Comparative pharmaceutico-analytical study of Rasamanikya prepared by two different Shodhana media of Haratala (orpiment)

Dipali Parekh, Sarika Makwana, Prashant Bedarkar, Biswajyoti Patgiri
Department of Rasa Shastra and Bhaisajya Kalpana, ITRA, Jamnagar, Gujarat, India

Abstract

Introduction: Foremost, Rasamanikya is described in Rasendra Chintamani by Acharya Dhundhuknath. It is a formulation that is prepared from the arsenical drug, i.e., orpiment (Haratala). Haratala is classified under Uparasa Varga in Rasa classics and is also included under Schedule E1 in D and C act 1940. In classics, there are so many media mentioned for purification process (Shodhana) of orpiment. In the present study, Kushmanda Swarasa (juice of Benincasa hispida [Thunb.] Cogn) and Churnodaka (lime water) are adopted as the purification media for orpiment. Aim: The aim of this study was to standardize the pharmaceutical procedure of Rasamanikya and develop a comparative analytical profile of both the formulation, i.e., Rasamanikya prepared by Kushmanda Swarasa and Churnodaka Shodhita Haratala. Materials and methods: The study was carried out in two stages as follows: Shodhana of Haratala and preparation of Rasamanikya by Kupipakwa method. Both the samples of Rasamanikya were analyzed for organoleptic and physicochemical parameters. The samples of final products were also analyzed through sophisticated analytical parameters, i.e., X-ray diffraction (XRD), Inductively coupled plasma-atomic emission spectroscopy (ICP-AES), CHNS and O, Field emission gun-scanning electron microscopy (FEG-SEM), Fourier transform infrared spectroscopy (FTIR) and Thermo-gravimetric analysis (TGA). Results: Average 2 h duration was required for the preparation of Rasamanikya formulation from 600 g of purified orpiment. In XRD analysis, both samples have different diffraction patterns. In ICP-AES analysis, both samples have the same percentage of arsenic. More percentage loss was noted in the TGA of Rasamanikya prepared with Churnodaka Shodhita Haratala than that of Kushmanda Swarasa Shodhita Haratala. Conclusion: Rasamanikya prepared by two different media of Shodhita Haratala did not found to have a substantial difference in pharmaceutical procedure. However, there was a considerable difference in the analytical study. Kupipakwa procedure can be used for large-scale preparation.

Keywords: Churnodaka, Haratala, Kushmanda Swarasa, Rasamanikya

Introduction

Rasamanikya is described in Rasendra Chintamani by Acharya Dhundhuknath.[1] This formulation is a well-known drug in Ayurveda that is judiciously used in practice by physicians. This formulation is included under the essential drug list framed under the Ministry of Ayush.[2] The final product color resembles Manikya (ruby). It is being used in various Kushta Roga (skin diseases), Shwasa (asthma), Vicharchika (eczema), Bhagandara (fistula-in-ano), Vatarakta (gout), and Phiranga Roga (syphilis).[3] Orpiment is the only ingredient in the formulation of Rasamanikya[4] which is included in the schedule E1 drug list (poisonous substances in Ayush). In Rasashastra classics, orpiment is categorized under Uparasa Varga.[5] In classics, there are several purification (Shodhana) media described for orpiment.[6] Shodhana is a process of purification and detoxification; by which physical and chemical blemishes, toxic materials are eliminated and substances are made more efficacious.

Address for correspondence: Dr. Dipali Parekh, Department of Rasa Shastra and Bhaisajya Kalpana, ITRA, Jamnagar - 361 008, Gujarat, India. E-mail: dipali178@gmail.com

How to cite this article: Parekh D, Makwana S, Bedarkar P, Patgiri B. Comparative pharmaceutico-analytical study of Rasamanikya prepared by two different Shodhana media of Haratala (orpiment). AYU 2022;41:197-207.

Submitted: 11-Sep-2019 Revised: 13-Feb-2020
Accepted: 04-Aug-2021 Published: 24-Feb-2022
suitable for further processing.\textsuperscript{[7]} Specific media has an important role in rendering a drug therapeutically active without causing side effects/adverse effects.\textsuperscript{[9]} In Ayurveda classics, there are three procedures involved in the manufacturing of Rasamanikya from Haratala, but there have been some modifications with the advancements of scientific tools such as Kupipakwa method, fuse bulb method, and blow lamp\textsuperscript{[9]} [Table 1]. From all that methods in the present study, Kupipakwa method has been used for the preparation of Rasamanikya for minimum product loss and advantage of bulk preparation. The standard operating procedure for the preparation of Rasamanikya is based on the melting and self-cooling of orpiment.\textsuperscript{[10]}

A study has been carried out on analytical validation of Rasamanikya prepared by Abhraka Samputa method using Churnodaka (lime water) Shodhita Haratala.\textsuperscript{[11]} There was another study that emphasized the analytical aspect of Rasamanikya prepared by Sharava Samputa, Abhakra Patra Samputa, Valuka Yantra, and bulb method using Kushmanda Swarasa Shodhita Haratala.\textsuperscript{[12]} Likewise, another study was carried out on the pharmaceutico-analytical evaluation of Rasamanikya prepared by Abhakra Patra, Sharava Samputa, and bulb method from Churnodaka (lime water) and Kushmanda Swarasa (juice of Benincasa hispida [Thunb.] Cogn) Shodhita Haratala\textsuperscript{[13]} [Table 2].

