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Review Article

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A REVIEW ON APPLICATION AND IMPORTANCE OF ANALYTICAL METHODS FOR METALLIC PREPARATIONS (INCINERATED ASH) W.S.R. TO XRF AND XRD

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ABSTRACT

Standardization of herbominral drugs is important aspect for safety and efficacy. In Ayurvedic literature different bhasma pariksha's were mentioned for the assessment of good quality bhasma, but it should be cross verified and assessed with some modern analytical parameters. So for the qualitative and quantitative analysis of such metallic preparation different methods were described in modern chemistry, among which XRF and XRD techniques are most useful and commenly applicable for most of herbomineral preparations. Before going for the analytical tests for any drug, it is very important to know about the basic introduction, application, feasibility and importance of these analytical methods. So this review article is planned to provide the scientific knowledge for the application of suitable analytical methods wsr to XRF & XRD.

KEYWORDS: XRF, XRD, Analytical methods, Incinarated Ash, Bhasma, standardization.

INTRODUCTION

Metallic preparations (bhasma/ sindur/ pottali/parpati) are being used since years ago in Ayurveda therapeutics. Proper textual SOP's should be followed for the preparations of such medicines, otherwise it may lead to some safety and efficacy issues. So stringent precautions should be taken before using such metallic preparation for treatment purposes. Standardization is the important step for the preparation of any pharmaceutical product. It can be divided in to three steps, raw material standardization, process standardization and final product standardization. In modern chemistry there are different analytical methods explained. The main purpose of these analytical methods as follows

- Identification of compounds (Raw material standardization)
- Qualitative analysis
- Quantitative analysis
- Functional groups analysis
- Particle size analysis etc.

Suitable standardization method should be selected, as per the nature of drug and its probable constitution. All these analytical methods were generally applicable in the field of chemistry and pharmaceutical quality control for various purposes. In Ayurvedic pharmacopeia of india (API), various physiochemical standardization methods for herbal and herbo-mineral preparations were mentioned. But as expenditure for all these analytical methods are too high, without any funding source it is not feasible to perform all the prescribed analytical tests. So one can select the appropriate methods for the particular formulation as per nature and requirement of that drug. This review article is the small effort for the introduction, application and importance of analytical methods for metalic preparations (incinerated ash) like bhsama, sindura, pottali and parpati with special reference to X-ray fleurocense and X-ray diffraction.

AIM

Understanding the Scientific introduction and applicability of analytical methods w.s.r. to XRF and XRD.

OBJECTIVES

Online and offline literature review of analytical methods for drug standardization through different sources.

MATERIAL AND METHODOLOGY

As this is review article, this section gives the scientific introduction, applicability and importance of the analytical methods w. s. r. to XRF and XRD.

1. XRF: X-ray fluorescence

It is described under following heads

- Introduction to XRF

- Fundamental Principles of X-ray Fluorescence
- Instrumentation of XRF
- Users manual, Sample collection and preparation
- Application of XRF
- Merits and demerits of XRF techniques

1.1 Introduction to XRF

An X-ray fluorescence (XRF) spectrometer is a device that uses x-rays to conduct routine chemical analysis of rocks, minerals, sediments, and fluids in a generally non-destructive manner. It operates similarly to an electron microprobe using wavelength-dispersive spectroscopy (EPMA). An XRF is primarily utilised for bulk examinations of bigger fractions of geological materials because it is generally unable to do analyses at the small spot sizes typical of EPMA work (2–5 microns). One of the most popular ways for analysing major and trace elements in rocks, minerals, and sediment is the use of x-ray spectrometers due to their stability and convenience of use, relative ease of sample preparation, and low cost.[1]

1.2 Fundamental Principles of X-ray Fluorescence[1],[2]

The XRF technique is based on core ideas shared by a number of different instrumental techniques that use electron and x-ray interactions with samples, such as X-ray spectroscopy (e.g., SEM-EDS), X-ray diffraction (XRD), and wavelength dispersive spectroscopy (microprobe WDS).

