Received: 15 Oct 2025	Revised: 15 Nov 2025	Accepted: 15 Dec 2025

Review Article

IJRPS
The Power of Wisdom

SCITEKHUB

ISSN: 3048-5606

"*KAJJALI* AS THE BASE OF MERCURIAL FORMULATIONS: A REVIEW OF ITS CHEMISTRY, CHARACTERISATION AND SAFETY"

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FUNDING INFORMATION:
None

How to cite this article:
Abhay Gandhi, "Kajjali as the base of mercurial formulations: a review of its chemistry, characterisation and safety" International Journal of Rasa Shastra and Pharmaceutical Sciences. 2025;2(4):20-24. Sri. 2025.1007.ijrps.04.04

ABSTRACT

Background: *Kajjali*, the black powder produced by triturating purified mercury with purified sulphur, is the starting point for most mercurial formulations of *Rasa Shastra*, including *kupipakva rasayanas* such as *Rasasindura* and *Makaradhwaja* and many compound *rasa* preparations. Its quality determines the safety of everything made from it. **Objective:** To review the chemistry of *kajjali* formation, the analytical evidence on its composition and particle size, and the evidence on its toxicity. **Methods:** A critical narrative review of characterisation studies using X-ray diffraction, electron microscopy, elemental and thermal analysis, and of in vitro, zebrafish and rodent studies on *kajjali* and *kajjali*-derived products. **Results:** Trituration converts metallic mercury and sulphur into black cubic mercuric sulphide (metacinnabar, β-HgS) mixed with unreacted orthorhombic sulphur. With adequate trituration, free mercury falls to undetectable or minimal levels. Reported particle sizes are in the range of tens to a few hundred nanometres for well-triturated samples; in one study, particles narrowed from 185–661 nm at 22 hours to 100–171 nm at 120 hours. The sulphur ratio governs the proportion of unreacted sulphur (TGA mass loss 45.9% for 1:1 and 80.5% for 1:6) and crystallite size. HgS is far less bioavailable and toxic than mercuric chloride or methylmercury, and zebrafish and cell studies suggest lower toxicity of processed mercurials, but long-term mammalian data are lacking. **Conclusion:** *Kajjali* is a chemically definable, testable intermediate. Instrumental end-points for free mercury, phase composition and particle size should replace reliance on organoleptic tests alone.

KEYWORDS: *Kajjali*; Mercury; Metacinnabar; Mercuric sulphide; *Rasasindura*; *Rasa Shastra*; Characterisation

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INTRODUCTION

Mercury (*parada*) holds a central place in *Rasa Shastra*, and almost every mercurial preparation begins with *kajjali*. The classical definition is simple: purified mercury and purified sulphur are triturated together, without any liquid, until a fine, smooth, lustreless black powder resembling collyrium (*kajjala*) is obtained[1,2]. The proportion of sulphur to mercury varies from equal parts (*samaguna*) to six times the weight of mercury (*shadguna*), and the product may be used directly or as the base for *kupipakva rasayanas* such as *Rasasindura* and *Makaradhwaja* and for compound formulations[3,4].

Kajjali is therefore the point at which elemental mercury, one of the most hazardous materials in the pharmacopoeia, is converted into a compound intended for internal use. If the conversion is incomplete, every downstream product carries free mercury. This review brings together the analytical and toxicological evidence on *kajjali* to show what is known about its chemistry, what end-points can be used to judge its completion, and what remains to be established about its safety.

METHODS OF THE REVIEW

This is a critical narrative review. Literature was identified through PubMed, PubMed Central, Crossref-indexed records, journal archives and publisher databases using the terms *kajjali*, black sulphide of mercury, mercuric sulphide, metacinnabar, *Rasasindura*, mercurial Ayurvedic formulation, characterisation and toxicity. Studies were included if they reported instrumental analysis of *kajjali* or a *kajjali*-derived product, or toxicological data on these materials. Reference lists of retrieved articles were screened for additional studies.

CLASSICAL PREPARATION AND QUALITY TESTS

In classical practice, mercury first undergoes *shodhana*, often with lime powder, garlic, rock salt or herbal juices, and sulphur is purified by melting and filtering it into milk with ghee. The two are then ground in a stone mortar, typically for many hours or days. The traditional end-points are physical: the powder must be black and lustreless, with no visible mercury globules even under sunlight, must fill the lines of the fingers (*rekhapurnatva*), must be smooth (*shlakshnatva*) and must float on water (*varitaratva*)[2,5].

