Research Article

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STUDY OF QUALITY CONTROL OF VANGA DHATU WITH SPECIAL REFERENCE TO GRAHYAGRAHYATVA CRITERIA

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ABSTRACT

In Rasashatra the word Grahyagrahyatva is used in context with raw drug selection. Grahya means acceptable and Agrahya is not acceptable. Thus, they signify the quality control techniques. Selection of appropriate raw material is the first and foremost step in Drug Standardisation. These classical textual norms, being in Sanskrit and in ancient terminology, cannot be interpreted by the suppliers or geologists. This creates problems while procuring raw material and leads to confusion regarding the appropriate mineral intended by ancient texts. Many a times there are minor variations in the composition of minerals that cause variation in their colour. May be, this minor variation in composition brings about major change in its pharmacological properties. If co-relations could be established between ancient criteria and mineralogical properties, standardisation of raw materials in terms of objective norms can be accomplished. An attempt is being made for quality assessment of Vanga (Tin). Regarding Grahyagrahyatva of Vanga, all parameters highlight physical or chemical properties. The Grahyagrahyatva norms were tested with parallel modern analytical techniques e.g. Grutva and Laghutva criteria with specific gravity. Also well designed proforma and visual scales were developed to assess the data which appears to be subjective. But assessed methodically and thus converted into numerical data for applying statistics. In this short term project research attempts were made to assess Grahyatva of collected 16 Vanga samples. Grahya and Agrahyatva assessment match with the assessment done by analytical methods to satisfactory and expected extent.

Keywords: Vanga, Grahyagrahyatva, Standardization, Assessment, Criteria.

INTRODUCTION

Herbal products are gaining more and more popularity throughout the world and lot of research work is being carried out globally. Figures from a study undertaken a few years ago in the United States suggested that as high as 67.6 % of the population had used complementary and alternative therapy at least once in their lifetime. 'Ayurvedic' especially 'Rasashastra' medicines possess power of fulfilling the increasing demands of alternative medicines from the globe. Though time tested, though formulated by sages, it is now right time for an 'Ayurvedic' pharmacies to prove the efficacy of their medicines. Mineral medicines, however, are eyed cautiously by modern scientific world due to various reasons. These include inconsistent production practices and insufficient proved evidences of safety, efficacy and standardization. Recently there have been some scientific publications questioning the safety of Ayurvedic metallic/ herbo-mineral products. Following this, several developed countries have prohibited the use of not only herbo-mineral products but also some of the herbal products reported to be contaminated with heavy metals. Keeping in view the fact that it is our heritage and needs to be subjected through well planned research in order to bring it to international platform as India's unique contribution, many efforts have been done since the 20th century. The way to achieve acceptance of modern scientific fraternity is to ensure authentic and validated practices in the fields of identification, selection, preservation, pharmaceutical procedures, standardisation, compounding and dispensing of Ayurvedic medicines. GMP (Good Manufacturing Practices) was enforced in India on 23rd June, 2000. The objectives of GMP comprise of 1.Safety 2. Efficacy 3. Acceptability of medicine. For these goals to be fulfilled, the journey begins from raw materials. Proper identification and standardisation are basic requirements in this regard. The mineral drugs are in much need of these aspects owing to the fact of potential toxicity.

"Jatimadbhirvishudhaishca Vidhina Parisadhitai: / Rasoparasalohadyai: Soota: Sidhyati Naanyatha //"
- Rasaratnasamucchaya 5/216
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The reference from Rasaratnasamuccaya indicates the significance of the authentic and unadulterated raw material and appropriate techniques of processing it, in order to achieve the desired effects of a pharmaceutical product.[1] The ancient way of raw material standardisation of Rasadravyas is through narration of Grahya i.e. acceptance and Agrahya i.e. rejection criteria. These criteria though may appear superficial to a casual observer, reveal much information about the constitution of Rasadravyas. These criteria need to be deciphered with the help of modern sciences like Physics, Chemistry, Mineralogy and Metallurgy etc., which can prove a crucial step towards standardisation of raw materials. In raw material standardization previous work was conducted for Tamra (Copper), Loha (Iron), Gairika and Godanti. 'Rasashastra' mainly deals with study of mercury, metals, minerals and marine products and their use in medicinal formulations. Among them metals are predominantly used. 'Vanga' is one such metal added in the class of 'Putiloha'.[1] 'Vanga' has major contribution in