- By interacting with radiation, atoms behave in a way that enables the investigation of major and trace elements in geological rocks by x-ray fluorescence. Ionization of materials is possible when they are energized by high-energy, short-wavelength radiation (like X-rays).
- An outer electron takes the place of the lost inner electron in an unstable atom if the radiation's energy is high enough to loosen a securely bound inner electron. Because the inner electron orbital's binding energy is lower than that of the outer one in this situation, energy is released.
- Fluorescent radiation refers to the radiation that is emitted and has a lower energy than the X-rays that are incident as the main source. The resultant fluorescence X-rays can be utilized to determine the abundances of elements that are present in the sample because the energy of the released photon is indicative of a transition between particular electron orbital's in a particular element.[1],[2]

1.3 Instrumentation of XRF

- The behavior of atoms when they contact with X-radiation makes it possible for XRF to analyze major and trace elements in geological materials. When a sample is irradiated by a powerful X-ray beam, or incident beam, some of the energy is scattered but some is also absorbed within the sample in a manner dependent on the sample's chemistry. According to the application, targets other than Rh, such as W, Mo, and Cr, can also be used to produce the incident X-ray beam.
- In turn, the stimulated sample produces X-rays along a range of wavelengths corresponding to the different kinds of atoms that are present in the sample.
- By ionizing and ejecting electrons from the lower (typically K and L) energy levels, the sample's atoms absorb X-ray energy.
- Electrons from an outer, higher energy orbital replace the expelled electrons. Due to the inner electron orbital's lower binding energy compared to the outer one, energy is liberated when this occurs.[3]

1.4 Users manual, Sample collection and preparation

- If suitable standards are provided, almost any solid or liquid substance can be analyzed. For rocks and minerals, standard commercial instruments for a sample that weighs at least a few grams of material, though the sample that is taken can be much greater.
- Rock samples that are several times larger than the largest grain or particle in the rock are obtained for XRF chemical analysis. When it can be separated into a tiny representative sample of a few tens to hundreds of grams, this first sample is then subjected to a series of crushing operations to reduce it to an average grain size of a few millimeters to a centimeter.
- The composition of the crushing instruments, which will unavoidably contaminate the sample to some ex tent, must be considered especially at this point.[4]

1.5 Application of XRF:[5]

X-Ray fluorescence is used in a wide range of applications, including

- Soil surveys & Production of cement
- Research in sedimentary, and metamorphic petrology
- Mining (e.g., measuring the grade of ore) and metallurgy (e.g., quality control)
- Environmental studies (e.g., analyses of particulate matter on air filters)
- Field analysis in geological and environmental studies (using portable, hand-held XRF spectrometers)
- Petroleum industry (e.g., sulfur content of crude oils and petroleum products)
- Manufacturing of ceramic and glass

1.6 Merits and demerits of XRF techniques[2]

Table no. 01: Showing Merits and demerits of XRF techniques.

Sr no	Merits of XRF	Demerits of XRF
1.	• Bulk chemical analyses of major elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P) in rock and sediment	• XRF has the ability to detect X-ray emission from virtually all elements, depending on the wavelength and intensity of incident x-rays.
2.	• Bulk chemical analyses of trace elements (>1 ppm; Ba, Ce, Co, Cr, Cu, Ga, La, Nb, Ni, Rb, Sc, Sr, Rh, U, V, Y, Zr, Zn) in rock and sediment detection limits for trace elements are typically on the order of a few parts per million	• In practice, most commercially available instruments are very limited in their ability to precisely and accurately measure the abundances of elements with Z<11 in most natural earth materials.
3.		• XRF analyses cannot distinguish variations among isotopes of an element, so these analyses are routinely done with other instruments
4.	-	• XRF analyses cannot distinguish ions of the same element in different valence states, so these analyses of rocks and minerals are done with techniques such as wet chemical analysis or Mossbauer spectroscopy.
5.		• Applicable for Relatively large samples, typically > 1 gram
6.		• Materials that can be prepared in powder form and effectively homogenized.
7.		• Materials containing high abundances of elements for which absorption and fluorescence effects are reasonably well understood

2. XRD: X-ray Diffraction

It is described under following heads

- Introduction to XRD
- Histrorical review of XRD
- X- ray definition
- Introduction to Crystallography
- XRD Analysis-Summary
- Braggs law : (X – ray diffraction and Braggs Law)
- Principles of XRD
- Disadvantages of XRD

