Research Article

Available online through
www.ijrap.net

IJRAP
ISSN 2229-3566

COMPARATIVE STUDY OF RASAMANIKYA (AN AYURVEDIC FORMULATION) WITH PURIFIED HARTALA (ORPIMENT)

Madhamshetty Hariprasad, Sawant Ranjeet S*, Bhingare S. D

Senior Medical writer II at Novartis Healthcare Pvt. Ltd; Vittal Rao Nagar, Madhapur Hyderabad, Andhra Pradesh, India

Assistant professor, Dept. of Rasashastra and Bhaishajya Kalpana, Govt. Ayurved College, Vazirabad road, Nanded, Maharashtra, India

P.G. Scholar, Dept. of Sharir Rachana, Govt. Ayurved College, Vazirabad road, Nanded, Maharashtra, India

Received on: 06/01/2011 Revised on: 13/02/2011 Accepted on: 09/03/2011

ABSTRACT

Hartala (Orpiment) is being in practice widely in Ayurvedic formulations in spite of its toxic nature. Rasamanikya is the drug prepared from only Hartala is proved to be much effective in various disorders like Vata-rakta (Gout), Kushtha (Skin disorders), Shwasa (Bronchial asthma), etc. This study was undertaken to understand the basic difference between these two forms of Arsenic. One is Hartala (As_2S_3) and Rasamanikya (As_2S_2).

The study includes -1. Purification of Hartala (Orpiment) 2. Preparation of Rasamanikya. and 3. Comparison of purified Hartala and Rasamanikya.

Hartala purified with help of Juice of Kushmand i.e. *Benincasa hispida* Linn. by dolayantra (process of steaming) Method. Rasamanikya prepared by four different methods and compared to get most standard product.

On chemical analysis it was found that Arsenic percentage was highest in Rasamanikya prepared by electric bulb method and least when prepared in Abhraka patra samput. The percentage of Sulphur was found to be high when prepared in Abhrakapatra samput and least in Sharav Samput method. On comparing Purified Hartala and Rasamanikya it was found that there was reduction in bulk density, moisture content and ash value from purified Hartala to Rasamanikya. It shows that preparation of Rasamanikya from purified Hartala is its conversation in to easily absorbable and more potent form. On ESCA analysis it was found that there is no elemental arsenic present in both samples which is toxic in nature, but in the form of sulphide complex form.

KEYWORDS: Ayurveda, Rasashastra, Hartala, Rasamanikya, ESCA

***Corresponding Author**

Dr. Ranjeet S. Sawant, Assistant Professor, Department of Rasashastra and Bhaishajya Kalpana, Government Ayurved College, Vazirabad Road, Nanded, Maharashtra State Pin code – 431601

INTRODUCTION

Ancient texts of Rasashastra have described a few important minerals and classified them on the basis of their usefulness for specialized process of mercury in the following groups i.e. Maharasa, Uparasa and Sadharana rasa. The minerals comes under Uparasa are Gandhaka (Sulphur), Gairik (Iron Oxide), Kasis (Ferrous Sulphate), Kankshi (Alum), Hartala (Orpiment), Manashila (Realgar), Anjana (Stybnite), Kankustha (Resin obtained from Gambose tree).[1]

Uparasa in general are useful for Parad Bandha (Production of bonds of mercury with other elements), Marana process (Calcinations) of Metals and Minerals and also for potentiating of mercury for Lohavedha (Boring in to body) and Dhatuvedha (process of converting base metals in to gold or silver) purpose.

Out of these Uparasa, Hartala (Orpiment) is highly potent mineral which is included in the list of poisonous drugs by Drug and Cosmetics Rule 1940 (Schedule E) because of its highly toxic nature in its crude form.[2]

Rasamanikya is the formulation prepared with only Hartala by heating it. It is the best remedy for several chronic diseases like Kushtha (Skin disorders), Shwasa (Bronchial Asthma).[3] Many pharmaceutical procedures developed in medieval period and adopted to process the metals and minerals to ascertain their conversation into biologically effective, absorbable and pharmaceutically suitable forms.

