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Characterization and comparative physico-chemical studies of Manahshila (traditionally used arsenic mineral) and the corresponding polymorphs of realgar (As_4S_4)

Vinamra Sharma[1,*], Amiya K. Samal[2], Anand K. Chaudhary[1] and Rajesh K. Srivastava[2]

[1]Department of Rasa Shastra, Faculty of Ayurveda, Institute of Medical Sciences, and
[2]Centre of Advanced Study in Geology, Institute of Science, Banaras Hindu University, Varanasi 221 005, India

This communication presents characterization and comparison of the physico-chemical properties of different varieties of Manahshila with the corresponding polymorphs of realgar. Three varieties of Manahshila have been described in Ayurveda, viz. Shyamangi, Kanavirak and Khandakhya; the last two are acceptable therapeutically. Khandakhya contains high percentage of arsenic than Kanavirak. In this study, both samples of Manahshila have been collected. Their physical and chemical properties have been correlated with the polymorphs of realgar. XRD study classifies Kanavirak as alacranite and Khandakhya as realgar. EDXA study confirms 51.33% and 68.14% of arsenic in alacranite and realgar samples respectively. This work correlates the ancient description of Manahshila with contemporary mineralogical classification (polymorphs) of mineral realgar.

Keywords: Alacranite, Manahshila, physico-chemical studies, polymorphs of realgar, mineralogical classification.

REALGAR (red arsenic – an arsenic-containing mineral drug) has long been used in traditional Indian medicines for the treatment of diseases of respiratory and digestive systems, skin diseases, psychological disorders and certain eye disorders[1–3]. Recently, it has been demonstrated that it is clinically effective for the treatment of patients with refractory or relapsed acute promyelocytic leukaemia (APL) and other hematopoietic malignancies[4–6]; this has given rise to an upsurge of research on its oldest to newest forms. Generally, inorganic realgar is highly toxic and carcinogenic[7,8]; however, Ayurveda has emphasized that a strong poison may be converted into a safe and potent therapeutic drug by applying specific pharmaceutical processes as described in the Ayurvedic literature (e.g. shodhana, marana, etc.)[9]. The drug Manahshila, one of the arsenicals, has been identified as realgar due to its similar chemical and physical properties. Ayurveda has advocated proper method of shodhana (purification and detoxification from the unwanted elements by intervention

*For correspondence. (e-mail: dr.vinamrasharma@gmail.com)

Table 1. Description of mineral Manahshila from an Ayurvedic perspective

Category	Details	
Broadly classified group	Uparasa	
Acceptable characters	Devoid of stone, easily powdered, heavy in weight, red similar to the colour of lotus flower with shining luster.	
Shodhana	Process	Method
	Bhavana (levigation)	With Ardraka/Agasthya Patra Swarasa/Bringharaja/Matulunga Swarasa for seven times
	Swedana (boiling under liquid bath)	(a) In Dola Yantra with Churnodaka/goat urine for three days (b) With Bringharaja Swarasa for 12 h
Therapeutic uses	Agnimandya (digestive impairment), anaha (distension of abdomen due to obstruction to passage of urine and stools), kasa (cough), svasa (asthma), kshaya (phthisis), kandu (itching), bhuta badha (psychological disorders), bhuta upadrava (microbial infection) and jvara (fever).	
Dose	5.0–7.5 mg	
Adverse effects due to administration of unpurified Manahshila	Mandagni (digestive impairment), ashmari (renal calculi), malavishtambhakari (constipation), mutrakriccha (painful micturation), mutradaha (burning micturation), mutorodha (obstructed micturation).	
Antidote	Oral administration of Madhu (honey) and Godugdha (cow's milk) for three days	
Formulation	Internal use	Shwasakutthar rasa, trilokyachintamani rasa, kshayakesari rasa, manashiladhi ghrita, rasarajarasa mrutasanjeevani rasa, kalagnibhairava rasa and shilasinduram
	External use – used as anajan (collyrium) or lepa (external application)	For eye disorders – Manashil anjana/varti and candrodaye varti. For tropical application – paradadi lepa and tutthadi lepa for upadamsha roga (Syphilis/soft chancre/chancroid)

of some herbal juices or inorganic liquid media) before recommending it for therapeutic purposes[10]. However, the collection of genuine sample is prerequisite for desired therapeutic efficacy of any substance.