2.1 Introduction to XRD[5]

X-ray Diffraction (XRD), which is a versatile, non-destructive technique that reveals, detailed information about the chemical composition and crystallographic structure of materials. It is utilized in a variety of settings ranging from chemistry and materials to geology and biological sciences.[6]

X-ray powder diffraction (XRD) is quick analytical method used to determine the phase of crystalline materials which reveal information on unit cell dimensions also. The material under analysis is finely powdered, homogenized, and the bulk composition is calculated on average.[5]

2.2 Historical review[7],[9]

- **1912: Maxwell von** Laue first discovered X-ray diffraction
- Determined that X-rays would be scattered by atoms in a crystalline solid if there was similarity in the wavelength of X-rays and the interatomic distances of the crystalline material.
- A primary use of XRD analysis is the identification of materials based on their diffraction pattern. As well as phase identification, XRD also yields information on how the actual structure deviates from the ideal one, owing to internal stresses and defects.

- Formula of Brags law : $2d\sin\theta=n\lambda$

λ = wavelength of the x-ray
θ = scattering angle
n = integer representing the order of the diffraction peak
d = inter-plane distance of (i.e atoms, ions, molecules)

- **1913: Sir William H. Bragg** and and his son **Sir W. Lawrence Bragg** derived the equation known as Bragg's Law to define diffraction as a function of the angle of incidence
- This law determined why the cleavage faces of crystals appeared to reflect X-ray beams at certain angles of incidence (θ). This is due to constructive interference.[9]
- Simulated the experiment, using visible light and tiny arrays of dots and pinholes to mimic atomic arrangements on a much larger scale.
- These experiments provided similar patterns to X-rays but were safer to work with than X-rays.
- **1914: von Laue** awarded Nobel Prize for discovery of X-ray diffraction by crystals and showing X-rays are electromagnetic waves

- **1915: Braggs** awarded Nobel Prize for their work determining the crystal structure of diamond, NaCl and ZnS.[7],[9]

2.3 X – Rays

- X-rays are electromagnetic radiation with very *short* wavelengths and *high* energy.
- X-rays have high energy and they penetrate opaque material, but are absorbed by materials containing heavy elements. As an x-ray beam travels through a substance its intensity decreases with distance traveled through the matter.
- Only a small range of characteristic x-rays are widely used for diffraction. Their K_a lines are used. The K_b line which is always present with K_a, at a slightly shorter wavelength, is filtered out using an absorbing film. The effective penetration of these x-rays determines the maximum thickness of specimens which can usefully be studied by XRD.[10]

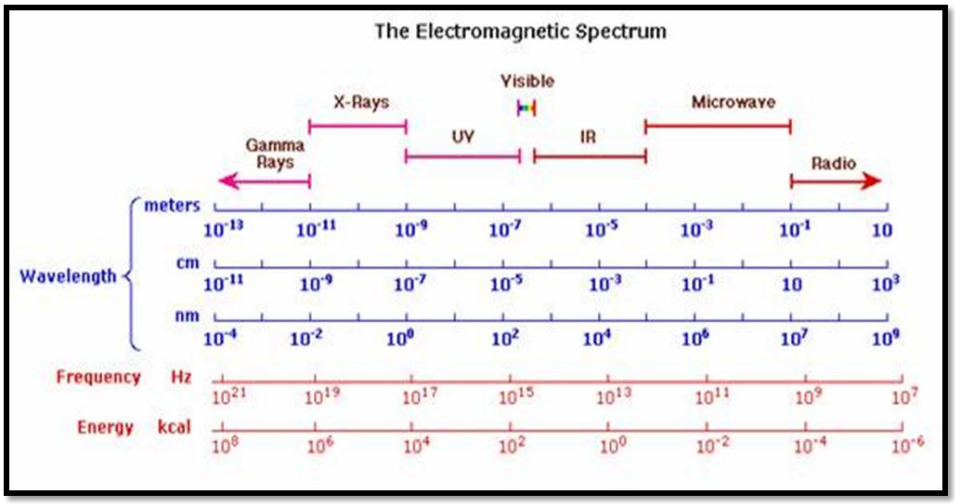

Figure no 01: Showing The electromagnetic spectrum.

