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

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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 *Kushtha Roga* (skin diseases), *Shwasa* (asthama), *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

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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

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Revised: 13-Feb-2020 **Published:** 24-Feb-2022 suitable for further processing.^[7] Specific media has an important role in rendering a drug therapeutically active without causing side effects/adverse effects.^[8] 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^[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.^[10]

A study has been carried out on analytical validation of *Rasamanikya* prepared by *Abhraka Samputa* method using *Churnodaka* (lime water) *Shodhita Haratala*.^[11] There was another study that emphasized the analytical aspect of *Rasamanikya* prepared by *Sharava Samputa*, *Abhraka Patra Samputa*, *Valuka Yantra*, and bulb method using *Kushmanda Swarasa Shodhita Haratala*.^[12] Likewise, another study was carried out on the pharmaceutico-analytical evaluation of *Rasamanikya* prepared by *Abhraka Patra*, *Sharava Samputa*, and bulb method from *Churnodaka* (lime water) and *Kushmanda Swarasa* (juice of *Benincasa hispida* [Thunb.] Cogn) *Shodhita Haratala*.^[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.^[14]

Kushmanda juice and lime water have been the most widely used reference media for the purification of orpiment.^[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

Different methods				
Classical methods	Adopted method			
Haratala with Abhrakha Patra Sharava Samputa method ^[16]	Glass bulb method ^[9]			
Haratala with Abhrakha Patra direct over coal ^[17]	<i>Antardhooma Kupipakwa</i> method ^[18]			
Haratala directly kept in Sharava &Sharava Samputa done ^[9]	Open <i>Sharava</i> method ^[14]			
-	Antardhooma Kupipakwa method ^[19]			

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 Grahya Lakshana.^[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).[21] Lime water was prepared as per the reference of Rasatarangini (lime: water ratio, 1: 240).^[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.^[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.^[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.^[14] The *Kacha Kupi* (glass bottle) with three layers

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].



Figure 1: *Haratala Shodhana.* (a) Unripe *Kushmanda* fruit (b) Grinding of unpeeled *Kushmanda* in mixture grinder (c) Paste was taken in cotton cloth and pressed, juice was collected (d) Mixing of *Churna* (lime) and water (e) *Churnodaka* was filtered through four folded cotton cloth (f) *Ashuddha Haratala* (g) Pounding of *Ashuddha Haratala* in *Khalwa Yantra* (h) Four folded *Pottali* with *Ashuddha Haratala* (i) *Pottali* was dipped in to *Kushmanda Swarasa* and *Swedana* was done in *Dolayantra* (j) Washing of *Haratala* with hot water (k) Washing for three times (I) Then dried

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



Figure 2: Preparation of *Rasamanikya* (a) Powder of *Shuddha Haratala* (b) Filling of glass bottle (c) Yellowish fumes observed, Accumulation of sulfur on neck of *Kupi* (d) Melting of *Haratala* (e) Positive *Sheeta Shalaka* test (f) Breaking of *Kupi* (g) *Rasamanikya* in *Kupi* (h) *Rasamanikya*

Table 2: Different media mentioned for Shodhana of Haratala

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

Table 3: Equipment specifications for Haratala Shodhana

Name of Equipment	Dimension		Capacity
Stainless steel	Depth	15. 24 cm	3 <i>l</i>
vessel	Diameter	22 cm	
	Circumference	45.72 cm	
Heating device	Gas burner with cylinder	L.P.G.	14.5 kg capacity
Cotton cloth	1 x 1 meter		
Thermometer	-		Mercury thermometer (0°C-360°C)
Rod	12 cm		
Measuring cylinder	-		Maximum : 2 <i>l</i>
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 orpiment started after 30 min. Complete melting of orpiment 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 orpiment 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 orpiment, purified orpiment 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 orpiment 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 (orpiment) toxicity in Rasa classics.^[28] The major constituents of Benincasa hispida fruits were volatile oils, flavonoids, glycosides, saccharides, proteins, carotenes, 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 2.21 Kushmanda juice [Table 5] was sufficient for 500 g of impurified orpiment 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 1 Churnodaka (lime water) was sufficient for 500 g of impurified orpiment 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 orpiment. 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

Equipment	Specifications	Capacity
Vertical EMF	Outer chamber - Thick mild steel powder coated	-
	Inner chamber - Inner ceramic board muffle placed vertical sideways silicon carbide rod heating elements and embedded with ceramic fibre to avoid heat loss.	
	O; L=40.5 cm, B=40.5 cm, H=50.5 cm	
	I; L=14 cm, B=14 cm, D=29 cm	
Kacha Kupi	L- 27.7 cm	750 ml
	Neck C- 8.5 cm	
	Middle C- 22.7 cm	
	Neck diameter- 1.6 cm	