In ancient Indian alchemy, Manahshila has been described as an orange–red crystalline mineral categorized under the category of uparasa (a group of mineral drugs)[11]. More than 40 compound formulations for internal and external administration have been mentioned in the Ayurvedic formulary of India, in which Manahshila is used as a major ingredient[12,13] (Table 1). It is considered as one of the best rasayana drugs/rasayanaagrah[2] (best nutrient to body and mind with adaptogenic, neuroenhancing and immuno-endocrino modulator properties). Texts written after the 12th century AD provide a detailed description of Manahshila[14,15]. Most authors have identified three varieties of Manahshila, viz. shyamangi, kanavirak and khandakhya (Table 2); each has its own specific physical properties. The last two varieties display properties of shining red-coloured crystals, devoid of external impurity, heavy in weight and easily powdered[16]. Therapeutically, it is always recommended for its use only after purification process[17]. On the other hand, in contemporary science, three polymorphs (having similar chemical structure with different crystalline bonds of the atoms) of realgar (As_4S_4) have been identified[18] (Table 3), which match with the description of Manahshila described in the ancient rasa shastra (metal–mineral medicines) texts.

It is customary to use all the varieties of Manahshila by the name of realgar; however, this is not true in all cases. Thus, this study compares characteristics of different varieties of Manahshila with the corresponding polymorphs of realgar. Two samples of Manahshila collected in the present study (Figure 1), were characterized using X-ray diffraction (XRD), energy diffraction X-ray analysis (EDXA), and scanning electron microscopy (SEM) to fulfil the primary objective of the study. This work will also be helpful to recognize authentic samples of Manahshila using the current perspectives.

Two samples of Manahshila, identified according to characteristics as explained in Ayurveda were collected from the Department of Rasa Shastra, Faculty of Ayurveda, Institute of Medical Sciences, Banaras Hindu University (BHU), Varanasi, India, and coded as M1 and M2. Both samples have been selected for shodhana separately. For the shodhana process, raw sample was pulverized in a stony mortar and pestle. Then the powdered material was levigated (bhavana) with fresh extracted ginger juice in sufficient quantity until proper and complete drying of the material. The same procedure was repeated again by adding sufficient quantity of fresh juice of ginger. Thus, total seven bhavanas were performed to obtain detoxified (shuddha) Manahshila samples, which have been recoded as M3 (M2) and M4 (M1).

XRD study of all the four samples (M1, M2, M3 and M4) was carried out at the Centre of Advanced Study in Geology, Institute of Science, BHU. The diffraction pattern was obtained on a PANalytical X'Pert Pro diffractometer fitted with a copper tube (CuKα radiation) and xenon detector, scanned over a range 5°–70° 2θ using a 1/2° fixed divergence slit and 1/4° receiving slit with a step size of 0.0250, 1.20 sec/step, and total run time of 56 min 2 sec at 45 kV and 40 mA[19]. The standard Inorganic Crystal Structure Database (ICSD) was used for comparison of the measured data in a PANalytical X'Pert

Table 2. Classical description of physical properties of different types of Manahshila

Physical properties	Shyamangi	Kanavirak	Khandakhya (R.R.S.[14])/ Dwikhanda (A.P.[15])
Colour	Yellowish-red with blackish tint (shyama rakta sagaura; R.R.S.) Red like cinnabar (hingulavat rakta; A.P.)	Coppery red (tamraabha; R.R.S.) Red (A.P.)	Excessive red (atiraktangi; R.R.S.) Comparatively less red to pale (kinchitarakta ch rakta; A.P.)
Luster	Bright (atideeptika; A.P.)	Bright (tejaswani; R.R.S.)	–
Others	Heaviest in weight (bharadya; R.R.S.)	Brittle (churnarupa; A.P.) Heaviest in weight (atibharayukta; A.P.)	Heavy in weight (R.R.S. and A.P.) Brittle (churnibhuta; R.R.S.)
Acceptable variety	No	Yes (A.P.)[15]	Yes (R.R.S.)[14] due to comparatively large amount of satva

*A.P., *Ayurveda Prakash*; R.R.S., *Rasa Ratna Samucchaya*.