many 'Rasashastra' formulations like 'Suvarna-Raj-Vangeshwar', 'Lakshmivilas Rasa', 'Nityananda Rasa' etc. which are abundantly used in practice and possess broad spectrum therapeutic benefits.[2] Thus it is decided to study about this unique metal used in 'Prameha', 'Klaibya', 'Pradara', Kushtha' etc. which are main problems today.[1] Administration of metallic formulation in human body must be done very cautiously. Our ancient 'Acharyas' were well aware of this fact. Therefore right from the selection of raw drug up to the final product, various selection criteria and standardization tests were mentioned in 'Rasashastra' texts. For example in case of 'Vanga Dhatu' text quotes-

"Dhavalam Mrudulam Snigdham Drutadravam Sagauravam/
Nihshabdam Khuravangam Syaat, Mishrakam Shyaamshubhrakam //"
- Rasaratnasamucchaya 2/154

'Grahya Khuraka Vanga' characterized as it is white in colour, soft, its lustre is like silver, melts quickly on heating, heavy and does not produce any sound while melting or hammering and 'Agrahya Mishraka Vanga' is blackish white in colour.[1] While talking about metals, the methods of smelting, refining and processing have evolved over the period of many years. Today 100 percent pure metal can be obtained by the techniques of electro refining. But this could not have been the case in the times the Rasashastra texts were compiled. The metal refined at that times would contain many trace elements, which can be separated easily today. Therapeutic as well as toxicological effects should also be considered in context with these trace elements while considering these raw materials. It might be the case that today the raw material used perhaps is not the same, which was expected to the pioneers of Rasashastra at that time. Thus a research in raw material analysis regarding metals appears very appealing. Regarding Grahyagrahyatva of Vanga, the texts mention 22 parameters of Grahya Vanga and 8 parameters of Agrahya Vanga. These all parameters highlight some or the other property, physical or chemical of the Vanga. In this research attempts are made to apply them to the collected samples. If the mentioned Grahyagrahyatva norms can be tested with a parallel modern analytical techniques this would be much easier to explain. Also there is need to design the scales to assess the data which appears to be subjective. This is the main aim of this short research project and sincere efforts are conducted in this direction.

Aim and Objectives

Aim

To study Quality Control of 'Vanga Dhatu' with special reference to 'Grahyagrahyatva' assessment

Objectives

- To make efforts to study and enlist 'Grahyagrahyatva' (acceptance and rejection) criteria of 'Vanga Dhatu' from important 'Rasashastra' texts.
- To enlist and study the criteria for 'Grahyagrahyatva' on collected samples of 'Vanga Dhatu' with the help of well designed proforma. (Data base preparation of conventional parameters and modern parameters)
- To make efforts to establish significant range of 'Grahya Vanga Dhatu' for pharmaceutical purpose by comparative assessment of conventional and physicochemical parameters.

MATERIAL AND METHODS

Literary Review

Synonyms of Vanga from various Rasashastra texts

Table 1: Synonyms of Vanga and their meanings

Category	Synonyms of Vanga	Meaning
Gatisucaka	(Indicating motion)	
	Vangam[1]	
	Rangam[3]	
Swabhava Nidarshaka	(Indicating nature)	
	Trapu, Trapupam[4]	Trapate – Mixed with other metals
	Trapus Lajjayam	Shy at touch of fire
Karmabodhaka	(Indicating action)	
	Piccatam, Uccatam[5]	The metal which can be easily cut down or engraved or pressed or molded
	Shukraloha[3]	Nutritive to sperms

Thus, synonyms are self explanatory and helps in better understanding of physical, metallurgical, pharmaceutical, medicinal properties of Vanga along with its uses, history, places of occurrence etc. Therefore study of synonyms reflecting above mentioned various aspects of Vanga are necessary for understanding various aspects of Vanga.