One such beautiful example is preparation of Rasamanikya from Hartala. Hartala and Rasamanikya are both compounds of Arsenic, which in given impure form prove to be fatal but work like ambrosia if properly subjected to Standard operative procedure mentioned in Rasashastra.

So an attempt was made to study Hartala and Rasamanikya with special reference to their physicochemical properties.

AIM AND OBJECTIVE

1. Purify Hartala by procedure mention in RRS (Rasaratna Samucchaya)
2. Prepare Rasamanikya by various methods.
3. Compare purified Hartala and Rasamanikya w.s.r.t. Physico-chemical properties

MATERIAL AND METHODS

Step 1: Purification of Crude Hartala

Raw Hartala sample procured from market and identified at reputed drug testing laboratory.

Materials

- Crude Hartala (Orpiment) procured from market – 100 gms.
- Kushmand Swarasa (juice of fruit of *Benincasa hispida* Linn. – As per requirement
- Dola Yantra (special apparatus mentioned in Rasashastra texts for steaming of various substances)

Method

100gms of crude Hartala was crushed into small pieces. Kushmand Juice filled in to earthen pot. Pottali of cotton cloth was made with crude Hartala kept in it. This pottali hung in pot with help of wooden stick and subjected to steam in Kushmand Swarasa (Juice) for 3 hrs. It was then allowed to cool and Hartala was removed and washed with lukewarm water. After drying it was weighted.[4]

Step 2: Preparation of Rasamanikya

Rasamanikya is prepared by four methods out of which 3 are mentioned in classical books and fourth one is new method.

Method 1: Preparation of Rasamanikya By Sharav Samputa Method

Materials

- Purified Hartala
- Kushmand Swarasa
- Curd
- Sharav Samputa (Earthen container with lid)
- Pyrometer
- Coal fire

Procedure

30gms of purified Hartala braked in to small particles (same as shape of rice) were subjected to bhavana (immersing with liquids) for 3 times with Kushmand Swarasa (juice) and 3 times with sour curd. Then it was washed and dried. 25 gms of it was kept into sharav samputa and joint was sealed with china clay. To favor the monitoring of internal temperature, a detector rod was placed in gap between both sharavas and sealed. The Samputa was heated by means of moderate coal fire till the lower basin become red hot. Maximum temperature exceeded till 660^{o}C. Total time required for heating was 30 min. Then content were collected after the whole apparatus got cooled itself.[5]

Method 2: Preparation of Rasamanikya By Abhrakpatra Samputa Method

Materials

- Purified Hartala
- Kushmand Swarasa
- Curd
- Abhraka patra (White mica thin sheets)
- Pyrometer
- Coal fire

Procedure

30gms of purified Hartala was subjected to bhavana (immersing with liquids) for 3 times with Kushmand Swarasa (juice) and 3 times with sour curd. After bhavana Orpiment was washed with lukewarm water. On drying it was broken in to particle as small as rice grains. 25 gms of that Hartala was kept on one thin mica sheet and covered with another sheet of same size. These sheets sealed around their margins with help of china clay. After drying properly, this samputa was subjected to high temperature (Coal fire) till the granules inside turn red in color. After self cooling, Rasamanikya inside obtained carefully.[6]

Method 3: Preparation of Rasamanikya By Valuka Yantra Method.

Materials

- Purified Hartala
- Kushmand Swarasa
- Curd
- Abhraka patra (White mica thin sheets)
- Pyrometer
- Coal fire

Procedure

30gms of purified Hartala was subjected to bhavana (immersing with liquids) for 3 times with Kushmand Swarasa (juice) and 3 times with sour curd. After bhavana orpiment was washed with lukewarm water. On drying it was broken in to particle as small as rice grains. 20gms of that Hartala was kept on one thin mica sheet and covered with another sheet of same size. These sheets sealed around their margins with help of china clay. This samputa was kept into sharav samputa and

joint was sealed with china clay. This whole apparatus was kept in to Valuka Yantra. This Valuka Yantra subjected to moderate heat (0 to 360^{o}C) for 3 hrs. After self cooling Rasamanikya inside obtained carefully.[7]

Method 4: Preparation of Rasamanikya by Bulb Method

Materials

- Purified Hartala
- Kushmand Swarasa
- Curd
- Glass bulb (electric bulb)
- LPG stove.