Table 4: Equipment specifications for *Rasamanikya* preparation

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 arsonic 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 (Ashuddha 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 5: Observations & results of 4 batches of Haratala Shodhana	y Kushmanda Swarasa & Churnodaka
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Batch Ashuddha Haratala		uddha Haratala		Kushmanda Swa	nrasa	S	huddha Harata	ala
	Wt. (g)	Color	Vol. (l)	pH before Shodhana	pH after Shodhana	Wt. (g)	% Yield	Color
Ι	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	-
				Churnodak	а			
Ι	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

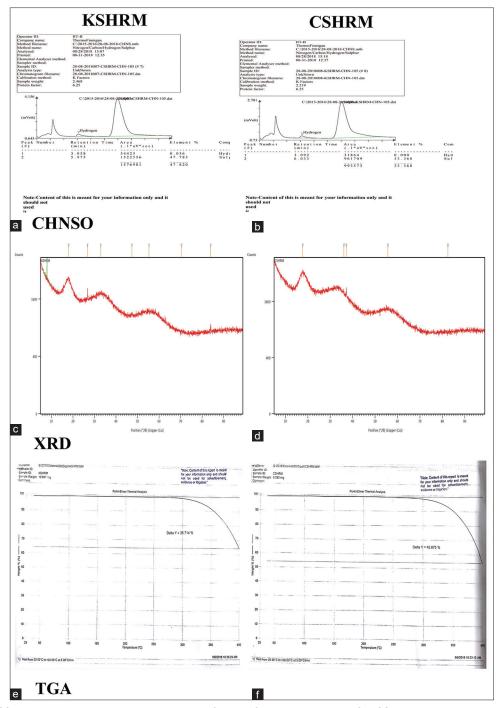


Figure 3: (a) CHNSO of Rasamanikya prepared with Kushmanda Swarasa Shodhita Haratala. (b) CHNSO of Rasamanikya prepared with Churnodaka Shodhita Haratala. (c) XRD analysis of Rasamanikya prepared with Kushmanda Swarasa Shodhita Haratala. (d) XRD analysis of Rasamanikya prepared with Churnodaka Shodhita Haratala. (e) TGA of Rasamanikya prepared with Kushmanda Swarasa Shodhita Haratala. (f) TGA of Rasamanikya prepared with Churnodaka Shodhita Haratala. (f) TGA of Rasamanikya prepared with Churnodaka Shodhita Haratala.

change in the chemical constitution of samples [Table 12]. The crystallite size was calculated from XRD pattern following the Scherrer equation $t = \lambda \times 0.94/(\beta \times \cos\theta)$. Here, the crystallite size for (h k l) plane, λ is the wavelength of the incident X-radiation (CuK α [1.540598 A]), β is the full width at half maximum in radians, and θ 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

 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 <i>Sheeta Shalaka</i>
01:00	409	Melting continued
01:15	406	Mud like consistency
01:30	403	On <i>Sheeta Shalaka</i> test blackish color material observed
01:45	404	Fumes decreased
02:00	403	Complete melt, <i>Sheeta Shalaka</i> test positive. EMF switched off.

oxides, in RM which are comparatively more toxic. Probable oxides absent from both the samples may be oxides of Arsenic trioxides, (As2O4) 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

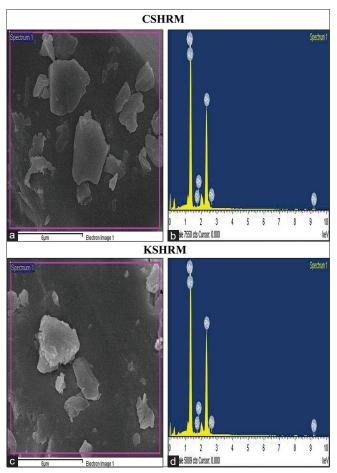


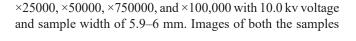
Figure 4: (a) FEG-SEM (Crystal structure) analysis of *Rasamanikya* prepared with *Churnodaka Shodhita Haratala*.(b) FEG-SEM analysis of (elements) *Rasamanikya* prepared with *Churnodaka Shodhita Haratala*. (c) FEG-SEM (Crystal structure) of *Rasamanikya* prepared with *Kushmanda Swarasa Shodhita Haratala*. (d) FEG-SEM (elements) of *Rasamanikya* prepared with *Kushmanda Swarasa Shodhita Haratala*.