One comprehensive study about various Shodhana media and six different methods of preparation concluded that Rasamanikya prepared by Kupipakwa method stands economical (least loss), less time-consuming, best in terms of reproducibility.\textsuperscript{[14]}

Kushmanda juice and lime water have been the most widely used reference media for the purification of orpiment.\textsuperscript{[15]} No study has been carried on the comparative study of these purification media with Kupipakwa method, the most economical way of Rasamanikya preparation. Still, large-scale production is difficult by well-established methods of Rasamanikya preparation. Correspondingly, Kupipakwa method was adopted for the study as a feasible, convenient method for large-scale production. This comparative pharmaceutical initiation may be further advantageous and open the window of additional scope for Ayurveda pharmaceutics and researcher. Hence, this study applied Swedana (sudation) method of Haratala Shodhana in Kushmanda juice and lime water and Kupipakwa method for preparation of Rasamanikya. This comparative pharmaceutico-analytical study is an attempt to develop a standard operative procedure for the most productive method of Rasamanikya preparation.

### Materials and methods

Ashuddha Haratala (impurified orpiment) and lime were procured from the Department of Rasashashtra and Bhaishajya Kalpana (RS and BK), Institute of Teaching and Research in Ayurved (ITRA), Jamnagar. Haratala was selected as per classical Grahyakovaksha.\textsuperscript{[20]} Kushmanda (B. hispida [Thunb.] Cogn) was purchased from local market of Jamnagar. Authentication of Kushmanda fruits was done through the expert of Pharmacognosy Laboratory of ITRA. Pharmaceutical procedures for the preparation of Rasamanikya were carried out at RS and BK department. Both final product samples were analyzed for organoleptic, physicochemical parameters at Pharmaceutical Laboratory, ITRA, Jamnagar. Sophisticated analysis (X-ray diffraction [XRD], Fourier transform infrared spectroscopy [FTIR], Inductively coupled plasma-atomic emission spectroscopy [ICP-AES], etc.) of final products of Rasamanikya has been carried out at the Department of Sophisticated Analytical Instrumental Facility and Metallurgical Engineering and Materials Science, Indian Institute of Technology Bombay.

### Shodhana of Haratala

Shodhana of orpiment was carried out by Swedana (sudation). Kushmanda juice was prepared with manual extraction (Nishpidana method).\textsuperscript{[21]} Lime water was prepared as per the reference of Rasatarangini (lime: water ratio, 1: 240).\textsuperscript{[22]} The small pieces of impure orpiment (Ashuddha Haratala) were tied in the four folded cotton cloth and immersed into the liquid media, i.e., Kushmanda juice and lime water separately. Continuous mild heating (85°C–90°C) was given for 3 h.\textsuperscript{[23]} After 3 h, cloth bundle (Pottali) was removed from liquid media and orpiment was taken out from cloth bundle. Then, it was washed three times with hot water. Treated liquid media and hot water were discarded by the landfilling method in a nonagricultural and noncommercial area. Then, it was subjected to dry in the open air. It was collected and stored in an airtight glass container. The purification of orpiment in both liquid media is shown in Figure 1 [Table 3].

### Preparation of Rasamanikya

Rasamanikya was prepared as per the reference of Rasa text Bharatiya Rasa Shashtra.\textsuperscript{[24]} In this reference, Valuka Yantra is used and corking is described for Rasamanikya preparation. A slightly modified method was adopted using an electric muffle furnace (EMF) as a heating device instead of Valuka Yantra like some previous studies in this direction.\textsuperscript{[14]} The Kacha Kupi (glass bottle) with three layers

---

**Table 1: Different methods of Rasamanikya preparation**

| Classical methods | Adopted method |
|-------------------|----------------|
| Haratala with Abhraka Patra Sharava Samputa method\textsuperscript{[16]} | Glass bulb method\textsuperscript{[9]} |
| Haratala with Abhraka Patra direct over coal\textsuperscript{[17]} | Antardhooma Kupipakwa method\textsuperscript{[9]} |
| Haratala directly kept in Sharava &Sharava Samputa done\textsuperscript{[9]} | Open Sharava method\textsuperscript{[14]} |
| - | Antardhooma Kupipakwa method\textsuperscript{[19]} |
of clay smear of cotton cloth (Kapadmitti) was filled with powder (#40) of purified orpiment (Shuddha Haratala). A filled glass bottle was kept in EMF. The temperature of EMF was settled at 400°C. After the complete melting of orpiment, Sheeta Shalaka test was found positive and then EMF was switched off. After self-cooling, a glass bottle was taken out from EMF and the layers of clay smear of cotton cloth were removed with the help of the knife. Afterward, kerosene oil-soaked cotton thread was tied one inch above the final product in the glass bottle. Then, the thread was ignited and allowed to burn completely and the sprinkling of water was done on ignited glass bottle to break the glass bottle. Final product was collected from the bottom of the glass bottle and stored in an airtight glass container after being triturated to fine powder. Complete melting of orpiment and formation of ruby red color product confirmed by the Sheeta Shalaka test was considered as an endpoint of the procedure. The standard operating procedure for the preparation of Rasamanikya in EMF was adopted from the previous research work.[25] Figures related to the preparation of Rasamanikya are depicted in Figure 2 [Table 4].

Analysis of raw drug (Ashuddha Haratala: Impurified orpiment and media used for purification), intermediate material (Shuddha Haratala: Purified orpiment) and final product (Rasamanikya)

Organoleptic (like color, taste, smell and touch) and physicochemical parameters (pH, specific gravity and total solid content) of purified orpiment and media used for purification were analyzed. Organoleptic parameters and physicochemical parameters (loss on drying, ash value, and acid-insoluble ash) of both samples of Rasamanikya were carried out.[26] Sophisticated instrumental analytical techniques such as XRD, ICP-AES, CHNS and O, Field emission gun-scanning electron microscopy (FEG-SEM), FTIR and Thermogravimetric analysis (TGA) of both samples of Rasamanikya were carried out.