Procedure

30gms of purified Hartala was subjected to bhavana (immersing with liquids) for 3 times with Kushmand Swarasa (juice) and 3 times with sour curd. After bhavana orpiment was washed with lukewarm water. After drying it was broken in to particle as small as rice grains. 20gms of that Hartala was kept in empty fused electric bulb and heated gently with help of LPG stove. The contents were found melting, liberating yellow fumes followed by white fumes. The color of content inside was turned in to dark red. At this stage heating stopped and allowed for self cooling. The content inside collected carefully.

RESULTS

Coding Of Sample For Analytical Study

Sample 1 - Purified Hartala
Sample 2 - Rasamanikya by Valuka Yantra method
Sample 3 - Rasamanikya by Sharav samputa method.
Sample 4- Rasamanikya by bulb method
Sample 5 - Rasamanikya by Abhrakpatra samputa method

Analytical Study (Chemical Analysis)

Estimation of Arsenic and Sulphur

All the above samples were subjected to Iodometric method mentioned in 'Pharmacopeial standards for ayurvedic formulations' for determination of Arsenic and IS: 3383-1982 for determination of Sulphur as shown in **table 1**.[8]

As Rasamanikya is being prepared by Abhrakpatra samputa method in all pharmaceutical companies, it was decided that further Analysis and comparison will be done between 'Purified Hartala' and 'Rasamanikya prepared by Abhrakpatra samputa method'.

Physical Analysis

Coding Of Sample For Physical Analysis

Sample 1 - Purified Hartala
Sample 2 - Rasamanikya Abhrakpatra samputa method

Estimation of Bulk Density

For determination of bulk density, 2gms of each sample is taken and volume was measured by filling the powders in cylinder and pressure was applied to make as possible as compact and result obtained is shown below in **table2**.

Estimation of Moisture Content

For determination of Moisture content, 2gms of each sample is kept in glass bottle and placed in the desiccator. These samples were dried at 110^{o}C and result obtained is shown below in **table 3**.

Estimation of Total Ash and Acid Insoluble Ash

About 3gms of accurately weighed sample was taken in platinum dish and incinerated by gradually increasing heat till it is free from carbon. It's allowed to cooled and weighed.

Total ash obtained above is boiled with 25 ml dilute HCl for 5 minutes. The insoluble matter was collected on ash less paper. This paper washed with 10 ml water twice and air dried. Then it was ignited in tarred platinum dish and weighed after cooling. Result obtained is shown below in **table 4**.

ESCA – Electron Spectroscopy for Chemical Analysis

Electron Spectroscopy for Chemical Analysis **(ESCA)** is an analysis technique primarily used in the identification of compounds on the surface of a sample. It utilizes X-Rays with low energy (typically 1-2 keV) to knock off photoelectrons from atoms of the sample through the photoelectric effect. The energy content of these ejected electrons is then analyzed by a spectrometer to identify the elements where they came from.[9]

ESCA of Purified Hartala

The scan of purified Hartala shows that elements such as Arsenic, Sulphur, Oxygen, Carbon and Silica are present in the sample. Arsenic was found in complex state having binding energy peak at 43.3 ev as in 3d and 142.5 ev as in 3P. The elemental Arsenic has value of 42.0ev. Hence it was observed that Arsenic is in sulphide complex form. The presence of S 2P in the survey scan also supports the above observation. Again arsenic found to be in the form of (As Me 3) having binding energy 211.1 ev as in 3S.

ESCA of Rasamanikya Prepared Abhrakpatra Samputa Method

The scan of Rasamanikya shows elements such as Arsenic, Sulphur, Oxygen, Carbon and Silica are present in the sample. Arsenic was found to be in the form of complex state having binding energy 43.6 ev as in 3d and 142.5 ev as in 3P. The elemental Arsenic will have value of 42.0 ev binding energy. So it confirms the presence of Arsenic in sulphide complex form. The presence of S 2P in the survey scan also supports the above observation.