List of Grahyagrahyatva criteria

Grahyagrahyatva criteria were compiled from 30 Rasashastra texts. 22 Grahya and 8 Agrahya criteria were found in concerning with Vanga.

List of 'Grahya' (Inclusion Criteria) Norms

Table 2: List of 'Grahya' (Inclusion Criteria) Norms

Grahya Criteria	R. T.	R. R. S.	R. A.	A. P.	A. K.	B. R. R.	R. P. S.	R. C.	R. C. M.	R. K. D.	Y. R.
Candrabham[4]				+							
Candraloha Samaprabha[3]	+										
Dhavala[1,5,7]		+			+	+		+	+		+
Drutadravam[3,1,5]	+	+			+	+		+	+	+	+
Gaurava[1,5,8]		+			+	+		+	+		+
Khurakara[4]				+							
Kshurakara[4]				+							
Laghu			+								
Mridu[1,2,5]	+	+	+		+	+		+	+	+	+
Nishabda[1,2,5]	+	+			+	+		+	+		+

List of 'Agrahya' (Exclusion Criteria) Norms

Table 3: List of 'Agrahya' (Exclusion Criteria) Norms

Agrahya Criterias	R. T.	R. R. S.	R. A.	A. P.	A. K.	B. R. R.	R. P. S.	R. C.	R. C. M.	R. K. D.	Y. R.
Shyamshubhraka[1,5]		+			+	+		+	+		+
Dhusara[3]	+										
AnyaDhatu Vimishrita[3]	+										
Mishraka[3,8]	+								+		
Krishna[3]	+										
Kathina[3]	+										
Ruksha[3]	+										
Drave Atikathina[3]	+										

R.T. - Rasatarangini, R.R.S.- Rasaratnasamuccaya, A.P.- Ayurved Prakash, A.K.- Anandakanda, R.P.S.- Rasaprakasha Sudhakara, R.C.- Rasacintamani, R.C.M.- Rasendra Cudamani, R.K.D.- Rasakamadhenu, Y.R.- Yogaratnakara

Total 19 criteria of Grahya Vanga and 7 criteria of Agrahya Vanga were divided according to organoleptic assessment i.e. Shabda, Sparsha, Rupa, Rasa and Gandha.

Critical study of Grahyagrahyatva criteria of Vanga

For proper assessment of Grahyagrahyatva, the primary step would be complete understanding of the meaning conveyed by the Sanskrit terms. For this purpose, the adjectives regarding the appearance of Vanga were enlisted and their meanings were searched from the Sanskrita-English dictionary of Monnier-Williams.[11]

E. g. Candrabham

Chandravat Aabha Yasya Sa: |
Candra – Pu. Devata, Soma.
Having a brilliancy or hue of light, the Moon
Abha– Looks like, Glittering or Shining like.
Candrabham - Looks like, Glittering or shining like moon.

Subjective assessment

After scrutiny of each Grahya and Agrahya criteria of Vanga, literary meaning i.e. Artha Nishchiti was done.

Procurement of Vanga samples

Total 16 samples of Vanga were procured from various sources like mine, local market and pharmacies and were labelled according to GPS – Global Positioning System. Samples were coded as 'S-1' to 'S-16'.

Proforma for assessment of 'Vanga' samples

The proforma was validated by research guide, statistician and the senior faculties in the department. The proforma includes information about expert and guidelines for assessment of samples. Precise meanings of Grahya and Agrahya criteria are enlisted from dictionary meanings. The Grahya and Agrahya criteria incorporated in proforma are assessed organoleptically by the experts.