Results and observations of pharmaceutical procedure

Boiling of media started within 20 min in Kushmanda juice and 15 min in lime water during the purification of orpiment. A sulfurous smell was felt after 20–25 min from both purification media. Color of orpiment converted into shiny yellow from dirty yellow and media converted into dark orange from the whitish green after the purification in Kushmanda juice media. [Table 5] Color of Haratala (orpiment) converted into dull yellow from dirty yellow and media converted into...
Table 2: Different media mentioned for Shodhana of Haratala

| Shodhana media       | Reference                                      |
|----------------------|------------------------------------------------|
| Churna Kanji         | Aanand Kanda, Kriyakaran (1/55-56)             |
| Kushmanda Swarasa    |                                                |
| Tila Taila           |                                                |
| Triphala Kashaya     |                                                |
| Musta                | Basavarajayam (25/116-118)                    |
| Kshara Jala          | Brihat Rasa Raj Sundar, p. 145                 |
| Godugdha             |                                                |
| Vatadugdha           |                                                |
| Shalmali Toya        |                                                |
| Tilakshara Jala      | Rasa Jala Nidhi part-2 2, p. 158-159          |
| Mahishamutra         |                                                |
| Kanya Swarasa        |                                                |
| Churnodaka + Musta Swarasa |                                 |
| Sarpunkha Swarasa    |                                                |
| Nimbu Swarasa + Water|                                                |
| Kokila Pakwa Ikshu Rasa |                                        |
| Kimshuka Kasundravra |                                                |
| Vata Praroha Swarasa | Rasa Kamdhenu (Dhatu Sangraha Pada) 4/64      |
| Brhmamulakrarta Kvatha|                                              |
| Gruhvari             | Rasa Tarangini 11/19-25                       |

Table 3: Equipment specifications for Haratala Shodhana

| Name of Equipment         | Dimension     | Capacity            |
|---------------------------|---------------|---------------------|
| Stainless steel vessel    | Depth 15.24 cm| 3 l                 |
|                           | Diameter 22 cm|                     |
|                           | Circumference 45.72 cm |             |
| Heating device            | Gas burner with L.P.G. cylinder | 14.5 kg capacity |
| Cotton cloth              | 1 x 1 meter   |                     |
| Thermometer               | -             | Mercury thermometer (0°C-360°C) |
| Rod                       | 12 cm         | Maximum : 2 l       |
| Measuring cylinder        | -             |                     |
| S. S. Tray                | 18.5 x 29.5   |                     |

whitish from yellowish after the purification in lime water media. An average 2.2 l and 2.4 l of Kushmanda juice and lime water were used for 500 g of Haratala, respectively [Table 5]. An average 0.9% and 1.1% loss were found in both the media, respectively [Table 5]. During preparation of both samples of Rasamanikya settled peak temperature, i.e., 400°C of EMF, was reached within 25 min. Melting of purified opiment started after 30 min. Complete melting of opiment was observed after 2 h of heating which was confirmed by Sheeta Shalaka test [Table 6 and Graph 1]. An average 1.58% w/w loss was observed during the pharmaceutical process of Rasamanikya prepared by Kushmanda Swarasa Shodhita Haratala (KSHRM). An average 1.83% w/w loss was observed during the pharmaceutical process of Rasamanikya prepared by Churnodaka Shodhita Haratala (CSHRM) [Table 7].

Results and observations of analytical study

The organoleptic parameters of media (i.e., Kushmanda juice and lime water) and impurified and purified opiment before and after purification are described in Tables 8 and 9. The organoleptic parameters of both samples of Rasamanikya are mentioned in Table 9. The physicochemical parameters of Shodhana media are presented in Table 10. The physicochemical parameters of impurified opiment, purified opiment and Rasamanikya are described in Table 11. Results of sophisticated analysis, i.e., XRD [Table 12], ICP-AES [Table 13], CHNSO [Table 14], FEG-SEM [Table 15, Figures 3 and 4], FTIR [Table 16] and TGA [Table 17] of both the samples, are tabulated. Hanawalt analysis and Fink method[27] of exploration of data of XRD pattern of a powder for comparison of samples were applied for evaluation of similarities and dissimilarities among diffraction pattern of different samples KSHRM and CSHRM.