DISCUSSION

Hartala is being in practice vividly in ayurvedic formulations in spite of its toxic nature. Rasamanikaya is

the drug which is proved to be much effective in skin diseases and bronchial asthma.

The concept of shodhana (purification process mentioned in ayurveda) is to remove and detoxify the impurities to enhance efficacy of material. Many references are mentioned in ayurveda texts about Hartala Shodhana, out of which many authors have indicated Kushmand Swarasa (Juice of Fruit of *Benincasa hispida* Linn.). Due to its Madhura Rasa and Sheet Guna, it subsides Ushna and Tikshana guna of Hartala. Hence it is considered as antidote of Hartala. Thus Hartala was subjected to Kushmand swarasa for its purification.

Various pharmaceutical methods are described in Rasashastra texts for preparation of Rasamanikaya. By these methods Rasamanikaya was prepared in four different methods.

Colour of Rasamanikya

The colour of all four samples prepared by different methods in their powder form was similar and it was red.

Duration of Procedure

It was found that Rasamanikya prepared by Abhraka patra samputi method took least time where as maximum time was consumed by Valuka Yantra Method which is shown below in **table 5**.

Temperature Requirement

Abhraka patra samputi method was prepared under comparatively low temperature where as for Valuka Yantra Method high temperature was needed which is shown below in **table 6**.

Loss Of Weight During Process

Weight loss was less in Sharav Samput method and more in fused Electric bulb method which is mentioned below in **table 7**.

Chemical Analysis

On chemical analysis it was found that Arsenic percentage was highest in Rasamanikya prepared by electric bulb method and least when prepared in Abhraka patra samput. The percentage of Sulphur was found to be high when prepared in Abhrakapatra samput and least in Sharav Samput method.

The difference in As% and S% between all four samples could be mainly due to following reasons:

1. Medium of heating used in procedure
2. Oxygen supply in procedure

Medium of Heating in Procedure

While using Abhrakapatra and electric bulb as medium for transferring heat, it was given directly to Purified Hartala. While using Sharav samput as medium, heat was transferred from sharava to Purified Hartala after it got heated. In Valuka Yantra method temperature maintained constant and very less amount of heat was transferred to purified Hartala constantly.

Oxygen Supply During Procedure

There was less oxygen supply in Abhrakapatra Samput method, Sharav Samput method and Valuka Yantra method during procedure. Relatively there was abundant oxygen supply during the preparation of Rasamanikya by electric method.

Pharmaceutical Standards For Rasamanikya

The text "Pharmacopeial standards for Ayurvedic formulations" has mentioned standard percentage of arsenic and sulphur in Rasamanikya i.e. 59 to 61% w/w for arsenic and 38 to 41% w/w for sulphur.[10]

ESCA Analysis

After analysis of Purified Hartala and Rasamanikya by ESCA it was found that binding energy of arsenic in purified Hartala increased to that of in Rasamanikya below in **table 8**.

In both samples Arsenic is in form of sulphide complex. There is difference in one complex peak between Purified Hartala and Rasamanikya i.e. Arsenic is not found to be in form of complex (AsMe3) having binding energy 211.1 eV as As in 3S as it is found in Purified Hartala.

CONCLUSION

By pharmaceutical analysis we can say that Abhrakapatra Samput method is standard to prepare Rasamanikya by considering colour, duration of preparation and minimal weight loss in final product.

After chemical analysis we can conclude that Rasamanikya prepared by Abhrakapatra method is standard based on principles mentioned in text "Pharmacopeial standards for Ayurvedic formulations"

The different methods mentioned for preparation of Rasamanikya in different texts may be due to their utilization in different indications.

On comparing Purified Hartala and Rasamanikya it was found that there was reduction in bulk density, moisture content and ash value from purified Hartala to Rasamanikya. It shows that preparation of Rasamanikya from purified Hartala is its conversation in to easily absorbable and more potent form.

