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Kinetic Chemistry of *Shodhana* w. s. r to *Nirvapa* and *Dhalana*

Author: Lalitha M Vatar[1]

[1]Department of Rasashastra and Bhaishajya Kalpana, Taranath Government Ayurvedic Medical College & Hospital, Ballari, Karnataka, India

ABSTRACT

In Ayurvedic system of medicine, metal/mineral-based formulations are being used since time immemorial. Our ancient scholars, who encouraged the use of metals and minerals for the treatment purpose, were also aware of their toxicity in general. None of them has advised the use of drugs in the crude form internally. Moreover, in crude form these drugs will not absorb so easily. Qualitative alteration is done for the improvement, enhancement, modifications, lowering untoward effects or any such procedure is nothing but *samskara*. Without *Shodhana Samskara, Rasasastra* is handicapped as no medicament can be prepared without the prior removal of impurities that is why *Shodhana* of every substance, utilized in *Rasashastra* is described at the very beginning. The *Nirvapa* & *Dhalana* are not only one of the *shodhana* method but also pre-procedure for further process like *Marana, Dhatu Pistinirmana-khalviya/parpati/ kupipakwa / pottali Kalpana.*

Key Words *Shodhana, Nirvapa, Dhalana,* kinetics, *Vanga, Rajata*

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INTRODUCTION

Shodhana is the process in which the *Mala* or *Dosha* are eliminated, to make metallic substance suitable for *Marana*, Regulation of physico-chemical attributes. "*Shodhanam karma vigneyam dravyadosha nivaranam"*[1] *"Uddishteroushadhaihi sardham kreeyate peshanadikam Mala vicchittae yattu Shodhanam tadiochytae"*[2] *Shodhana* can be classified into two types 1. *Samanya:* General process of Shodhana for all the drugs of a particular group e.g., *Samanya Shodhana* of *Dhatu*, 2. *Vishesha:* Specific process for a particular drug e.g *Vishesha Shodhana* of Vanga in *Churnodaka*.

धात्वादेर्वह्नितप्तस्य जलादौ यन्निषेचनम्।

स निर्वापः स्मृतश्चापि निषेकः स्नपनञ्च तत् ॥ **(R.T 2/40)**[3]

Substances like metals and minerals are heated to red hot and immersed in the liquid (decoctions, oil, juice etc.) are named as *Nirvapa* or *Snapana* or *Nisheka*.

संद्रावितस्य द्रव्यस्य द्रवे निक्षेपणन्तु यत्। ढालनं तत्समुद्दिष्टं रसकर्मविशारदैः ॥ **(R.T 2/36)**[4]

The action of pouring the molten metal into another liquid is known as *Dhalana*.

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***Samanya shodhana* by *Nirvapa & Dhalana* told for *dhatu*:**

तैले तक्रे गवां मूत्रे ह्यारनाले कुलत्थजे ।
क्रमान्निषेचयेत्तप्तं द्रावे द्रावे तु सप्तधा ॥
स्वर्णादिलोहपत्राणां शुद्धिरेषा प्रशस्यते ॥ **(RRS 5/29)**

The thin sheets (*kantakavedhi patra*) of any of these metals are heated to red-hot over fire and dipped into the following liquids: *Tilataila, Takra, Gomutra, Āranāla* and *Kulattha kwatha* for seven times successively, in total for one drug it will be 35 times of heating and dipping. This process will purify all the metals in general.

In the process of *Nirvapa* & *Dhalana* changes occurs in three stages.

1) Phase of heating.

2) Phase of quenching

3) Post-quenching interaction between hot solid material and cold liquid media. Physical & chemical changes occur in all these 3 phases

AIMS AND OBJECTIVES

1. To validate the process of *Rajata Nirvapa* and *Vanga Dhalana*.
2. Role of Media used in *Shodhana.*
3. The probable mode of kinetic chemistry, theories, concepts in *Nirvapa* & *Dhalana*.

MATERIALS AND METHOD

Silver and Tin were selected according to *Grahya lakshana* and by AAS analysis silver (99 %) Tin (99.5%) content in the sample was identified.

METHODOLOGY

Shodhana- Samanya shodhana of Rajata and Vanga in *Tila taila, Takra, Gomutra, Aranala* and *Kulattha kwatha* for seven times in each media successively and ***Vishesha Shodhana*** - *Nirvapa* of *Rajata* in *Nimbu swarasa* and *Dalana* of *Vanga* in *choornodhaka* for seven times was carried out.