Discussion

Rasamanikya is copiously used for the treatment of various ailments in Ayurveda. Shodhana is the prerequisite for any drugs used in Rasa Shastra. Purification of opiment is most important in an account of its safety and efficacy purpose in formulations containing arsenical in it. Kushmanda Swarasa with Jeeraka (Cuminum cyminum) and Sita (sugar candy) is given as an antidote for Haratala (opiment) toxicity in Rasa classics.[28] The major constituents of Benincasa hispida fruits were volatile oils, flavonoids, glycosides, saccharides, proteins, carotenoids, vitamins, minerals, β-sitosterin, and uronic acid.[29] A research study shows that flavonoids can flush out arsenic from the body.[30] The pH of lime water is highly alkaline. It might helped to remove alkaline-soluble impurities from the mineral.[31] Lime water is used primarily as a softening agent. As the pH is raised, the hydrogen ion concentration decreases, shifting the equilibrium toward the reactants and releasing arsenate to the solution. Calcium is enhancing the surface adsorption of arsenic onto the solids in solution. The reduction in arsenic leachability at higher pH values is most likely due to the divalent cation effect of calcium and not due to the formation of a calcium arsenate solid.[32] Average 2.2 l Kushmanda juice [Table 5] was sufficient for 500 g of impurified opiment for Swedana (sudation) process (3 h of duration) in 2.5 l capacity of cylindrical stainless steel vessel. Average 0.9% [Table 5] loss was observed during the process. Average 2.4 l Churnodaka (lime water) was sufficient for 500 g of impurified opiment for Swedana process (3 h of duration) in 2.5 l capacity of cylindrical stainless-steel vessel. Average 1.1% [Table 5] loss was observed during the process. The reason for loss after the process of purification may be due to the elimination of impurities from opiment. The salient principle in the preparation of Rasamanikya is melting of the ingredient and
self-cooling to get a settled product. The same aim is taken into consideration during Kupipakwa method. The melting point of orpiment (Haratala) is 300°C to 325°C.[33] Set temperature of EMF at 400°C was achieved within 25 min with the appearance of yellow fumes and white fumes while white fumes were observed within the initial 10 min. White fumes may be an indication of arsenical compounds. Orange tinge molten crystalline product was observed in the Sheeta Shalaka test after the complete melting of Haratala which indicates the compound formation. 98.42% yield of blackish ruby red product with KSHRM (Rasamanikya prepared by Kushmanda Swarasa Shodhita Haratala) and 98.17% yield of shiny ruby red product with CSHRM (Rasamanikya prepared by Churnodaka Shodhita Haratala) were obtained [Table 7]. The negligible loss was seen in the preparation by this method. The reason might be the absence of Krama Agni (increasing temperature pattern) in this modified method of Kupipakwa. Hence, there are fewer chances to lose material in the final product that is commercially cost-effective.

After Shodhana of orpiment in Kushmanda Swarasa pH of media was increased from 5.9 to 6.83 [Table 5]. After Shodhana of orpiment in Churnodaka, pH of media was decreased from 11.3 to 9.1. The maximum adsorption of arsenite (III) and arsenate (V) appears at pH values of 8 and 4, respectively. Minimum adsorptions of both are at pH 12 and their adsorptions increase again at higher pH values such as 13 and 13.5.[34] The absorption of arsenicals is largely dependent on the pKa values.[35] Absorption rates of arsenate and dimethylarsinic acid at pH 5.5 are much higher than those reported at pH 7.2, while the absorption rate of monomethyl arsenic acid was low for both pH 5.5 and pH 7.2.[36] Specific gravity and total solid content of media increased after the Shodhana process which indicates accumulation of impurities, concentration of media, and dissolution of arsenic and sulfur into the media as shown by approximately 1% loss of the product after Shodhana [Table 5]. The contents of organic and inorganic media in the preparation are also reflected in the loss on drying which was 1.14, 0.85, 0.02, 0.84, and 0.1 in ASH (Aushuddha Haratala), KSH (Kushmanda Shodhita Haratala), CSH (Churnodaka Shodhita Haratala), KSHRM, and CSHRM, respectively, which indicates the presence of the lesser amount of moisture with inorganic media (Churnodaka) than organic media (Kushmanda juice). The ash value was 0.34%, 0.39%, 0.42%, 1.74%, and 1.69% of ASH, KSH, CSH, KSHRM and CSHRM respectively, which indicates the fewer amount of inorganic material. Undetectable acid-insoluble ash in all samples indicates the absence of impurities and ready absorbability of the product in the gastric media.

The XRD graph of both samples of the Rasamanikya is zigzag which indicates loss of crystalline structure and acquiring amorphous form [Figure 3c, d and Figure 4a, c]. It is well acknowledged that at a higher temperature, arsenic sulfides loose crystallinity. Consequently, it has an unknown crystal structure which is confirmed from FEG-SEM images in the present study. Data of diffraction at the first 3 or 6 strongest intensity lines did not match exactly with each other, suggesting that the chemical composition and crystallite composition of both samples are different from each other suggesting a significant

---

### Table 4: Equipment specifications for Rasamanikya preparation

| Equipment | Specifications | Capacity |
|-----------|---------------|----------|
| Vertical EMF | Outer chamber - Thick mild steel powder coated | 750 ml |
| | Inner chamber - Inner ceramic board muffle placed vertical sideways silicon carbide rod heating elements and embedded with ceramic fibre to avoid heat loss. | |
| Kacha Kupi | L - 27.7 cm | |
| | Neck C - 8.5 cm | |
| | Middle C - 22.7 cm | |
| | Neck diameter - 1.6 cm | |

### Table 5: Observations & results of 4 batches of Haratala Shodhana by Kushmanda Swarasa & Churnodaka

| Batch | Ashuddha Haratala | Kushmanda Swarasa | Shuddha Haratala |
|-------|-----------------|------------------|-----------------|
|       | Wt. (g) | Color | Vol. (l) | pH before Shodhana | pH after Shodhana | Wt. (g) | % Yield | Color | Wt. (g) | % Yield | Color |
| I     | 500     | Dirty golden yellow | 2.2     | 5.9 | 6.83 | 497 | 99.4 | Shiny yellow |
| II    | 500     | Dirty golden yellow | 2.2     | 5.9 | 6.83 | 496 | 99.2 | Shiny yellow |
| III   | 500     | Dirty golden yellow | 2.2     | 5.9 | 6.83 | 494 | 98.8 | Shiny yellow |
| IV    | 500     | Dirty golden yellow | 2.2     | 5.9 | 6.83 | 495 | 99.0 | Shiny yellow |
| Avg.  | 500     | - | 2.2 | - | 495.5±1.291 | 99.1±0.258 | - |

