TOXICOLOGICAL AND HUMAN RISK ASSESSMENT OF HARATAL (ORPIMENT/AS$_2$S$_3$)

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ABSTRACT

With the evolution of civilization and its development, chronic heavy metal poisoning came to light, one of them is α-allotropic form of arsenic; i.e. Haratal (arsenic trisulphide). Agadatantra the special branch of Ayurveda mainly deals with the toxicological aspect of Ayurveda and the pioneer Ayurveda classic “Sushruta Samhita” 1st described haratal as a heavy metal and highlight its toxicodynamic, toxicokinetic along with poisoning sign symptoms.

KEYWORDS: Arsenic trisulphide poisoning, Heavy metal toxicity, Ayurveda drugs occupational toxicity, Orpiment

INTRODUCTION

Heavy metal and minerals compound are most commonly used in the therapeutic management of Ayurveda. Among those compounds the use of Parad (mercury /Hg), Haratal (orpiment/AS$_2$S$_3$), Manashila (realgar /AS$_2$S$_3$) and Gouripasana (white arsenic / AS$_2$O$_3$) etc is common. However reference about the use of metal mentioned in the pioneer ayurveda text charaka samhita but the authentication of metal compound and its medicos legal use is well developed by acharya Nigarguna. However in the present scenario Haratal (orpiment/AS$_2$S$_3$) has several medical and industrial preparations. Even Haratal (orpiment/AS$_2$S$_3$) has history as being used in treating Piles, Epilepsy, Erysipelas etc. 1.

Toxicological analysis

Haratal (orpiment) is considered as nucleus of rasaaushadhi (herbo-mineral formulations). The word “orpiment” is derived from the latin “Auripigmentum” or “golden paint”. It is also known for its bright yellow colour. The Ayurveda profession has a long history with regards to the use of Haratal (orpiment/AS$_2$S$_3$) for knowing its toxic effect. “The father of Indian surgery” - Sushruta first described Haratal as a metallic poison 2. Haratal (orpiment/AS$_2$S$_3$) is an inorganic arsenic compound which contains 61% arsenic and 39% sulphur 3.

Suicidal poisoning is common by taking a large amount of Haratal (orpiment/AS$_2$S$_3$) 4, 5. Haratal (orpiment/AS$_2$S$_3$) has been used for suicidal purpose because it is inexpensive, easily available in market, sweet taste and high toxic value. Dr.J.B.Mukherjee and R.N.Karmakar in the year of 2000 have cited a case where a lady of West Bengal (India) took a sweetmeat of butter, flour and yellow sulphide of arsenic at 6p.m. toxic signs and symptom appeared 6 hours later and she died after 39 hours. Her stomach contained coarsely powdered of yellow arsenic 6.

Haratal’s (orpiment/AS$_2$S$_3$) accidental poisoning is not uncommon when the orpiment is widely used as main ingredients of herbo- mineral pharmaceutical industries and as a pigment agent in art industry for painting dolls, toys, and wooden poles and as moderate cytotoxic agent in chemotherapy, aphrodisiacs, external dermatological application. Injudicious use of haratal (orpiment/AS$_2$S$_3$) as cytotoxic agent, over dosing of haratal containing medication, improper manufacturing process and therapeutic modification, prolong use of haratal (orpiment/AS$_2$S$_3$) containing ointment over skin or open wound and applications into uterus for abortion can lead to accidental poisoning. Workers in deferent herbo-mineral pharmaceautics and art industries are suffered from accidental haratal (orpiment/AS$_2$S$_3$) poisoning due to exposed of haratal (orpiment/AS$_2$S$_3$) dust and aerosol. Medicinal and industrial deposition of haratal (orpiment/AS$_2$S$_3$) may also be a cause of elevated arsenic level in ground water in India 7.

Previously orpiment was the poison of choice for assassinations creeds. Haratal (orpiment/AS$_2$S$_3$) when used for homicidal purposes is commonly given in curries and dal, to mask their colour 8.

Haratal (orpiment/AS$_2$S$_3$) is very commonly used for abortifacient purpose 9, 10. It is locally applied on abortion stick in form of paste or ointment and put into uterus for procuring abortion and may leads to systemic poisoning 11, 12. Bengali chemical examiner in 1945 annual reports has cited a case, where a woman inserted cotton wool swab smeared with haratal (orpiment/AS$_2$S$_3$) in to her vagina to produce abortion; on having failed to get the desired results, she took orally also and died from its effect. Arsenic was detected in her viscera as well as the cotton wool swab 13.