On chemical analysis it was found that decrease in arsenic level in Rasamanikya compared with purified Hartala.

On ESCA analysis it was found that there is no elemental Arsenic present in both samples which is toxic in nature, but in the form of sulphide complex form.

REFERENCES

1. Kulkarni SB, editor, Rasaratnasamucchaya, 1st edition, Kolhapur, India. Shivaji university Sanskrit and Prakrit series.1970 page 50-51
2. Malik V, editor, Drug and Cosmetics Act 1940, 18th edition, Lucknow, India. Eastern Book Company. 2005 page 282

3. Tripathi I, editor, Rasavidyotini hindi commentary. In Rasendrasarsangraha, 4th edition,Varanasi, India. Chaukhambha Orientalia 2006 page 48.
4. Mishra SN, editor. Siddhaprada Hindi commentary, In Bhaishajya Ratnavali, 1st edition, Varanasi, India. Chaukhambha Surbharati publication 2005 page 42
5. Mishra SN, editor. Siddhaprada Hindi commentary, In Bhaishajya Ratnavali, 1st edition, Varanasi, India. Chaukhambha Surbharati publication 2005 page 872
6. Shastri k, editor, Prasadini Commentory. In Rasataringini, 11th edition, New Delhi, India. Motilal Banarasidas publications 2004 page 258
7. Shastri k, editor, Prasadini Commentory. In Rasataringini, 11th edition, New Delhi, India. Motilal Banarasidas publications 2004 page 257
8. Pharmacopeial standards for ayurvedic formulations, 1st edition, New Delhi, India. Yugantar Publication WH 27, 1987 page 647
9. ESCA- en.wikipedia.org/wiki/X-ray_photoelectron_spectroscopy (last modified on 18 February 2011 at 03:06.) Available from http://en.wikipedia.org/
10. Pharmacopeial standards for ayurvedic formulations, 1st edition, New Delhi, India. Yugantar Publication WH 27, 1987 page 272

Table 1: Determination of Arsenic and Sulphur in sample obtained after purification of Hartala and preparation of Rasamanikya by various methods.

Sample	Arsenic (%)	Sulphur (%)
1	61.9	37.7
2	61.8	33.3
3	63	30.7
4	64.1	35.2
5	57.9	38.8

Table 2: Determination of Bulk density in sample of Purified Hartala and Rasamanikya prepared Abhrakpatra samputa method.

Sample	Bulk Density
1	1.672
2	1.01

Table 3: Determination of Moisture content in sample of Purified Hartala and Rasamanikya prepared Abhrakpatra samputa method.

Sample	Loss on drying at 110^0C (%)
0	0.46
1	0.12

Table 4: Determination of Total and Acid insoluble Ash in sample of Purified Hartala and Rasamanikya prepared Abhrakpatra samputa method.

Sample	Total ash (%)	Acid insoluble ash (%)
1	0.02	Negligible
2	0.054	Negligible

Table 5: Time (duration) required in each procedure of preparation of Rasamanikya by four different methods.

Sr. No.	Method of preparation	Time taken
1	Abhrak Patra Samput	3 min.
2	Electric bulb	10 min.
3	Sharav Samput	30 min.
4	Valuka Yanra	3 hrs.

Table 6: Temperature required for preparation of Rasamanikya by four different methods.

Sr. No.	Method of preparation	Required temperature
1	Abhrak Patra Samput	300°C
2	Electric bulb	500°C
3	Sharav Samput	Internal temp – 660°C
4	Valuka Yanra	370°C

Table 7: Loss of weight observed during process of preparation of Rasamanikya by four different methods.

Sr. No.	Method of preparation	Weight of Hartala taken (Gms)	Weight of Rasamanikya obtained (Gms)	Weight loss (%)
1	Sharav Samput	25	23	8%
2	Abhrak Patra Samput	25	23	8%
3	Valuka Yanra	20	18	10%
4	Electric bulb	20	17.5	12.5%

Table 8: Binding energy observed in Arsenic, Arsenic in purified Hartala and Arsenic in Rasamanikya.