Instrumental studies show how these processes perform in practice. In one batch, purification recovered about 89% of mercury, with the largest loss (about 7.3%) during trituration with lime, and about 94.5% of sulphur; 225 g each of mercury and sulphur were then ground by hand for about 78 hours, giving 447 g of *kajjali* (about 99.3% yield) that passed all the classical tests[5]. In another study, 300 g each of mercury and sulphur were triturated for up to 120 hours; the lustre of mercury diminished but was still visible in sunlight beyond 94 hours[6]. These observations illustrate how slowly the last traces of free mercury disappear, and why visual tests alone are a weak end-point.

CHEMISTRY OF KAJJALI FORMATION

1. Phase composition

Mercury reacts with sulphur at room temperature under mechanical activation to form mercuric sulphide. Two polymorphs exist: red trigonal α-HgS (cinnabar), which is the stable form at room temperature and the main constituent of *Rasasindura* after sublimation, and black cubic β-HgS (metacinnabar), which forms under mechanochemical conditions. X-ray diffraction of *samaguna kajjali* identified cubic HgS (metacinnabar), with the strongest reflection at $2\theta \approx 26.4–26.5°$ ($d \approx 3.38–3.4$ Å), together with reflections of orthorhombic sulphur[5,7]. Studies at different trituration times show the three main reflections of cubic HgS, (111), (220) and (311), in all samples[6]. Some authors label the black product as cinnabar; the reported cubic reflections indicate that the black phase is metacinnabar, and consistent use of these terms would avoid confusion.

2. The role of sulphur ratio

Because classical texts prescribe different mercury-to-sulphur ratios, the role of excess sulphur has been investigated directly. A comparison of *samaguna* (1:1) and *shadguna* (1:6) *kajjali* found that both were two-phase mixtures of HgS and orthorhombic α-sulphur, with more free sulphur in the 1:6 product. Energy-dispersive analysis gave mercury-to-sulphur weight ratios of about 59:41 and 19:81, and thermogravimetric mass losses attributed to unreacted sulphur were 45.9% and 80.5%, respectively. X-ray photoelectron spectroscopy found only mercury and sulphur, with no change in surface oxidation state, and no free mercury was detected by XRD in either sample[8]. Excess sulphur therefore does not change

the mercury compound formed, but it dilutes it and changes the physical properties of the powder.

3. Elemental composition and impurities

Energy-dispersive analysis of one *samaguna kajjali* batch gave 88.8% mercury and 11.2% sulphur by weight, with no other elements detected[5]. Atomic absorption spectroscopy found lead, cadmium, arsenic and zinc within acceptable limits in both *samaguna* and *shadguna* samples[8]. Testing for unintended metals in the starting mercury and sulphur, and in the final product, is an essential and often neglected step.

PARTICLE SIZE AND TRITURATION TIME

Table 1. Selected characterisation studies of *kajjali*

Study	Hg:S ratio and trituration	Main phases	Particle or crystallite size	Other findings
Srinivasulu et al. 2012	1:1 (*samaguna balijarita*)	Cubic HgS (metacinnabar), free orthorhombic sulphur	Not reported	Strongest HgS reflection at 2θ = 26.5°
Sharma et al. 2018	1:1, about 78 h by hand	Metacinnabar with some orthorhombic sulphur	About 90% of particles 60–200 nm on SEM; a few 1–2.5 µm	EDX 88.8% Hg, 11.2% S; passed classical tests
Joshi et al. 2021	1:1 and 1:6	HgS with α-sulphur; more free sulphur at 1:6	SEM average 39 nm (1:1) and 61 nm (1:6); crystallites 21 and 53 nm	No free Hg by XRD; TGA mass loss 45.9% and 80.5%
Kestwal and Mitra 2025	1:1, sampled at 4–120 h	Cubic HgS; free Hg decreasing with time	SEM 185–661 nm (22 h), 158–601 nm (94 h), 100–171 nm (120 h)	Lustre visible in sunlight beyond 94 h

Trituration time affects both free mercury and particle size. Sampling during a 120-hour trituration showed particle sizes narrowing from 185–661 nm at 22 hours to 100–171 nm at 120 hours, with free mercury decreasing and becoming minimal at 120 hours[6]. Other studies have reported most particles in the 60–200 nm range after about 78 hours[5], or averages of 39–61 nm by SEM in *samaguna* and *shadguna* products[8]. As discussed in the review of *bhasma* characterisation in this series, these are image-based sizes and crystallite sizes, not number-based distributions, and should be described as such.

Comparisons of traditional hand trituration with mechanised methods have also been reported[9]. Mechanisation can shorten preparation time and improve reproducibility, but only if the end-point is defined by measurement rather than by elapsed time.