Total 4: Numbers of experts were consulted and were divided in three groups

Name of group	No. of experts
Ayurvedic academicians, Teachers and Practitioners	6
Ayurvedic Pharmacists and Research scholars	7
Metallurgists and Geologists	6

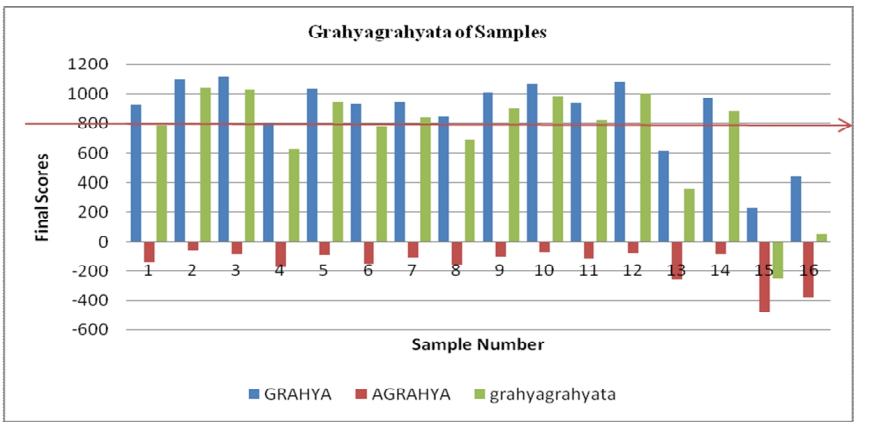
Method of Assessment

Each criterion was scored from 1 to 100 for each sample. Data was entered to the spread sheet. Accuracy and validity of data was checked while doing the data entry. Data was rearranged according to 19 observations of a single sample with Grahya 19 and Agrahya 7 observations. Calculation of scores was done. Then statistical calculations were done with the help of 'ANOVA test' and 'Kolmogorov- Smirnov Test'. After the statistical assessment, 3 highest scoring samples were selected as Grahya and 3 lowest scoring samples were selected as Agrahya samples, which were further subjected to analytical study.

Table 5: Final scores, Ranks and Revised names of Grahya and Agrahya samples

Sample No.	Final Score	Rank	Grahya and Agrahya samples	Revised Sample Name
2	1042	1	GRAHYA SAMPLES	G1
3	1030	2		G2
12	1005	3		G3
13	362	14	AGRAHYA SAMPLES	A1
16	56	15		A2
15	-254	16		A3

Grahyagrahyatva of 16 samples



Graph 1: Final Grahyagrahyatva of 16 samples

Above graph represents Grahyagrahya assessment of 16 samples. Positive bars are above X- axis in blue colour represents Grahyatva, negative bars below the X-axis in red colour represents Agrahyata and Green bars represents Grahyagrahyatva of 16 samples.

Analytical Assessment

3 Grahya and 3 Agrahya samples were subjected for further analysis. Results were as follows.

Table 6: Analytical results of Grahya and Agrahya samples

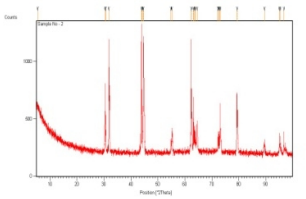
S. No.	Tests	Sample G1	Sample G2	Sample G3	Sample A1	Sample A2	Sample A3
1.	Hardness	9.4	6.8	12.2	56.8	32.9	12.5
2.	Specific Gravity	7.28	7.05	7.28	7.05	10.51	10.65
3.	Melting Point	239° C	234° C	259° C	257° C	337° C	333° C
4.	Electrical Conductivity	450 mA	850 mA	1200 mA	400 mA	200 mA	75 mA
5.	XRF	Sn- 97.66 %	Sn- 97.06 %	Sn- 96.53 %	Zn- 98.21 %	Pb- 85.62 %	Pb- 89.3 %

Reflectivity

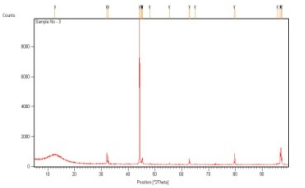
- Sample G1 and G3 are highly reflecting samples.
- Sample A3 shows some amount of reflectivity, less than G3 and more than A2.
- Reflectivity of sample G2, A1 and A2 is 50 % to that of sample G1 and G3.