Rajata Nirvapa procedure and observation. Table.1

Vanga Dhalana procedure and observation. Table.2

Some important considerations during *Nirvapa* & *Dhalana* process:

- Heating should be done until the complete red hot /molten state of metals or minerals.
- The ladle should be inert; it must not react with the material during heating.
- Red hot/molten material should be quenched immediately.
- After quenching materials should be allowed to complete coolness in liquid media.
- Each time the Drava dravya (liquid media) should be taken freshly. During interval of processing in another liquid media the material should be completely dry.

The amount of liquid media must be sufficient to immerse the material completely.

Probable Mechanism behind *Nirvapa* & *Dhalana*

According to *Rasashastra (Aptopadesha pramana)*

Ghana Dravya (Pruthvi+jala mahabhuta)

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Agni samskara (tapana/dravana jala mahabhoota level reduces, *Tejo mahabhuta* increases) Heating

Tapta/Dravita Dravya Nimajjana in Drava dravya

After *Svanga sheeta of Dravadravya, Dravya* is taken out

Samyak Prakshalana (with ushna jala & dried)

Quenching Process

Nirvapa and *Dhalana* can be compared to Quenching. Changes occur in 3 stages

1) Phase of heating.
2) Phase of quenching.
3) Post-quenching interaction between hot solid material and cold liquid media.

1) Phase of heating/ melting:

Physical change: Metals are solid, closed packed crystal structure in which particles are closed together in a lattice form and vibrate in their fixed position. In solids, the atoms/molecules are held in a fixed arrangement by bonds, which are governed by electrostatic forces.

Chemical changes observed in Nirvapa and Dhalana. Table 3

Collision theory[6]–States that when suitable particles of the reactant hit each other, only a certain amount of collision result in a perceptible or notable changes, Increasing the temperature of the reaction increases the speed at which particles move. This increases the number of effective collisions; the collisions have a higher energy and therefore the rate of reaction is increased.

Chemical change:

When the Copper and Tin is heated until it glows dull red in the presence of oxygen, the heat speeds up oxidation and tin oxide is formed.

The probable reaction may be:

$$2Cu + O_2 \longrightarrow 2CuO$$

$$2Sn + O_2 \xrightarrow{\Delta} 2SnO$$

At the stage of heating -inter atomic distance - weakening of bondage, Oxidation, Collision theory, Thermodynamic-1st law, Exothermic reaction occurs.

2) Phase of Quenching:

When the Red hot/ molten metal is quenched, the liquid media immediately penetrates inside and water-soluble impurities get dissolved in it due to breaking of bonds. **Quenching**[7] is a process of cooling a metal very quickly. It prevents low-temperature processes, such as phase transformations from occurring by only providing a narrow window of time in which the reaction is conductive to thermodynamics and kinetics as well. It is an efficient way to control mechanical and metallurgical characteristics of metals. During instant cooling, recrystallization occurs along with the reformation of grain boundaries. In this reconstituted structure, each grain is surrounded by the molecules of liquid media, may be imposing its properties on that purified mineral.

At the stage of quenching-breaking of bond, Thermochemistry-Enthalpy change occurs.

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3) Post quenching interaction between liquid media and minerals during instant cooling:

Repeated heating and successive quenching, treats individual reduced grains as separate entities and further reduces the grain size, reduce hardness, impose the properties of various media, cause the colour changes. During cooling stage - Corrosion, Surface chemistry- Recrystallisation-grain boundary, Acid –base theory occurs.

Kinetic chemistry

- **Griffith theory:**[8]

Griffith proposed that brittle material contains many fine cracks. All solids contain flaws and microscopic cracks. A flaw is any structural weakness that may develop into a crack under strain like heat. The weakest flaw in a particle determines its fracture strength. Usually, the surfaces of particles are irregular. The applied force by the form of heat is initially taken on high portion of the surface. As a result, high stress may be set up locally in the particles. The bond at this place becomes weak, which may be responsible for flaws. The particle with the weakest flaw fractures most easily and produced largest possible pieces. In the next step, another weakest flaw fractures by this way particle size are reduced.

- **Grain Boundary and RecrystalisationTheory**[9]**:** A grain boundary is the interface between two grains or crystallites, in a polycrystalline material. Grain is nothing but the microscopic crystalline areas of a mineral limited by the boundaries known as "Grain boundaries."

- **Speed of Quenching**: This is because, if grain retardation i.e., reduction in the grain size and increase in the grain boundary area must be achieved immediate quenching of the metal after sufficient exposure to heat is of prime importance.

- **Role of Quenching Media:** The quenching media during quenching are selected to obtain specified physical properties with minimum internal stress and distortions. A quenching medium must cool the metal at a cooling rate favorable to produce the desired results, The liquids used - Weak / Strong acids, Weak / Strong bases, Enzymes, Herbo-mineral entities.

- **The volume of quenching** as a metal is quenched; the liquid absorbs the heat and thus decreases the cooling rate.