**Churnodaka**

| I     | 500     | Dirty golden yellow | 2.4     | 11.3 | 9.1 | 493 | 98.6 | Dull yellow |
| II    | 500     | Dirty golden yellow | 2.4     | 11.3 | 9.1 | 496 | 99.2 | Dull yellow |
| III   | 500     | Dirty golden yellow | 2.4     | 11.3 | 9.1 | 494 | 98.8 | Dull yellow |
| IV    | 500     | Dirty golden yellow | 2.4     | 11.3 | 9.1 | 495 | 99 | Dull yellow |
| Avg.  | 500     | - | 2.4 | - | 494.5±1.291 | 98.9±0.258 | - |

Data: Mean±SD
Parekh, et al.: Rasamanikya preparation form two different Shodhana media of Haratala

AYU | Volume 41 | Issue 3 | July-September 2020

The crystallite size was calculated from XRD pattern following the Scherrer equation \( t = \frac{\lambda}{B \times \cos \theta} \times 0.94 \). Here, the crystallite size for \((h k l)\) plane, \(\lambda\) is the wavelength of the incident X-radiation (CuK\(\alpha\) [1.540598 Å]), \(B\) is the full width at half maximum in radians, and \(\theta\) is the diffraction angle for \((h k l)\) plane. The particle size of KSHRM and CSHRM was found to be 58.88 nm and 81.31 nm, respectively. Consequently, all samples have a maximum average particle size in the nano range confirmed as nanoparticles (below 100 nm).

In ICP-AES, the arsenic percentage was 59.05 and 58.37 in the samples of KSHRM and CSHRM, respectively [Table 13]. A decrease in the percentage of arsenic in KSHRM and CSHRM as compared with stoichiometric percentage of arsenic in orpiment is non-significant. Arsenic release in the
solution is affected by the pH. Introduction of more OH− ion into the solution or increasing the pH would result in a higher rate of dissolution.[37] Since the pH of Churnodaka is higher than Kushmanda juice, it might cause the leaching of more arsenic in the Shodhana process which is reflected later in the product. The presence of lead in both the test samples is within permissible limits. The presence of silica and magnesium in both samples may be due to the use of a glass bottle during the pharmaceutical procedure.

CHNS analysis is performed with inorganic material in the present study to determine the presence of any organic remains accumulated in the material during the pharmaceutical process. CHNS reveals that the percentage of sulfur was 33.368 and 47.783 in sample KSHRM and CSHRM, respectively [Tables 14 and Figure 3 a and b]. Upon stoichiometric analysis, 39% sulfur was present in Haratala (orpiment).[33] After the preparation of Rasamanikya, it was decreased in KSHRM and increased in CSHRM. This may be due to the heating process during the preparation of the final product, and a certain chemical reaction occurs with Shodhana media. Nitrogen and carbon were absent in both the samples. Complete absence of oxygen in both the samples of RM, i.e., KSHRM and CSHRM, denied the formation and presence of arsenic oxides, namely trivalent and pentavalent oxides, in RM which are comparatively more toxic. Probable oxides absent from both the samples may be oxides of Arsenic trioxides, (As2O3) 2 − group, (AsO3) 3 − group, (As2O5) 4 − group, arsenic (V) oxides, pharmacosiderite group, and uranyl arsenates.

FEG-SEM study reveals that the atomic percentage of As L in KSHRM was 89.65% and 89.59% in CSHRM. The weight

| Table 6: Observations during preparation of both the sample of Rasamanikya |
|---|---|---|
| Time (h:min) | Temp (°C) | Observations |
| 00:00 | 69 | Furnace started. |
| 00:10 | 283 | Mild white fumes started |
| 00:20 | 384 | Fumes increased |
| 00:25 | 402 | Yellow fumes started, more Sulfurous smell coming out |
| 00:30 | 406 | Melting started |
| 00:35 | 407 | Dense fumes were observed, orange tinge observed in Sheeta Shalaka |
| 01:00 | 409 | Melting continued |
| 01:15 | 406 | Mud like consistency |
| 01:30 | 403 | On Sheeta Shalaka test blackish color material observed |
| 01:45 | 404 | Fumes decreased |
| 02:00 | 403 | Complete melt, Sheeta Shalaka test positive. EMF switched off. |

| Table 7: Results of final products of Rasamanikya |
|---|---|---|---|---|
| Product | Batch | Wt. of Shuddha Haratala (g) | Weight of final product (g) | Yield after powdering (g) | % yield |
| KSHRM | I | 600 | 597.36 | 590.10 | 98.35 |
| II | 600 | 597.53 | 590.26 | 98.38 |
| III | 600 | 597.57 | 591.22 | 98.54 |
| Avg. | 600 | 597.49 | 590.47 | 98.42 |
| CSHRM | I | 600 | 597.32 | 589.12 | 98.19 |
| II | 600 | 592.26 | 587.89 | 97.98 |
| III | 600 | 595.78 | 590.04 | 98.34 |
| Avg. | 600 | 595.12 | 589.02 | 98.17 |

KSHRM-Rasamanikya prepared by Kushmanda Swarasa Shodhita Haratala, CSHRM-Rasamanikya prepared by Churnodaka Shodhita Haratala
percentage of As L was found to be 78.38% and 78.89% in samples of KSHRM and CSHRM, respectively [Table 15]. The As/Ca molar ratio in lime water might play an important role in the arsenic sulfide stabilization and affect its leaching behavior as used in prelandfilling waste management. [38] SEM images were taken at magnification of ×2500, ×5000, ×10000, ×25000, ×50000, ×750000, and ×100,000 with 10.0 kv voltage and sample width of 5.9–6 mm. Images of both the samples