KAJJALI IN DOWNSTREAM FORMULATIONS

In *kupipakva rasayanas*, *kajjali* is heated in glass bottles under a graded temperature programme, and HgS sublimes and recrystallises at the neck as red cinnabar. In the standardisation of *Makaradhwaja* using gold, mercury and sulphur in a ratio of 1:8:24, the *kajjali* was triturated for 24 hours before heating to about 600 °C over about 12 hours in an electric muffle furnace[4]. In compound formulations, *kajjali* is mixed with other *bhasmas* and herbal media. In Hridayarnava Rasa, made from *kajjali* and Tamra *bhasma*, XRD identified mercuric sulphide, copper sulphide and free sulphur[10]. Free mercury left in *kajjali* would be carried into all of these products, and in *kupipakva* preparations could volatilise during heating.

SAFETY EVIDENCE

1. Speciation and bioavailability

The central toxicological argument for *kajjali* is chemical speciation. Mercuric sulphide is very poorly soluble in water and gastrointestinal fluids, and its absorption is far lower than that of mercuric chloride or methylmercury[11]. Reviews of mercury-based herbo-metallic preparations and of cinnabar- and realgar-containing traditional Chinese medicines reach the same conclusion: total mercury content overstates the risk from HgS, but HgS is not inert, and long-term or high-dose use can lead to mercury accumulation[12,13]. The bioaccessibility of mercury from selected Ayurvedic medicines has been measured in simulated gastrointestinal fluids[14], and structural studies using X-ray absorption fine structure spectroscopy have examined mercury in *Rasasindura* to understand its putative low toxicity[15].

2. Experimental toxicity

In zebrafish, *Rasasindura* and *kajjali* have been compared with other mercury compounds for neurotoxicity[16], and Ayurvedic processing of α-HgS

produced distinct physicochemical properties and toxicokinetics[17]. *Rasasindura* has also been examined in NIH3T3 fibroblasts and zebrafish larvae[18]. Structural, chemical and safety studies have been reported for *samagandhak kajjali*[19]. A scoping review of *Rasasindura* safety found only five eligible peer-reviewed studies and concluded that acute, subacute and chronic toxicity studies in higher mammals were still needed[20]. Analytical work on mercury-, sulphur- and arsenic-containing Siddha formulations points to the same need for combining characterisation with safety testing[21].

3. What remains uncertain

The experimental evidence supports lower toxicity of well-made HgS than of soluble or organic mercury, but it does not define a safe dose or duration in humans. Key uncertainties are the degree of transformation of HgS in the gut, the contribution of any residual free mercury, the effect of long-term accumulation in kidney and brain, and whether gut microbiota or co-administered substances alter mercury uptake. No human pharmacokinetic study of *kajjali* has been identified.

PROPOSED QUALITY END-POINTS FOR KAJJALI

Based on the studies reviewed, the following instrumental end-points could complement the classical tests:

- **Free mercury:** absence of metallic mercury reflections on XRD, supported by a sensitive method such as thermal desorption or cold-vapour analysis of extractable elemental mercury, with a defined limit.
- **Phase composition:** identification of cubic HgS and quantification of free sulphur by XRD and thermogravimetry, with acceptance ranges for each classical ratio.
- **Mercury and sulphur content:** assay of total mercury and sulphur against the expected stoichiometry for the ratio used.
- **Unintended metals:** limits for lead, arsenic and cadmium in the raw materials and the product.
- **Particle size:** a defined method (for example laser diffraction or image analysis of a stated number of particles) and acceptance range.

Each of these end-points can be measured routinely and would allow *kajjali* to be released for further processing on the basis of data rather than elapsed trituration time.

RESEARCH GAPS

The most important gaps are: a validated method and limit for free mercury in *kajjali*; comparison of hand and mechanised trituration using the same instrumental end-points; dissolution and bioaccessibility testing of *kajjali* and its products in simulated gastrointestinal fluids; repeated-dose toxicity studies in rodents with tissue mercury measurement; and human biomonitoring of patients taking *kajjali*-based formulations at therapeutic doses.

CONCLUSION

Kajjali is chemically well defined: it consists of black cubic mercuric sulphide mixed with a ratio-dependent amount of unreacted sulphur, and well-made samples contain little or no free mercury and fine particles in the nanometre to sub-micron range. Longer trituration reduces both free mercury and particle size, and the sulphur ratio governs the free sulphur fraction. Mercuric sulphide is much less bioavailable than other mercury compounds, and experimental studies suggest lower toxicity for processed mercurials, but long-term mammalian and human data are lacking. Because *kajjali* is the base of most mercurial formulations, instrumental release criteria for free mercury, phase composition and impurities should be adopted as a priority.

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