Reflectivity of the material depends upon purity, roughness, ambient of sample etc.[12]

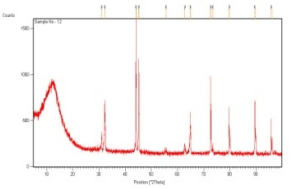
X-Ray Diffraction (XRD)



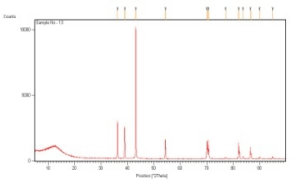
Graph 2: XRD of sample G1,



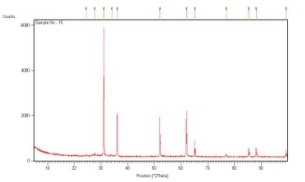
Graph 3: XRD of sample G2,



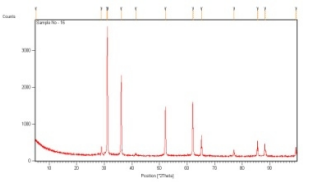
Graph 4: XRD of sample G3



Graph 5: XRD of sample A1,



Graph 6: XRD of sample A2,



Graph 7: XRD of sample A3

Sample XRD reports were matched with the standard XRD reports of US Research Nano materials, www.nanoshel.com, www.intechapen.com.

Table 7: XRD result of samples

Peak of Tin	In samples G1, G2 and G3.
Peak of Zinc	In sample A1.
Peak of Lead	In samples A2 and A3.

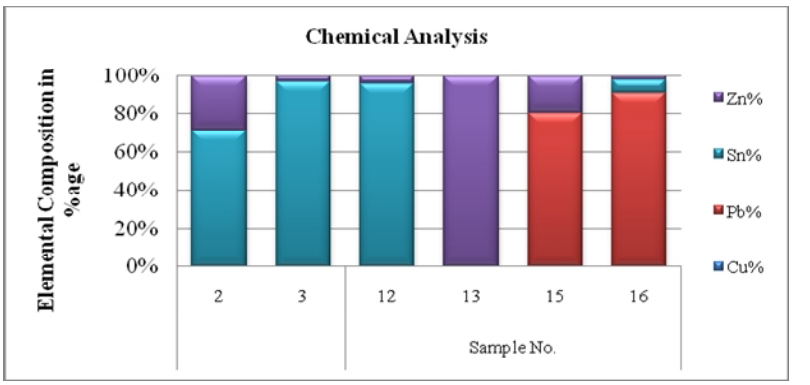
X-Ray Fluorescence (XRF)

Table 8: XRF result of samples

Element	Concentration	Sample No.
Tin	More than 96.5 %	G1, G2, G3
Zinc	More than 98.60 %	A1
Lead	More than 85 %	A1, A2

XRF reports shows presence of trace elements like Si, Fe, Ca, Mg, As, Al etc. in Vanga samples

Qualitative Analysis – Electrogravimetry



Graph 8: Chemical composition of samples[12]

Electrogravimetry confirms elemental assay as in XRD and XRF tests, Samples G1, G2 and G3 shows presence of Tin at maximum level, Sample A1 shows presence of Zinc and samples A2 and A3 shows Lead at maximum concentration.

Metallography

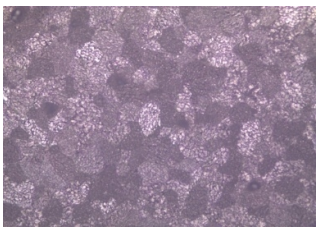


Photo 1: Microstructure of 'G1'

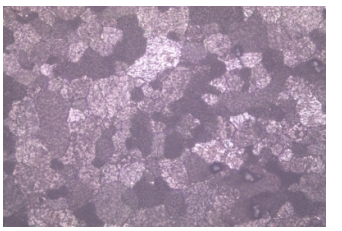


Photo 2: Microstructure of 'G2'

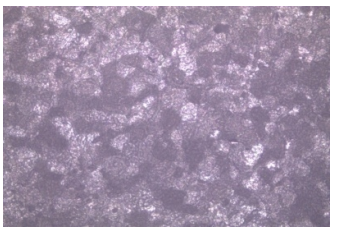


Photo 3: Microstructure of 'G3'