Table 1: Vernacular names Haratal (AS$_2$S$_3$)

| Native speaker | Name          |
|----------------|---------------|
| Assamese      | Haratala      |
| Bengali       | Haratala      |
| English       | Orpiment      |
| Gujarati      | Haratala      |
| Hindi         | Haratala      |
| Kamada        | Haridal, Haratala, Aradal  |
| Malayalam     | Aritalam      |
| Oriya         | Haratala      |
| Punjabi       | Haratala      |
| Tamil         | Ardidaram, Vellikuo pashanam |
Excretion
Sublingual > application on unbroken skin. Vagina, urethra, (intra peritoneum) > SC (subcutaneously) > Ingestion > rectum, (intravenous) > IP
In order of rapidity of action; Inhaled in gas / vaporous form

Mode of Absorption
In order of rapidity of action; Inhaled in gas / vaporous form > IV (intravenous) > IP (intra peritoneum) > SC (subcutaneously) > Ingestion > rectum, vagina, urethra, sublingual > application on unbroken skin.

Excretion – excreted mainly through renal system by producing acute kidney injury (AKI)

Therapeutic Indications: Arsha (haemorrhoids), Apasamra (epilepsy), Kustha (dermatological disorder), Bhagandara (fistula), Visarpa (erisipelas), Vishama Jwara (viral fever), Vrana (ulcers) etc.

Availability: Haratal (Orpiment) is found all over the world. It occurs naturally near volcanic structures and also byproduct coal combustion. In India it is found in Darjeeling district of state West Bengal and Bay of Bengal region and Kashmir naturally and manufactured in Surat.

Type of haratal: Haratal is two types i.e. - patra haratal and pinda haratal. Patra haratal is golden in colour and it’s containing thin layer. Patra Haratal is preferred for the therapeutically purposes.

Haratal X- RD (X-Ray diffraction): 250 gm patra Haratal (orpiment / AS₃S₂) was purchased from West Bengal (India) local market and authenticated at Sri Dharmasthala Manjunatheshwara college of Ayurveda pharmacy, Hassan Karnataka (India). The sample of Haratal was highly crystalline (~100%); monoclinic system pattern by using the powder diffraction. File data base of ICDD-ICPDS showed that it was purely AS₃S₂ with graph showed prominent peaks of Arsenic trisulphide with many impurities present in it.

Table 2: Toxicological properties as per Ayurveda classic

| Book | Rasa | Guna | Virya | Vipak |
|------|------|------|-------|-------|
| A.S. | Kasaya, katu | + | + | + |
| Ba. R. | Katu | + | + | + |
| Bh.P. | Kasaya, katu | + | + | + |
| R.N. | Katu | + | + | + |
| R.Ch. | Katu | + | + | + |
| R.J. | Katu | + | + | + |
| R.K.D. | Katsu, kasya, tikta | + | + | + |
| R.M. | - | + | + | + |
| R.A. | - | + | + | + |
| Y.R. | Kasaya, katu | + | + | + |
| R. Ch. | - | + | + | + |
| R.R.S. | Katu | + | + | + |
| M.N.P. | Kasaya, katu | + | + | + |

Table 3: Description of toxicant Haratal

| Formula | AS₃S₂ |
|---------|-------|
| Periodic Table | 33rd |
| Specific gravity | 3.5 |
| Appearance | Orange crystals |
| Density | 3.43 g cm-3 |
| Molar mass | 246.04 g mol⁻¹ |
| Melting point | 310.5 °C |
| Boiling point | 707 °C |
| Crystalllography | Monoclinic |
| Ash Value | 0.78 % |
| Acid Insoluble Ash | 0.42% |
| Water soluble ash | 0.68% |
| Loss on drying at 110 °C | 99.21% |
| Particle size | 6.6-1559 microns |
| Percentage of Arsenic and sulphur | Arsenic 61% Sulphur 39% |
| Taste | Sweetish followed by burning sensation in mouth. |