Table 3. Description of mineral realgar As_4S_4 (arsenic sulphide) and its polymorphs

Parameters	Alacranite (M1)	Realgar (M2)	Pararealgar*
Chemical formula	As_4S_4	As_4S_4	As_4S_4
Chemical composition (using EDXA)	Arsenic 51.33%; sulphur 20.85%	Arsenic 68.14%; sulphur 31.86%	Not verified
Colour	Red, orange–yellow tint	Dark bright red	Yellow to orange
Streak	Yellow–orange	Orange to reddish-orange	Bright yellow
Cleavage	Indistinct	Good in one direction	None
Fracture	Conchoidal	Conchoidal	Uneven
Luster	Vitreous, resinous, greasy	Adamantine, resinous, sub-metallic	Vitreous to resinous
Tenacity	Very brittle	Slightly sectile	Brittle
Hardness	1.5	1.5–2	1–1.5
Specific gravity	3.4–3.46	3.5	3.5–3.6
Crystal system	Monoclinic	Monoclinic	Monoclinic

*Note: The mentioned physical properties of alacranite and realgar are verified in this study. However, data on pararealgar are taken from external sources[21].

Figure 1. Raw samples M1 and M2 corresponding to alacranite and realgar respectively.

High Score (Plus) v3.X database. The EDXA and SEM studies were carried out at Central Instruments Facility, Indian Institute of Technology (BHU), Varanasi. The samples were analysed on a Penta FET Precision OXFORD Instruments – X-act ZEISS model no. 51-1385-046 after gold grid coating by Coater – Sputter QUORAM Q-150RES. Particles with different patches (spots) were analysed by EDXA to ascertain the presence of elements. SEM study was done on very fine-grained powder of the sample (M3) to examine under electron microscope of 15000×. The surface photograph and thereof particle size estimation of a single particle as well as clusters of particle were analysed.

The colour, odour and texture of samples M1–M4 have been examined thoroughly (Table 4). M1 was red with orange–yellow streak, whereas M2 was dark red with orange streak. M1 and M2 were turned into smooth orange powder after shodhana. Figures 2 and 3 and Table 5 present XRD and EDXA data of the studied samples respectively. SEM study of M3 shows that the particles are homogenously mixed. Minimum size of half of the particles ranges from 400 to 800 nm (with maximum size 15.55 μm) (Figure 4). Various crystallites in different shapes like rod-shaped, cubical and square-shaped are embedded in lumps to form bigger particles.

The physico-chemical correlation of three varieties of Manahshila and three polymorphs of realgar (As_4S_4) has been discussed. Realgar melts at 320°C and burns with a bluish flame, releasing fumes of arsenic and sulphur. It is polymorphous with alacranite and pararealgar[20]. Pararealgar (β-polymorph of As_4S_4) gradually forms from realgar as a result of long exposure to light[21]. In the crystal structure of realgar, each arsenic atom is bonded to two sulphur atoms and another arsenic atom. As the As–As bonds are weaker than the As–S bonds, certain

Table 4. Organoleptic characteristics of alacranite (M1), realgar (M2), purified realgar (M3) and purified alacranite (M4) samples

Sample	Colour	Texture	Odour
M1	Red with orange–yellow precipitate	Smooth, fine	Metallic
M2	Dark red with orange precipitate	Smooth, fine	Metallic
M3	Orange	Smooth, fine, powder	Characteristic
M4	Orange	Smooth, fine, powder	Characteristic

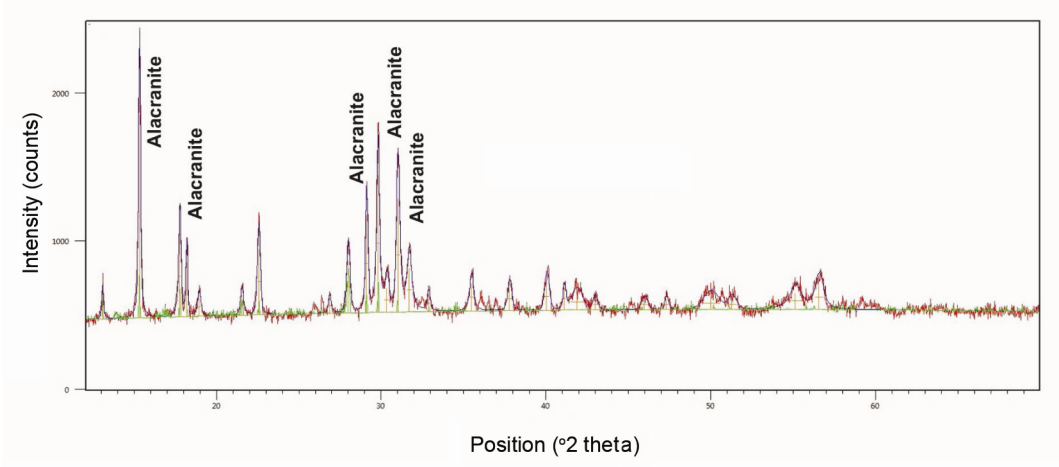

Figure 2. XRD scan of the sample M1, where five major peaks of alacranite are labelled. Other visible minor peaks also belong to alacranite.