Photo 4: Microstructure of 'A1'

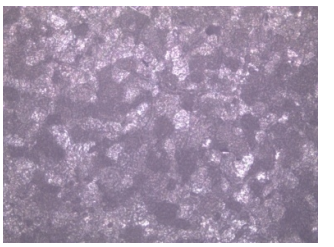


Photo 5: Microstructure of 'A2'

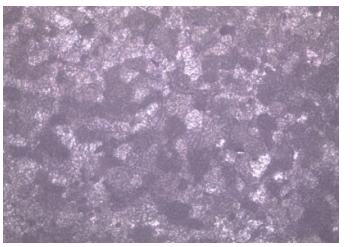


Photo 6: Microstructure of 'A3'

Metallography test represents the microstructure of metals. Above photographs shows grain structure of Vanga samples.

Grain structure

If metal undergoes any processing results into change in the grain structure of that metal. Microstructure can reveal process specificity of the metal.

Colour

Images of sample no. G1, G2 and G3 show microstructure of Tin. The white and bright part present in the images with their grain boundaries indicates presence of Tin. Image of sample A1 shows microstructure of Zinc. Brown coloured large patches with the grain boundaries indicate presence of Zinc.

Grain size

G2 and G3 are better than G1 while considering softness of metal due to presence of large sized grains present in sample G1 and G2.

Images of sample A2 and A3 are blurred, black in colour and do not shows grain boundaries. Specific etchant is used to stain grains of specified metal. Sample A2 and A3 possess lots of impurities in it. It is difficult to form an etchant to stain such material.

Statistics to analytical tests

For contemporary assessment of samples, above ten tests were executed. Results thus obtained show minor dissimilarities. It was indispensable to separate the samples, as acceptable and rejectable, on basis of analytical test results, with the help of statistics.

Table 9: Final result of subjective and analytical assessment

S. No.	Assessment done by Proforma Method	Assessment done by Analytical Method
A.	**Ranking of Grahya samples**	
	G1 - 1042	G2 - 102
	G2 - 1030	G1 - 98
	G3 - 1005	G3 - 92
B.	**Ranking of Agrahya samples**	
	A1 - 362	A3 - 36
	A2 - -254	A1 - 32
	A3 - 56	A2 - 24

It shows that, Grahya and Agrahya samples selected by subjective assessment match with the assessment done by analytical methods to satisfactory and expected extent.

DISCUSSION

Conceptual study

In early days, Vanga in small quantity was found in India as well as imported from neighbouring countries. At present, India import Tin from Malaysia. Grahyagrahyatva criteria as well as nomenclature (Naam Rupa Vidnyana) of Vanga also reveals Grahyagrahyatva assessment i.e. standardization of Vanga Dhatu. (Table 1), e.g. Trapu - Trapate – Mixed with other metals, Simhalam - Siloni - Previously found in Simhala Desha, Shwetarupyaka - Colour of Vanga is like silver.[4] Greek word for Casseterite-' Kassiteros' shows similarity with Sanskrit word 'Kastira'(Kaas, to shine). This argument has been used to explain the Eastern origin of Vanga Dhatu.[11] Rasashastra texts have mentioned 2 types of Vanga Dhatu – Mishraka and Khurakara as well as Shveta

and Krishna.[4] Among these, Khuraka from Grahya category is associated with shape, whereas, Mishraka depicts its mixed nature. These 2 types are also taken as standards for Grahya and Agrahyatva. In physical chemistry of Tin, 'Cry of tin' is the property observed for the identification and standardization.

Assessment of Grahyagrahyatva criteria of Vanga

For the proper assessment of Grahyagrahyatva criteria of Vanga, critical study of Grahyagrahyatva criteria is first and important step. Grahyagrahyatva criteria have been mentioned with relevance to nature, so as to ease their identification. E.g. Trapusamarupa, Shwetarupyaka these words used for Grahya Vanga indicating similarity of Vanga with silver.[4] Ayurveda texts have used such comparison because nature of parameters are seldom altered and hence exist for infinite period so as to guide further generations.

