ayurvedic Pharmacopoeia of India (Ministry of health & family welfare Gov. of India), Part 1, Vol. I, 1st Edition-1999, Published by The, controller of publication Delhi-54, Appendix-2, Pg. 214(2.2.7).
12. The Ayurvedic Pharmacopoeia of India (Ministry of health & family welfare Gov. of India), Part 1, Vol. I, 1st Edition-1999, Published by The, controller of publication Delhi-54, Appendix-2, Pg. 214(2.2.6).
13. Pharmacopoeial standards for Ayurvedic formulations CCRAS 518pp. 18. Standard Operative Procedure, of the procedure document, NIN Hyderabad.
14. Mullen D J E, Nowacki W, Zeitschrift fur Kristallographie, 136 (1972). 48-65, Refinement of the crystal structures of realgar, AsS and orpiment, As₂S₃, Locality: Lengnabach quarry Binnatal, Switzerland.
15. Bandeppa Sangolgi, Ganapathi rao and Sangameshwar Benne, PHARMASUTICAL STUDY OF HARATALA W.S.R TO ITS VARIOUS SHODHANA PROCEDURES - A RESEARCH ARTICLE.
16. Krupali Shailesh Jani, Prashant Bedarkar, Vinay J Shukla¹, Biswajyoti Patgiri Comparative pharmaceutico analytical study of Haratala (orpiment) Shodhana (purification) using different Shodhana media.