CONCLUSION

1) *Vanga* was in medicinal use from *Samhitha* period, later during the period of *Rasashastra*, evolved internal use of *Vanga* and *Rajatha* after *Shodhana, Jarana, Maranadi* procedures.

2) The main purpose of *shodhana* is to remove both the water soluble and fat-soluble impurities in the metal. Generally, liquids used for the primary processing of *Samanya* and *Vishesha shodhana* contains Weak/strong acids, weak/ strong bases, enzymes, solvents, inorganic contents, herbo-mineral entities and their specific *Prabhava*.

3) *Nirvapa* & *Dhalana* are the physiochemical and therapeutic transformation of a substance making it feasible, for the next process (e.g., *Marana, satvapatana, dhatupistinirmana.)* or directly for therapeutic use.

4) pH of *shodhana* media used, do play an important role in the structural changes in the metal as well as impose their properties on it during the process. Destruction of structure in the metal by converting to a granular form especially before marana.

5) By knowing the concepts/theories in modern chemistry, we can understand the reaction mechanisms in *Nirvapa & Dhalana*, it can be compared to Quenching process.

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Table 1 *Rajata Nirvapa* procedure and observation

Drava dravya	**Rajata Before *nirvapa***				**During Nirvapa**		**After *Nirvapa***			
	Colour	**Odour**	**Wt in Gms**	**Consistency**	**Sound**	**Splashing**	**Colour**	**Odour**	**Wt loss**	**Consistency**
Tila taila	White Shining	Odour less	154	Soft Malleable	Slight hissing sound	No Splashing	Metallic lusture slightly diminished	Oily Smell	0.50	*Rajata patras* become soft
Takra	Silver White Shining	Oily smell	153.5	Hard Disc shaped Metallic Mass Form	Loud hissing sound	Splashing with sound	Lost their luster	Curdy Smell	0	soft and fragile
Gomutra	White Less shining	Curd Smell	153.5	Hard Sharp Pointing Malleable Form	Loud Hissing sound	Splashing with sound	Pale White No Shining	Aromatic	0.25	hard Sharp Pointing Malleable Form Some Powder
Aranala	Pale white with no shining	Aromatic	153.25	Pieces Hard Sharp Pointing Metallic Form with Some Powder	Mild Loud Hissing Sound	Splashing With Sound	Pale White No Shining	Acidic Smell	1.75	Small Pieces, less Hard, sharp Pointing with Some Powder
Kulattha	Pale white with no Shining	Acidic smell	151.5	Small Pieces Hard with Some powder	Loud/loud hissing & Bubbling Sound	Splashing With Sound	Brownish White No shining	Odorless	0	Soft Small Pieces, less Sharp with More of Powder Form
Nimbu Swarasa	White No Shining	Odorless	151.5	Small Pieces, soft, fragile	Loud Hissing sound	More Splashing with Loud sound	Curdy White No shining	Odorless	0.25	Soft Small Pieces.

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Table 2 *Vanga Dhalana* procedure and observation

Drava dravya	***Vanga* Before *Dhalana***				**During Dhalana**		**After *Dhalana***			
	Colour	Odour	Wt in Gms	Consistency	Sound	Splashing	Colour	Odour	Wt loss	Consistency
Tila taila	White Shining	Odour less	880	Soft Malleable Strips Of tin in Metal	No sound	No Splashing	Silver White Shining	Oily Smell	3	Hard, Disc Shaped, Metallic Mass Form
Takra	Silver White Shining	Oily smell	877	Hard Disc shaped Metallic Mass Form	Mild sound	Splashing with sound	Oft White with Less Shining	Curdy Smell	15	Pieces, hard Sharp Pointing Malleable
Gomutra	White Less shining	Curd Smell	862	Pieces Hard Sharp Pointing Malleable Form	Loud Hissing sound	Splashing with sound	Pale White No Shining	Aromatic	14	Pieces, hard Sharp Pointing Malleable Form
Aranala	Pale white no shining	Aromatic	848	Pieces Hard Sharp Pointing Metallic Form with Some Powder	Mild Loud Hissing Sound	Splashing With Sound	Pale White No Shining	Acidic Smell	21	Small Pieces, less Hard, sharp Pointing with Some Powder
Kulattha	Pale white with no Shining	Acidic smell	827	Small Pieces Hard with Some powder	Loud/loud hissing &Bubbling Sound	Splashing With Sound	Brownish White No shining	Odorless	22.5	Soft Small Pieces, less Sharp with More of Powder Form
Choornodaka	White No Shining	Odor less	804.5	Soft Small Pieces, less Sharp with More powder forms	Loud Hissing& Bubbling sound	More Splashing with Loud sound	Curdy White No shining	Odorless	30	Soft Small Pieces, less Sharp with More of Powder Form