### Table 8: Organoleptic characteristics of Shodhana media

| Characters | Kushmanda Swarasa Before Shodhana | After Shodhana | Churnodaka Before Shodhana | After Shodhana |
|------------|----------------------------------|----------------|---------------------------|----------------|
| Color      | Greenish white                   | Dark orange    | Whitish                   | Yellowish      |
| Taste      | Sweet                            | Tasteless      | Tasteless                 | Tasteless      |
| Odour      | Specific                         | Sulfurous      | Odorless                  | Sulfurous      |
| Touch      | Mild sticky                      | Watery         | Glossy soft               | Touch          |

### Table 9: Organoleptic characteristics of Haratala & Rasamanikya

| Characters | AH - Ashodhita Haratala | KSH - Kushmanda Swarasa Shodhita Haratala | CSH - Churnodaka Shodhita Haratala | KSHRM - Rasamanikya prepared by Kushmanda Swarasa Shodhita Haratala, CSHRM - Rasamanikya prepared by Churnodaka Shodhita Haratala |
|------------|-------------------------|------------------------------------------|-----------------------------------|---------------------------------------------------------------|
| Color      | Dirty golden yellow     | Shiny yellow                             | Dull yellow                       | Blackish Ruby color                                          |
| Taste      | -                       | Tasteless                                | Tasteless                        | Tasteless                                                    |
| Odour      | Slight Irritable Odour  | Sulfurous Smell                          | More irritable sulfurous smell   | Odorless                                                     |
| Touch      | In layers rough in touch| In layers soft in touch                  | In layers soft in touch           | Glossy soft in touch                                         |

### Table 10: Physico-chemical parameters of Shodhana media

| Parameters          | Kushmanda Swarasa Before Shodhana | After Shodhana | Churnodaka Before Shodhana | After Shodhana |
|---------------------|----------------------------------|----------------|---------------------------|----------------|
| pH                  | 5.9                              | 6.83           | 11.3                      | 9.1            |
| Specific gravity    | 1.0148                           | 1.03024        | 1.0045                    | 1.005199       |
| Total solid content (%) | 0.1249                       | 1.23           | 0.0098                    | 1.25           |

### Table 11: Physico-chemical parameters of Haratala and Rasamanikya

| Parameters          | AH - Ashodhita Haratala | KSH - Kushmanda Swarasa Shodhita Haratala | CSH - Churnodaka Shodhita Haratala | KSHRM - Rasamanikya prepared by Kushmanda Swarasa Shodhita Haratala, CSHRM - Rasamanikya prepared by Churnodaka Shodhita Haratala |
|---------------------|-------------------------|------------------------------------------|-----------------------------------|---------------------------------------------------------------|
| Loss on drying      | 1.14                    | 0.85                                     | 0.02                             | 0.84                                                        |
| Ash Value (%w/w)    | 0.34                    | 0.39                                     | 0.42                             | 1.74                                                        |
| Acid insoluble ash (%w/w) | Nil                | Nil                                      | Nil                              | Nil                                                         |

### Table 12: Honawalt analysis and Fink method for differentiation of XRD pattern of first strongest 6 intensity lines

| 2θ (°) | Int (%) | D spacing | 2θ (°) | Int (%) | D spacing |
|--------|---------|-----------|--------|---------|-----------|
| 55.3297| 100.0   | 1.65906   | 17.6805| 100.00  | 5.01652   |
| 32.8980| 92.41   | 2.72035   | 37.1684| 73.15   | 2.41902   |
| 17.9604| 39.80   | 4.93895   | 82.4539| 14.92   | 1.16978   |
| 26.7569| 35.52   | 3.33188   | 36.0774| 14.55   | 2.48963   |
| 83.9043| 13.86   | 1.15226   | 55.6987| 11.24   | 1.65030   |
| 47.3699| 2.82    | 1.91915   | -      | -       | -         |

KSHRM - Rasamanikya prepared by Kushmanda Swarasa Shodhita Haratala, CSHRM - Rasamanikya prepared by Churnodaka Shodhita Haratala
suggest that samples are non-crystalline. They are foliated like multiple sheets clumped together and few agglomerates can be seen. There is a very wide range of variations in the size of particles/agglomerates. Both the samples have surface defects in the form of holes which looks like abrupt cooling of boiling sample. KSHRM is comparatively more foliated, regularly arranged sheets like particles along with holes at the surface which are hexagonal. CSHRM showed acicular, needle-shaped crystals at × 75000 magnification [Figure 4].

Fourier transform infrared spectroscopy (FTIR) was performed to detect the presence of functional groups or organic legends in Rasamanikya. An FTIR spectrum of Rasamanikya is taken in the region of 3700-450 cm⁻¹. A general overview of Rasamanikya indicates the presence of a large number of functional groups. Total 8 peaks were obtained in sample of KSHRM and 7 peaks obtained in the sample of CSHRM. Total 3 peaks were obtained in hydrogen stretching region in both the samples. No peaks were observed in any of the samples in triple-bond region (2700–1950 cm⁻¹) which indicate the absence of a highly complex structure. The carbonyl stretching vibration is characterized by absorption through double-bond region (1950 and 1550 cm⁻¹). Both samples had one peak in the double-bond region. Alkene, alcohol, and phenol groups were found in the both samples. Carboxylic acid and derivative groups were found only in KSHRM sample and alkyne group was not found in KSHRM sample. Accordingly, FTIR analysis strongly suggests the presence of many functional groups in both samples [Table 16].