Table 7: R	Table 7: Results of final products of <i>Hasamanikya</i>						
Product	Batch	Wt. of Shuddha Haratala (g)	Weight of final product (g)	Yield after powdering (g)	% yield		
KSHRM	Ι	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	Ι	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,

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



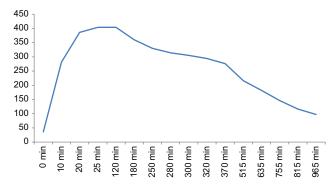




Table 9:	Organoleptic	characteristics	of Haratala	&	Rasamanikya

Characters	AH	KSH	CSH	KSHRM	CSHRM
Color	Dirty golden yellow	Shiny yellow	Dull yellow	Blackish Ruby color	Shiny Ruby red
Taste	-	-	-	Tasteless	Tasteless
Odour	Slight Irritable Odour	Slight sulphurous smell	More irritable sulphurous smell	Odorless	Odorless
Touch	In layers rough in touch	In layers soft in touch	In layers soft in touch	Glossy soft in touch	Glossy soft in touch

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

Table 10: Physico-chemical parameters of Shodhana media					
Parameters	Kushmand	a Swarasa	Churnodaka		
	Before Shodhana	After Shodhana	Before Shodhana	After Shodhana	
рН	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	KSH	CSH	KSHRM	CSHRM
Loss on drying	1.14	0.85	0.02	0.84	0.01
Ash Value (%w/w)	0.34	0.39	0.42	1.74	1.69
Acid insoluble ash (%w/w)	Nil	Nil	Nil	Nil	Nil

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

Table 12: Honawalt analysis and Fink method for differentiation of XRD pattern of first strongest 6 intensity lines					
	KSHRM			CSHRM	
° 2 θ	Int (%)	D spacing	° 2 θ	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

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

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

Table 14: CHNSO analysis of tw	o samples of <i>Rasamanikva</i>
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Element	Nitrogen %	Hydrogen %	Sulphur %	Carbon %	Oxygen %
KSHRM	Nil	Nil	33.368	Nil	Nil
CSHRM	Nil	0.036	47.783	Nil	Nil
WOUDD (D :1	11 72	1 1 0	C1	11

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

Table 15: Field emission gun-scanning electron microscopy analysis of two samples of *Rasamanikya*

Element	KSH	IRM	CSHRM		
	Weight %	Atomic %	Weight %	Atomic %	
Mg K	0.00	0.00	0.00	0.00	
Si K	0.54	1.64	0.67	2.02	
As L	78.38	89.65	78.89	89.59	
Pb M	21.08	8.72	20.45	8.40	
Totals	100.00	-	100.00	-	

KSHRM - Rasamanikya prepared by Kushmanda Swarasa Shodhita Haratala, CSHRM - Rasamanikya prepared by Churnodaka Shodhita Haratala 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.^[39] Pharmaceutically 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 16: Fourier transforms infrared spectroscopy analysis of *Rasamanikya* prepared by *Kushmanda Swarasa Shodhita* Haratala and Rasamanikya prepared by *Churnodaka Shodhita Haratala*

Functional class	Range (nm)	KSHRM	CSHRM
Alcohols & Phenols	3200-3550	3427.03	3434.19
		O-H (H-bonde	d), usually broad
Alkanes	2850-3000	2924.70, 2853.94	2922.93, 2853.06
		CH3, CH2&	CH2 or 3 bands
Alkanes	1630-1680	1631.30	1629.60
		C=C (symmetry	reduces intensity
Carboxylic Acids &	1210-1320 (acids)	1316.19	-
Derivatives		O-C (somet	imes 2-peaks)
Alcohols & Phenols	970-1250	1033.48	1117.59, 1022.10
		(C-O
Alkanes	880-995	968.62	-
		=С-Н	& =CH2
Alkynes	600-700	-	601.47
		C-H de	formation
Unknown	-	586.18	-

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

Comple Name Initial terms (%) Initial $ut (0)$ Final $ut (0)$ 0/ loss Final terms (%)	
Sample Name Initial temp (°c) Initial wt. (%) Final wt. (%) % loss Final temp (°c) N	Max microvolt endo down (μ v)
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).^[40] 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.

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Conflicts of interest

There are no conflicts of interest.

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206

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