Sr. No.	Sample	Binding energy
1	Arsenic element	42.0 eV
2	Arsenic in purified Hartala	43.3 eV
3	Arsenic in Rasamanikya	43.6 eV

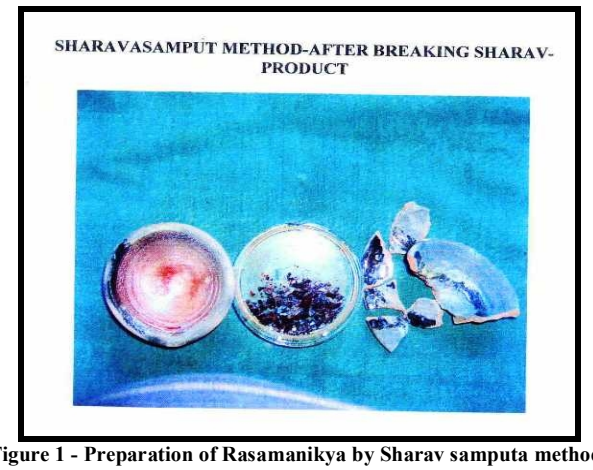

Figure 1 - Preparation of Rasamanikya by Sharav samputa method.

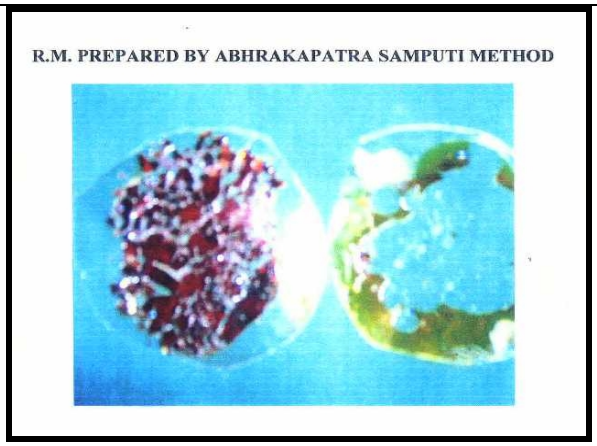

Figure 2 - Preparation of Rasamanikya by Abhrakpatra samputa method.

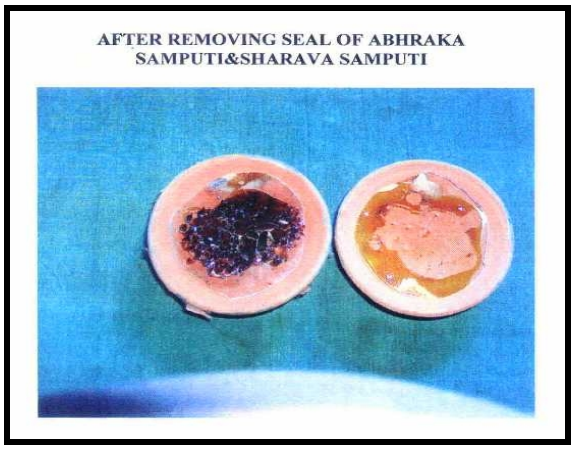

Figure 3 - Preparation of Rasamanikya by Valuka Yantra method.