2.4 Introduction to Crystallography

- Crystallography diffraction data provides information on the structures of crystalline solids. The symmetry in structures shows itself in the diffraction by the appearance and disappearance of characteristic reflections. The intensity of the diffracted beams depends on the arrangement and atomic number of the atoms in the repeating motif, called the unit cell. Unit cells describe the symmetry of all structures.[8],[9]

Key Concepts

- Crystal structures are the periodic arrangement of atoms in a crystal.
- Structures are defined using lattices (infinite array of points in space)
- Unit cells are used to describe the smallest repeating structure in a lattice of a crystalline material.
- These repetitions are what give rise to the constructive interference defined by Bragg's Law

2.5 XRD Analysis-Summary

From diffraction patterns one can find the crystal structure of an unknown material. In addition one can also determine factors such as the orientation of single crystals, or measure the size and shape of crystalline regions. There are several X-ray diffraction techniques. Two of the most common are:

- **Single crystal X-ray diffraction:** used to solve structure of crystalline materials ranging from inorganic compounds to complex macromolecules such as proteins or polymers. You can learn everything about a crystal structure, but requires a single crystal. Although obtaining single crystals is difficult, single crystal X-ray crystallography is a primary method for determining the molecular conformations of biological interest such as DNA, RNA and proteins.
- **Powder X-ray diffraction:** used to characterize crystallographic structure, grain size, and preferred orientation in polycrystalline or powder solid samples. This is a preferred method of analysis for characterization of unknown crystalline materials. Compounds are identified by comparing diffraction data against a database of known materials. It can be used to follow phase changes as a function of variable such as temperature, pressure.[8],[9]

2.6 Braggs law: (X – ray diffraction and Braggs Law)[9]

- X-rays have wavelengths on the order of a few angstroms (1 Angstrom = 0.1 nm). This is the typical inter-atomic distance in crystalline solids, making X-rays the correct order of magnitude for diffraction of atoms of crystalline materials
- When X-rays are scattered from a crystalline solid they can constructively interfere, producing a diffracted beam.
- Interference occurs among the waves scattered by the atoms when crystalline solids are exposed to X-

rays. There are two types of interference depending on how the waves overlap one another.

- Constructive interference occurs when the waves are moving in phase with each other. Destructive interference occurs when the waves are out of phase.
- The relationship describing the angle at which a beam of X-rays of a particular wavelength diffracts from a crystalline surface was discovered by Sir William H. Bragg and Sir W. Lawrence Bragg and is known as Bragg's Law

$$2d\sin\theta=n\lambda \quad (1)$$

- λ = wavelength of the x-ray
- θ = scattering angle
- n = integer representing the order of the diffraction peak.
- d = inter-plane distance of (i.e atoms, ions, molecules)