Samples

Constitution of Vanga sample depends upon geological surrounding. When Vanga is extracted from its mineral, it undergoes various extraction processes. It can be resulted into alteration in the shape, colour, traces etc. of Vanga, which further can affect Grahyagrahyatva of the sample.

Proforma findings

Chandrabham, Rupyabham and Shubhra are Varna i.e. colour criteria of Vanga.[1] Varna criteria are easy to assess by the naked eye at primary level. Hence, by this method, it is easy to identify samples while purchasing them from the market; it determines quality of Vanga sample. Nirmala, Swaccha and Shuddha criteria are used for assessment of purity of Vanga.[3] This assessment can be change with oxidation rate of the sample. Tin surface undergoes oxidation due to exposure to the air, giving its surface a blackish tinge. Therefore, the sample least reactant to air shows delayed discoloration and thus more Grahya. Mrudu and Kathina criteria of Vanga are shape dependent, assessment may change with the subject and are possible to get altered during recycling.[4] Khurakara and Kshurakara criteria of Grahya Vanga are shape dependent and not significant for assessment using proforma.[4]

Significance of Analytical Tests

Hardness Test

Pharmaceutics and Quantum of Energy i.e. Puta required to prepare Vanga Bhasma depends upon hardness.

Melting Point

The sample of Vanga which took less time to melt implies to criteria Drutadravam.[1,3] Melting point can be altered with addition of impurities in it.[12]

Shodhana process for Putiloha Varga is known as Dhalana and for other Loha Varga known as Nirvapana. If Vanga is given excess heat during Bhasma Nirmana, then Vanga loses its particle nature and reunites to solitary form. This process is called as Utthana. Drutadravam or Ushnasaham criteria explain the difficulty of early Punarutthana of Vanga.

Reflectivity

'Snigdha' has been mentioned as Grahya criterion for all metals, because metallic lustre is the general property of all metals.[1,3,4] Therefore, in order to check metallic lustre, all samples were subjected to Reflectivity Test.

Purity of Vanga

Purity of Vanga samples determined by XRD, XRF and chemical analysis; Purity assessment of Vanga samples is easier with the help of Grahyagrahyatva criteria than physico-chemical analysis. But adulteration at micro level may show toxic effects. Grahyata, Shudhata and Purity of Vanga show minute difference between them.

Analytical assessment

Table 10: Co-relation in subjective criteria and analytical assessment

Ayurvedic assessment criteria	Related analytical assessment
Kathin, Mrudu[4]	Hardness test
Guru, Laghu[1,3]	Specific gravity test
Drutadravam, Ushnasahatvam[1,3]	Melting point
Snigdh[1,3,4]	Reflectivity test
Nirmal, Swachha, Shuddha	XRD, XRF, Chemical analysis

CONCLUSION

Standard database was created for Grahya and Agrahya criteria of Vanga after studying Rasashastra texts. Also synonyms of Vanga reveal importance in the raw material standardization. Presently Vanga is imported mainly from Malaysia.

Shape of the sample also is very much important in the assessment of Grahyagrahyatva and the shape perhaps will make notable effect on various pharmaceutical procedures.

Analytical study of selected Grahya samples G1, G2 and G3 contains Tin in more than 96.5 % quantity. Agrahya sample no. A1contains Zinc- 98.60 %, A2 contains Lead- 85.62 % and A3 contains Lead- 89.3 %. In these samples, presence of Lead, Arsenic, Zinc and Silicon in Vanga is considered as Agrahya parameters. Samples A1, A2 and A3 were found Agrahya in Subjective assessment and were also rejected in chemical assessment. Impurity of Lead in small quantity can alter the colour of Vanga to a great extent. Humidity and oxygen affect the Tin surface and black coloured Tin oxide is formed on the surface of Vanga.

Chemical analysis shows percentage of Tin within it and Metallography test is helpful for assessing softness and purity of the metal. Raw material standardization correlates the ancient parameters with the current

physico-chemical parameters. Grahya and Agrahyatva assessment match with the assessment done by analytical methods to satisfactory and expected extent.

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