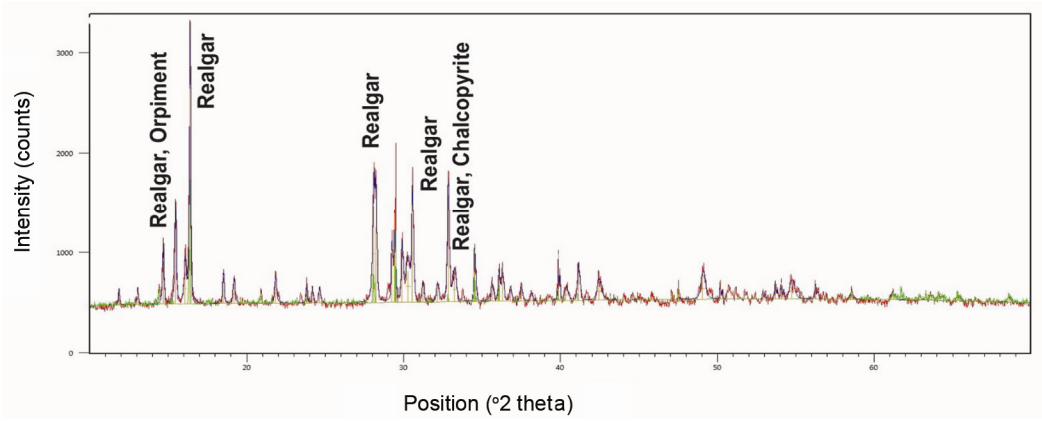

Figure 3. XRD scan of sample M2, where five major peaks of realgar, orpiment and chalcopyrite are labelled.

wavelengths of light interact with the crystal structure of realgar, breaking the weaker bonds between arsenic atoms and destabilizing the realgar structure, causing it to become powdery pararealgar without changing the overall chemical composition[22]. Alacranite (α-polymorph of As_4S_4) was first observed in association with barite–quartz calcite veins in the Alacran silver mine, Pampa Larga mining district, Chile in 1970 (ref. 23). In 1986, Popova *et al.*[24] have provided a detailed mineralogical description and a name for it. In alacranite, each arsenic atom is bonded to another arsenic atom and two sulphur atoms, while the sulphur atoms are bonded only to two arsenic atoms. The structural arrangement of molecules in alacranite is chemically similar to realgar bound together by van der Waals forces. The differences between alacranite and realgar have been demonstrated in the unit cell sizes and the packed structures of both minerals, which have been further confirmed through XRD study[25].

A wide range of internal and external applications of Manahshila is known since 200 BC. However, detailed description is available in the text of Indian alchemy only after the 12th century AD (Table 2). There are diverse opinions regarding the selection of genuine samples for therapeutic use. Some authors consider khandakhya variety to be the best because it contains high percentage of satva (i.e. somal)[14], whereas others recommend kanavirak

due to its physical properties[15]. By scrutinizing the properties of kanavirak and khandakhya varieties of Manahshila, it is observed that both varieties have similar characteristics. The established physical and crystallographic properties of polymorphs of As_4S_4 minerals have been correlated with the three varieties of Manahshila. Kanavirak has been considered as the best variety by Acharya Madhav, the author of *Ayurveda Prakash*, which has the similar properties to alacranite. On the other hand, Rasa Vagbhatta, the author of *Rasa Ratna Samucchaya* explained khandakhya variety as the best. In EDXA study, variation in arsenic has been observed from 51.33% to 68.14% in alacranite and realgar respectively. Thus, it is recommended that khandakhya may be considered as realgar.

All relative peaks are identified as alacranite with molecules of As_4S_4 in XRD analysis of M1 (Figure 2). The same sample was also studied after shodhana (M4), producing similar peaks as the raw sample (M1). In sample M2, most of the high-intensity peaks are identified as realgar (As_4S_4) with monoclinic structure. Some of the peaks (1 or 2) with low intensity are identified as orpiment (As_2S_3) and chalcopyrites ($CuFeS_2$), present in very low concentration (Figure 3). In nature, the sulphide minerals are generally associated with each other due to similar physico-chemical properties. The vast majority of sulphide minerals are part of hydrothermal sulphide ores[26]. After shodhana, XRD data of sample (M3) correspond to realgar, and no peak of associated minerals is identified. Moreover, some of the peaks also correspond to organometallic compounds, which may be added during shodhana through organic phyto-constituents and their reaction with metallic compound.