2.7 Principles of XRD

- Max von Laue discovered in 1912 that crystalline materials behave for X-ray wavelengths as three-dimensional diffraction gratings identical to the spacing of planes in a crystal lattice.
- X-ray diffraction is a widely used method for examining crystal structures and atomic distances.
- Constructive interference between monochromatic X-rays and a crystalline sample is the foundation of X-ray diffraction. A cathode ray tube produces the X-rays, which are then filtered to produce monochromatic radiation, focused by collimation, and pointed at the sample. When the circumstances are in accordance with Bragg's Law (n=2d sin), the interaction of the incident rays with the sample results in constructive interference (and a diffracted ray).
- This law establishes a connection between the lattice spacing and diffraction angle in a crystalline sample and the wavelength of electromagnetic radiation.
- Then X-rays are found, analyzed, and counted. Due to the powdered material's random orientation, all potential lattice diffraction directions should be obtained by scanning the sample through a range of 2 θ angles.
- Each mineral has a specific set of d-spacings, hence converting the diffraction peaks to d-spacings enables mineral identification. This is often accomplished by comparing the d-spacings with accepted reference patterns.
- The production of X-rays in an X-ray tube is the foundation of all diffraction techniques.
- The sample is hit with these X-rays, and the diffracted rays are captured. T
- The angle between the incident and diffracted rays is a crucial factor in all types of diffraction. Beyond this, the apparatus for powder and single crystal diffraction differs.
- An X-ray tube, a sample holder, and an X-ray detector are the three fundamental components of an X-ray diffractometer.
- In a cathode ray tube, x-rays are created by burning a filament to produce electrons, accelerating those electrons with a voltage toward a target, and then hitting the target material with those electrons.
- Characteristic X-ray spectra are created when electrons have enough energy to knock off the target material's inner shell electrons.
- An X-ray diffractometer's geometry is such that the sample spins at an angle θ in the direction of the collimated X-ray beam, and the X-ray detector rotates at an angle of 2θ to capture the diffracted X-rays.
- A goniometer is the device used to hold the angle and rotate the sample. For common powder patterns, data is gathered at fixed angles in the X-ray scan, ranging from 2 θ to 5° to 70°.
- XRD works on the principle of Bragg's equation, which can be described in terms of reflection of collimated X-ray beam incidence on a crystal plane of the sample that to be characterized. XRD is based on the wide-angle elastic scattering and is generally used for ordered material (specifically long-range order crystalline material), and is not preferred for disordered material.
- A beam of X-rays is passed through the specimen and is scattered, or diffracted, by the atoms in the path of the X-rays investigated. The interference occurring due to scattering of X-rays with each other is observed applying Bragg's law and a suitably positioned detector, and crystalline structure characteristics of the material are determined. All measurements are carried out in Angstroms (1 Å=0.1 nm or 10^{-10}m). To confirm the results obtained using XRD, they may be compared with microscopy techniques or other solid-state characterization techniques.
- However, XRD can be time-consuming and may require large amounts of sample (Das et al., 2014; Epp, 2016).
- Despite some limitations, XRD is widely used to determine the material structure at an atomic level. Another difficulty with XRD is that it is difficult to analyze the growing crystal in real time and therefore this technique gives results only from single confirmation or binding state (Cao, 2004; Sapsford et al., 2011; Zanchet et al., 1999).
- The next disadvantage of the XRD technique is the low intensity of diffracted X-rays, specifically for low atomic number material, with a comparison to electron diffractions (Cao, 2004).[8],[9]

2.8 XRD Benefits and Applications[8]

XRD is a non-destructive technique used to:

- Identify crystalline phases and orientation
- Determine structural properties:
  - Lattice parameters
  - Strain
  - Grain size
  - Epitaxy

- Phase composition
- Preferred orientation
- Measure thickness of thin films and multi-layers
- Determine atomic arrangement

2.9 Disadvantages of XRD

- XRD does, however, have certain limitations: Typically XRD analysis requires access to standard reference data. Preparation of samples often requires grinding them down to a powder. If the crystal sample is non- isometric, then the indexing of patterns can be complex when determining unit cells.
- XRD also has size limitations. It is much more accurate for measuring large crystalline structures rather than small ones. Small structures that are present only in trace amounts will often go undetected by XRD readings, which can result in skewed results.[8]

Figure no 02 and 03: Showing XRF spectrometer with the sample port on top and a set of samples in silver metallic holders in the sample changer in front.

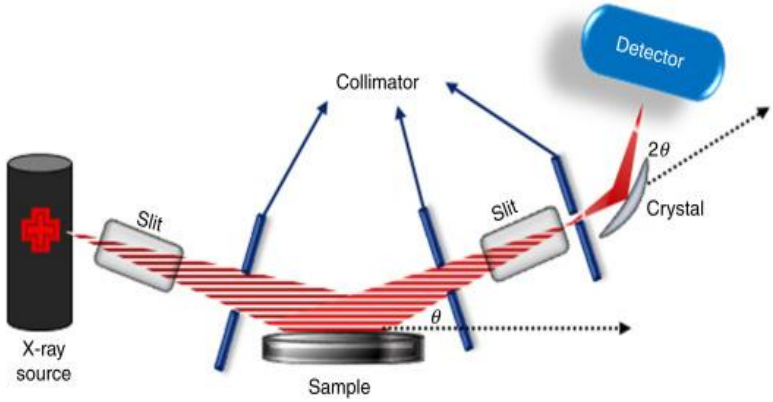

Figure no 04: Showing mechanism of XRD.