An increasing pattern of temperature at the rate of 5/min was adopted for TGA, and the maximum temperature given was 422. Up to 332°C mass loss was almost the same in both the sample but altered later on [Figure 3e and f]. Organic contents were present in KSHRM, so organo-arsenic compounds may cause more stability of the compound.[30] Pharmacologically also data supported with more product yield were found in KSHRM [Table 17]. As delta values of both the samples are different [Figure 3e and f]. Only one value of delta Y was observed in the curve which confirms that only one distinct event took place in both samples. This may be caused by

| Table 13: Inductively coupled plasma-atomic emission spectroscopy analysis of two samples of Rasamanikya (% in ppm) |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| Sample                          | Mg (%)          | Pb (%)          | As (%)          | Si (%)          |
| KSHRM                           | 0.019           | 0.00043         | 59.05           | 0.023           |
| CSHRM                           | 0.0047          | 0.00082         | 58.37           | 0.079           |

| Table 14: CHNSO analysis of two samples of Rasamanikya |
|---------------------------------|---------|---------|---------|---------|
| Element                         | Nitrogen | Hydrogen | Sulphur | Carbon | Oxygen |
| KSHRM                           | Nil     | Nil     | 33.368  | Nil    | Nil    |
| CSHRM                           | Nil     | 0.036   | 47.783  | Nil    | Nil    |

| Table 15: Field emission gun-scanning electron microscopy analysis of two samples of Rasamanikya |
|---------------------------------|---------|---------|---------|---------|
| Element                         | KSHRM   | CSHRM   |---------|---------|
| Mg K                            | Weight %| Atomic %| Weight %| Atomic %|
| Sil K                           | 0.00    | 0.00    | 0.00    | 0.00    |
| As L                            | 0.54    | 1.64    | 0.67    | 2.02    |
| Pb M                            | 78.38   | 89.65   | 78.89   | 89.59   |
| Totals                          | 100.00  | -       | 100.00  | -       |

| Table 16: Fourier transforms infrared spectroscopy analysis of Rasamanikya prepared by Kushmanda Swarasa Shodhita Haratala and Rasamanikya prepared by Churmodaka Shodhita Haratala |
|---------------------------------|---------|---------|
| Functional class                | Range (nm) |          |
| Alcohols & Phenols              | 3200-3550 | 3427.03  |
|                                |          | 3434.19  |
|                                |          | O-H (H-bonded), usually broad |
| Alkanes                         | 2850-3000| 2924.70, 2853.94| 2922.93, 2853.06|
|                                |          | CH3, CH2& CH2 or 3 bands |
|                                |          | C=C (symmetry reduces intensity |
|                                |          | C-O    |
|                                |          | O-C (sometimes 2-peaks) |
|                                |          | C-H deformation |
| Alkanes                         | 1630-1680| 1631.30  |
|                                |          | 1629.60  |
|                                |          | - |
| Carboxylic Acids & Derivatives  | 1210-1320| 1316.19  |
|                                |          | - |
| Alcohols & Phenols              | 970-1250 | 1033.48  |
|                                |          | 1117.59, 1022.10 |
|                                |          | - |
| Alkenes                         | 880-995  | 968.62   |
|                                |          | 601.47   |
|                                |          | - |
| Alkynes                         | 600-700  | 586.18   |
|                                |          | - |

| KSHRM – Rasamanikya prepared by Kushmanda Swarasa Shodhita Haratala, CSHRM – Rasamanikya prepared by Churmodaka Shodhita Haratala |
Table 17: Temperature and weight changes observed in TGA analysis of Rasamanikya

| Sample Name | Initial temp (°C) | Initial wt. (%) | Final wt. (%) | % loss | Final temp (°C) | Max microvolt endo down (μv) |
|-------------|------------------|----------------|--------------|---------|----------------|---------------------------|
| KSHRM       | 38               | 99.944         | 25.773       | 74.171  | 433            | 45.861                    |
| CSHRM       | 37               | 99.929         | 18.489       | 81.44   | 422            | 25.054                    |

KSHRM - Rasamanikya prepared by Kushmanda Swarasa Shodhita Haratala, CSHRM - Rasamanikya prepared by Churnodaka Shodhita Haratala

chemical reactions (decomposition and loss of water of crystallization, combustion, and reduction of metal oxides) or physical transitions (vaporization, evaporation, sublimation, desorption and drying). Therefore, their enthalpies are different suggesting a change of chemical composition which is supported with altered graphs of the change in microvolt endo down concerning temperature and time among both the samples [Figure 3e and f]. There is also a change in total mass as well as the pattern of mass loss concerning temperature and time among CSHRM and KSHRM. TGA data of these two samples indicated a significant difference in their chemical nature as well as in their chemical properties.

Conclusion
Rasamanikya prepared by two different media Shodhita Haratala (Kushmanda Swarasa Shodhita and Churnodaka Shodhita) do not have considerable difference at the pharmaceutical level. Significant analytically differences were found in these samples of Rasamanikya. Changes in the pH of both media during Shodhana suggest changes in the adsorption and absorption properties of orpiment. Variation in the percentage of sulfur and arsenic in CHNS and FEG-SEM analysis from their stoichiometric equivalent showed that both media act differently on the orpiment. In XRD and FEG-SEM analysis, both samples have different diffraction patterns and crystal structures. Nanoparticles of KSHRM were found to be 58.88 nm and 81.31 nm in CSHRM, respectively. In FTIR analysis, Rasamanikya prepared by Kushmanda Swarasa Shodhita Haratala has an additional functional group, i.e., carboxylic acid due to interaction with organic media (Kushmanda Swarasa). A non-significant difference was found in arsenic percentage from both samples in ICP-AES and FEG-SEM elemental analysis. In CHNSO analysis, the percentage of sulfur was found more in CSHRM owing to the alkaline role of media. Kupipakwa procedure with EMF produced 98.42% product in KSHRM and 98.17% in CSHRM which is commercially cost-effective and can be used for large-scale preparation.