Figure 4 - Preparation of Rasamanikya by bulb method

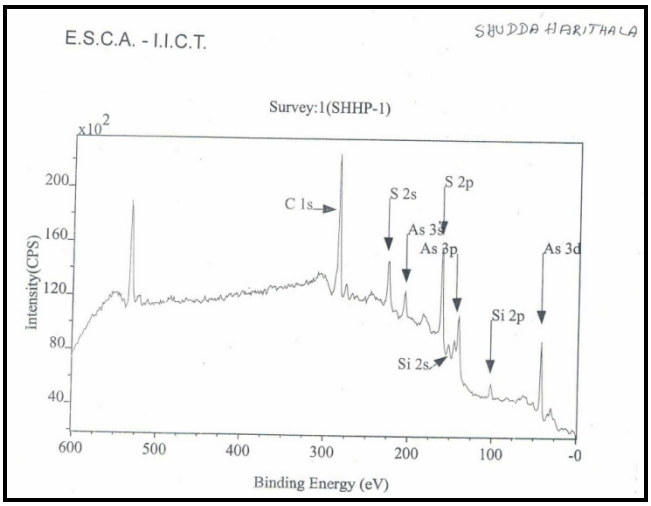

Figure 5 - ESCA of Purified Hartala

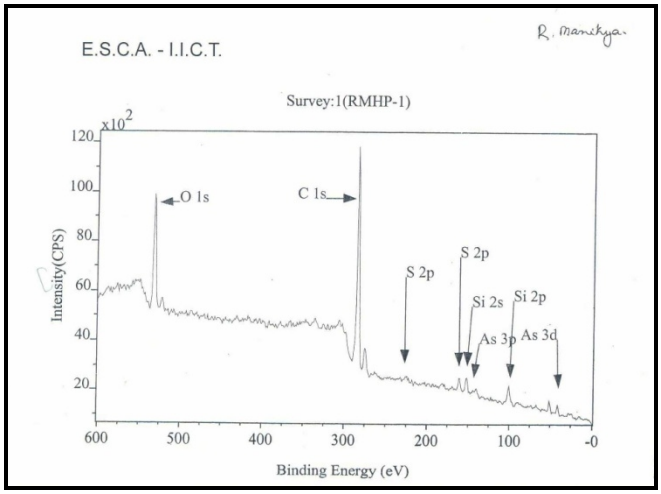

Figure 6 - ESCA of Rasamanikya prepared Abhrakpatra samputa method

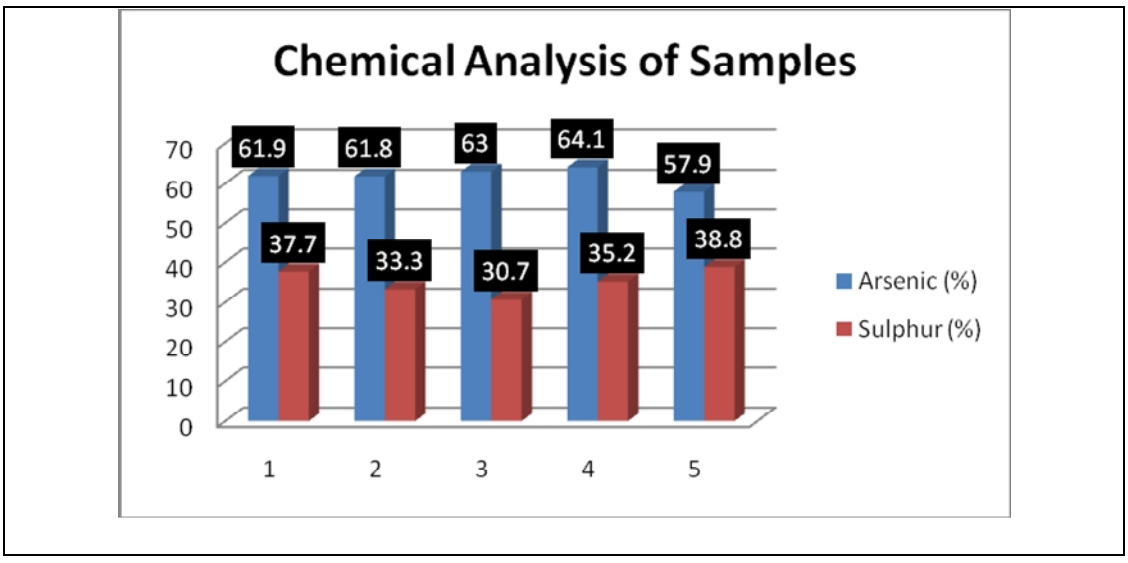

Figure 7 - Chemical Analysis of Sample of Purified Hartala (Sample 1) and Samples of Rasamanikya (Sample 2 to 5)

Source of support: Nil, Conflict of interest: None Declared