The objective of shodhana is detoxification of a mineral. This is achieved by a single or multiple processes like trituration followed by sublimation, roasting, etc. This concept modifies characteristics of a drug and enhances its therapeutic action for medicinal purposes[27]. For Manahshila, various pharmaceutical processes are described which can be performed by selecting the respective liquid medium mentioned under that pharmaceutical process. Fresh extracted juice of ginger (*Zingiber officinalis* Roscoe) is one of the commonly used media, in the process of Manahshila. In this study, an increase in the weight of Manahshila is observed after shodhana process, which is due to the addition of solid organic phyto-constituents from ginger juice. Similarly, levigation with ginger juice changes red colour of Manahshila powder into orange colour. EDXA study of shuddha Manahshila shows less percentage of arsenic. This may be due to addition of solid extract of ginger during the bhavana process. Thus 590 ml of ginger juice was absorbed in 300 g of Manahshila during the bhavana process seven times, resulting in an increase in weight by 36 g of Manahshila (final weight of shodhit Manahshila was 336 g). Shodhana of Manahshila by ginger juice involves several effective mechanisms. It may act as a phytochelation[28]. Phytochelatins are peptides which bind heavy metals by chelation, thus playing an important role in detoxification of heavy metals[29]. Ginger contains two significant sulphur-based amino acids (viz. cysteine and methionine), which can act as phytochelatins and render arsenic in the Manahshila nontoxic. Cysteine, a methyl donor peptide, helps in the process of methylation[30]. This is a process of detoxifying arsenic in the body through accelerated excretion. Ginger also preserves the level of glutathione, a natural antioxidant-recycling enzyme present in the blood. It acts as a detoxifying compound by combining with arsenic and excretes it via the bile. Arsenic poisoning reduces the level of glutathione and ingestion of ginger prevents the fall of glutathione in the blood. Hence, bhavana with ginger juice supports detoxification as well as combating its possible depletion due to arsenic. Nano-sized (10^{-9} m) range is known for its fast penetration and quicker action. In this study, half of the particles are in the nano range. It was found that nano-sized realgar particles could substantially enhance bioavailability[31].

The Ayurvedic Pharmacopoeia of India includes monograph of 21 metals and minerals; however, Manahshila is not included in this list. This detailed physico-chemical

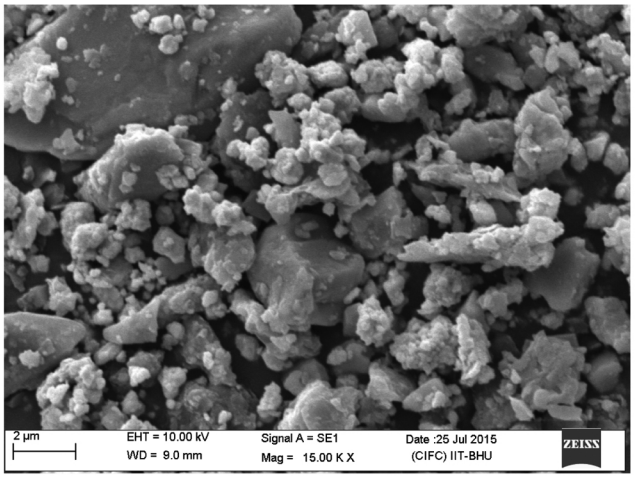

Figure 4. SEM image of sample M3 showing agglomerates of size range 400–800 nm.

Table 5. EDAX findings of alacranite (M1), realgar (M2) and purified realgar (M3) samples

	Weight %		
Element	M1	M2	M3
C K	27.81	–	43.97
O K	–	–	24.45
S K	20.85	31.86	9.31
As L	51.33	68.14	22.28
Total		100.00	

study of Manahshila may be helpful in the preparation of its monograph.

XRD and EDXA studies of two selected samples of Manahshila classified them as realgar (khandakhya) and alacranite (kanavirak) respectively, both accepted as the best varieties for therapeutic use. In the process of Manahshila, ginger juice has been used, which may subside the toxic effect of the drug by acting as a chelating agent. This has been verified through XRD study, as observed from the additional peaks of some organometallic compounds. Thus, this work provides a valid correlation between the traditional information on characterization and processing of Manahshila in toto and corresponding polymorphs of realgar, and confirms the most acceptable type, i.e. khandakhya to be realgar with formula As_4S_4.

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