Financial support and sponsorship
This study was financially supported by the IPGT and RA, GAU, Jamnagar.

Conflicts of interest
There are no conflicts of interest.

References
1. Mishra S, editor. Rasendrachintamani of Acharya Dhundhuknath, Kushtarogadhikara. Ch. 9, Ver. 128-131. 11th ed. Varanasi: Choukhamba Orientalia; 2011. p. 376.

2. Department of AYUSH, Ministry of Health and Family Welfare, Government of India, Essential Drugs List (EDL), March 2013. Available from: http://www.indianmedicine.nic.in [Last accessed on 2019 Aug 08].

3. Shashtri K, editor. Rasatarangini of Shadanand Sharma. Ch. 11, Ver. 88-89. 11th ed., Varanasi: Motilal Banarasidas Publication; 1979, p. 257.

4. Mishra S, editor. Rasendra Chinntamani of Acharya Dhundhuknath, Kushtarogadhikara. Ch. 9, Ver. 128-31. 11th ed. Varanasi: Chaukhamba Disentilation; 2011. p. 376.

5. Kalkarni DK, editor. Rasa Ratna Samucchya of Vagbhatta. Ch. 3, Ver. 1. Reprint ed. New Delhi: Meharchanda Lakshmandas Publicacion; 2010. p. 42.

6. Shah PK, Singh LB, Vaishnav PU, Kalsaria B. A critical review about Haratala (orpiment). J Ayurveda Integr Med Sci 2017;2:185-9. https://www.myresearchjournal.com/index.php/JAIMS/article/view/7725 [Last accessed on 2021 Sept. 16].

7. Rai P, Kumar N, Singh RS. Role of Media in the Pharmaceutical Processing of Krishna Vajra Abhraka – A Fourier Transmission Infrared Spectroscopy Study (FTIR). Biomed Pharmacol J 2009;2:73-8. https://biomedpharmajournal.org/vol2no1/role-media-in-the-pharmaceutica-processing-of-krishna-vajra-abhraka-a-fourier-transmission-infrared-spectroscopy-study-flir [Last accessed on 2021 Sept. 16].

8. Maurya SK, Seth A, Laloo D, Singh NK, Gautam DN, Singh AK. Sudhana: An Ayurvedic process for detoxification and modification of therapeutic activities of poisonous medicinal plants. Anc Sci Life 2015;34:188-97. https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4535066 [Last accessed on 2021 Sept. 16].

9. Anandakat HA, Sharma HS. Pharmaceutico clinical study of Rasamanikyam resulting its efficacy on Kshudrakushthas, MD Dissertation. Ch. 3, Part 1. Jamnagar: Dept. of Rasashastra, Gujarat Ayurved University; 1988. p. 67.

10. Shashtri K, editor. Rasatarangini of Shadanand Sharma. Ch. 11, Ver. 5. 11th ed. Varanasi: Motilal Banarasidas Publication; 2011. p. 244.

11. Gaidhani SN, Singh A, Lagad CE, Kumari S, Lavekar G, Padhi MM, et al. Validation and quality assessment of Rasamanikya – A classical herbo-mineral preparation. J Sci Ind Res 2011;70:871-4. http://onlin.nic.in/res.in/bitstream/123456789/12683/1/JSIR%2070%2810%29%20871‑874.pdf [Last accessed on 2021 Sept. 16].

12. Hariprasad M, Ranjeet S, Bhingare SD. Comparative study of Rasamanikya (An Ayurvedic formulation) with purified Haratala (Orpiment). IJRAP 2011;2:363-8. https://www.researchgate.net/publication/285735148 [Last accessed on 2021 Sept. 16].

13. Sud S, Sudheendra H, Sujatha K, Reddy PS. A comparative pharmaceutico-analytical evaluation of Rasamanikya prepared with three different methods. IJRAP 2011;2:1651-4. https://www.researchgate.net/publication/235908356 [Last accessed on 2021 Sept. 16].

14. Srimannarayana K, Patgiri BJ, Prajapati PK. Process standardization of Rasamanikya. AYU 2010;31:7-11. https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3215326 [Last accessed on 2021 Sept. 16].

15. Biradar S, Ruikdkin G, Prajapati PK. Haratala Shodhana – A review through Rasas Classics. Glob J Res Med Plants Indig Med 2016;5:107-13.

16. Shashtri K, editor. Rasatarangini of Shadanand Sharma. Ch. 11, Ver. 83-89. 11th ed. Varanasi: Motilal Banarasidas Publication; 1979, p. 257.

17. Shashtri K, editor. Rasatarangini of Shadanand Sharma. Ch. 11, Ver. 19. 11th ed. Varanasi: Motilal Banarasidas Publication; 1979, p. 258.

18. Dwivedi V. Bharatiya Rasashtra. 2nd ed. Datiya: Sharma Ayurveda Mandira; 1987. p. 299.

19. Pandey R, editor. Rasendra Sara Samgraha by Gopalakrishna Bhatta. Ch. 1, Ver. 191-194. Reprint ed. Delhi: Chaukhamba Sanskrit Pratishtha;