Table 4: Acute & chronic poisoning symptoms

| System | Acute poisoning | Chronic poisoning |
|--------|----------------|------------------|
| GIT    | Sweetish-metallic taste, nausea, vomiting, garlic odour breath, defecation is frequent and involuntary, odourless and watery resembling rice water. | Nausea, vomiting, loss of appetite, diarrhea/diarrhoea. |
| Renal  | Oliguria, uremia, albinuria, ARDS, micturition | Chronic nephritis, renal tubular necrosis |
| CVS    | Hypotension, pulmonary oedema, circulatory collapse | Hypotension, IHD, cardiac failure |
| Hepatic | Fatty infiltration | Hepatomegaly, cirrhosis of liver, jaundice |
| MS     | Pain in limbs, weakness | -------------------------- |
| CNS    | Headache vertigo, tremors, convulsions, general paralysis | Peripheral neuropathy, encephalopathy |
| Skin   | Alopecia, skin eruptions | Raindrop pigmentation, Airdich-Meers lines, alopecia |

Sign and symptoms: As it is inorganic arsenic trisulphide so it may follow arsenic poisoning sign and symptoms.

Medicolegal uses of Haratal (Orpiment / AS₃S₂)
- Depilatory in conjunction with lime in tanning industry
- Orpiment is widely used as pigments in arts and industry for painting dolls and toys, wooden poles etc.
- Orpiment is commonly used for abortifacient purpose
- Used as ingredients of herbomineral formulation.

DISCUSSION
The quintessence part of a research work is discussion. It gives the plausible reasons for the observed parameter of the study. Haratal (orpiment/AS₃S₂) is an inorganic arsenic compound which contains 61% arsenic and 39% sulphur. Arsenic is one of the 12 most abundant elements on earth. Today Arsenic is a common source as an acute hazard. Through drinking water, more than 200 million people globally are exposed to higher than safe levels of arsenic. The most affected areas are West Bengal in India and Bangladesh. Arsenic exists in nature in three allotropic forms, α (yellow), β (black), γ (grey), of the metallic state and in a number of ionic forms and Haratal is the α (yellow) allotropic forms of the arsenic. Haratal (orpiment/AS₃S₂) is main ingredients of herbo-mineral pharmaceutical industries. So haratal (orpiment/AS₃S₂) is considered as nucleus of rasaaushadhi (herbo-mineral formulations) and it is widely used as a pigment agent in art
industry for painting dolls, toys, and wooden poles and as moderate cytotoxic agent in chemotherapy, aphrodisiacs, external dermatological application. Haratal (orpiment/\text{AS}_3\text{S}_3) has been used for suicidal purposes because it is inexpensive and easily available and has high toxicity\textsuperscript{17}. Improper purification procedure of haratal (orpiment) in herbo-mineral pharmaceutical industries and art industry, over dose, prolong use or unexpected adverse reactions produce toxic symptoms like convulsion, burning sensation, fainting, cardiac pain and even death. INDIAN MINISTRY OF HEALTH AND FAMILY WELFARE DEPARTMENT declared haratal (orpiment/\text{AS}_3\text{S}_3) as a deadly metallic irritant poisonous substance and enlisted it in schedule “E” of poisonous drug, under THE DRUGS AND COSMETICS and RULES 1945. The experimental animal model showed solubility of Haratal (Orpiment/Arsenic trisulphide) is very low in water and it is poorly absorbed in gastrointestinal tract of Wistar albino rats. Haratal (Orpiment/Arsenic trisulphide) is expelled through urine and fecal matter due to fate of poison\textsuperscript{18,19}. So only a small portion of arsenic trisulphide was absorbed and reached to the blood stream which was not adequate to produce acute toxicity and orally safe up to 5gm/kg body weight of Wistar albino rats.

CONCLUSION

Haratal (orpiment/\text{AS}_3\text{S}_3) is a schedule “E” drug so it can only be dispensed on the prescription of registered Ayurveda medical practitioners. A proper post marketing pharmacovigilance surveillance required to observe quality, safety, and efficacy of all Haratal (\text{AS}_3\text{S}_3) containing herbo-mineral formulations like - Kasturi bhatara rasa, Chandakeshwara rasa, Thalaka bhasma, Nithyananda rasa, Vatarakthanthaka rasa, Rasendra gutika, Vatha gajankusha rasa, Vatarakthanthaka rasa, Kaphakethu rasa etc. More dose related toxicity study and toxicogenomical data required of haratal and it is containing substances to avoid the occupational health hazards of herbo-mineral pharmaceutical industries worker and environmental and human risk assessment.

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