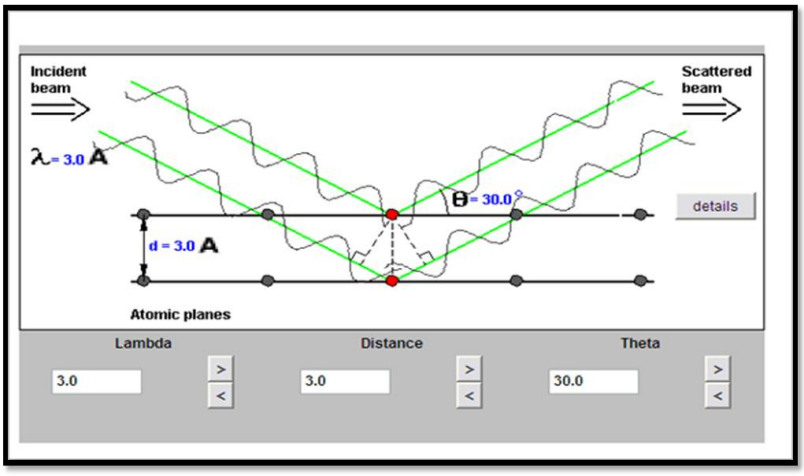

Figure no 05: Showing mechanism of XRD with Brags law.

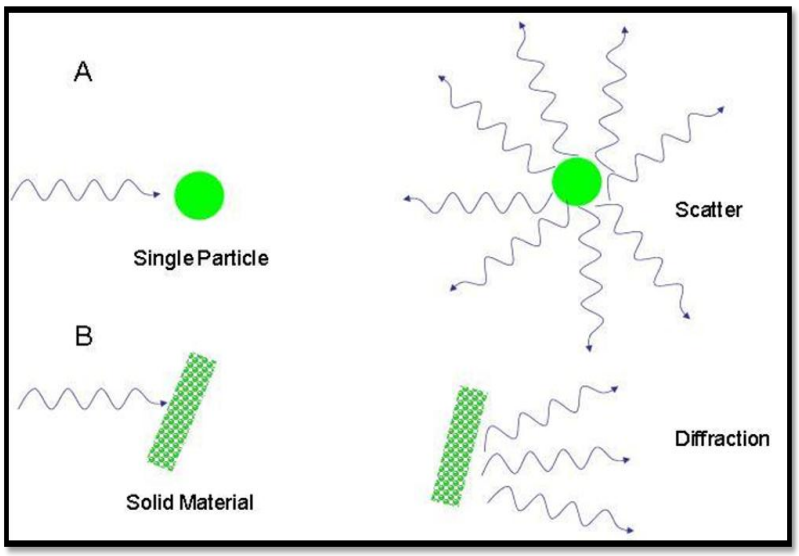

Figure no 06: Mechanism of XRD.

A. Fundamental When X-rays interact with a single particle, it scatters the incident beam uniformly in all directions.
B. When X-rays interact with a solid material the scattered beams can add together in a few directions and reinforce each other to yield diffraction. The regularity of the material is responsible for the diffraction of the beams.[6]

3. DISCUSSION AND CONCLUSION

This review work is discussed and concluded with following important key notes:

- An X-ray fluorescence (XRF) spectrometer is a device that uses x-rays to conduct routine chemical analysis of rocks, minerals, sediments, and fluids in a generally non-destructive manner.[1]
- XRF is the most popular analytical method used for major and trace elements in rocks, minerals, sediment as well as incinerated ash (bhasma).
- XRF s more convenient method with relative ease of sample preparation, and low cost.
- XRF will produces and assay by giving information on the chemical composition of your sample without indicating what phases they are present in your sample.
- X-ray diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions.
- X-ray diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds).
- XRD identifies and measures the presence and amounts of minerals and their species in the sample, as well as identify phases.
- X-ray diffraction analysis (XRD) is a technique used in materials science to determine the crystallographic structure of a material.
- XRD works by irradiating a material with incident X-rays and then measuring the intensities and scattering angles of the X-rays that leave the material with help of Brags law.[9]
- So this review work concluded that, XRF & XRD analytical techniques are most important techniques in Ayurvedic pharmaceutical science for the standardization and quality control purposes during the preparation of herbominearl formulation. It is widely used for the purpose of the identification of raw material, purity of raw material, quality control of finished drug as well as to analyze the chemical composition of the herbomineral formulations to evaluate the safety as well as efficacy.

4. Compliance with ethical standards

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5. Disclosure of Conflicts of interest: There is no conflict of interes.

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