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SULPHUR: SOURCES, CHEMICAL BEHAVIOUR, SHODHAN INDUCED TRANSFORMATIONS AND THERAPEUTIC POTENTIAL – AN INTEGRATIVE REVIEW

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ABSTRACT

Introduction: Sulphur is an essential macronutrient involved in amino acid synthesis, redox balance, and detoxification. In Ayurveda, it is known as Gandhaka and is therapeutically used after Śodhana to improve safety and efficacy. However, its chemical behaviour and pharmacological relevance require better integration with modern science.

Methods: This integrative review compiled data from authenticated databases, including PubMed and peer-reviewed journals. Information on sulphur sources, oxidation states, thermal behaviour, Śodhana-induced changes, and pharmacological activities was analysed.

Results: Sulphur occurs in animal, plant, inorganic, and environmental sources, mainly in reduced and oxidized forms. Its behaviour varies with oxidation state and temperature, showing structural transformations at higher temperatures. Śodhana significantly improves purity, particle size, and safety profile. Sulphur-containing compounds like triterpenoid thiane and gamma lactone exhibit antimicrobial, anti-inflammatory, and antineoplastic activities through mechanisms such as oxidative stress and apoptosis induction.

Discussion: Sulphur's biological and therapeutic effects depend on its chemical form and processing. Śodhana enhances its pharmacological properties, aligning traditional practices with modern scientific understanding.

Conclusion: Sulphur has significant nutritional and therapeutic value. Śodhana improves its safety and efficacy, while sulphur compounds show promising potential in modern drug development.

KEYWORDS: Sulphur, Śodhana, Sulphur compounds, Triterpenoid thiane, Gamma lactone, Antineoplastic activity.

INTRODUCTION

Sulphur is an essential macronutrient required for the synthesis of amino acids, proteins, vitamins, and antioxidants in the human body. It plays a vital role in cellular metabolism, detoxification, and maintenance of structural integrity of tissues. Sulphur-containing compounds like methionine, cysteine, glutathione, and taurine are directly linked to oxidative stress control and metabolic functions.[1]

In Ayurveda, sulphur (Gandhaka) is classified as an important mineral drug extensively used in Rasashastra formulations. After appropriate Śodhana (purification), Gandhaka is indicated in the management of skin disorders, infections, metabolic diseases and rejuvenative therapies (Rasayana). Classical texts such as Rasatarangini and Ayurveda Prakasha emphasize Śodhana to enhance safety, bioavailability and therapeutic efficacy. Despite its long traditional use, systematic correlation of Ayurvedic processing with modern chemical and pharmacological evidence remains limited, justifying the need for the present review. bro iska reference from authentic sources.[2]

MATERIALS AND METHODS

This review was developed through comprehensive collection of literature from **PubMed, ScienceDirect, and authentic peer-reviewed journals**. Data on the sources of sulphur ,percentage of sulphur , state of sulphur in food , behaviour change in sulphur as per change in temperature , changes after shodhan ,form of sulphur were compiled from published articles. All information, tables, and references have been retained from verified research articles and government-supported open-access repositories.

RESULTS

1. Sources of Sulphur

Sulphur is obtained from a wide range of foods:

S. N	SOURCE	EXAMPLES
1.	Animal source[3]	Eggs, meat, fish, milk, cheese
2.	Plant source[4]	Onion, garlic, broccoli, cabbage, cauliflower
		Legumes, nuts, cereals
3.	Natural sources[5]	*Gandhak* (purified sulphur) Hing (Ferula asafoetida L.) Lasuna [Allium sativum L.]
4.	Inorganic sources[6]	Sulphates in water and food additives
5.	Environmental and geological sources[7]	Sulphur from volcanic emissions (SO_2 , H_2S) , Sedimentary sulphide (FeS_2)

Table [8]

S.N	Name of sulphur drugs	Natural sources	Biological activities
1.	Gama lactone	Isolated from human urine	Anti inflammatory, inflammatory bowel disease treatment
2.	Triterpenoid thiane	Isolated from organic matter in *Holocene* and *pleistocene*	Apoptosis agonist , antineoplastic , anti eczematic anti psoriatic and dermatological properties
3.	Ajoenes	Isolated from allium sativum	Antibacterial , antiviral , antifungal
4.	Allicin	Isolated from allium sativum	Antibacterial , antiviral , antifungal

{*Holocene* – It refers to recent geological deposits . Rich in biogenic and sulfur-containing organic compounds .Frequently studied in geochemistry, paleoclimate, and natural product research}9

2. Percentage of Sulphur Present in foods [10]

1. Preserved / canned fish – 3.0g/kg
2. Sea food – 2.8g/kg
3. White meat (chicken , turkey) – 2.8g/kg
4. Cheese – 2.1g/kg
5. Fresh fruit – 87mg/kg
6. Oils and fats – 157 mg/kg
7. Beverages – 141mg/kg
8. Onion and garlic – 1.3g/kg

3. State of Sulphur Present in Food

In foods sulfur is most commonly found in **reduced organic forms** (thiols/thioethers: formal oxidation state ≈ −2, e.g. cysteine, methionine), and in **fully oxidized inorganic forms** (sulfate, +6). Intermediate oxidation states such as **sulfite (+4), thiosulfate {($S_2O_3^{2-}$) One sulphur is +5 (central sulphur, sulfate-like); One sulphur is −1 (terminal sulphur, sulfide-like), sulfoxides (+2)** and various **reactive sulfur species (RSS)** occur too but are generally less abundant and often transient or matrix-dependent.[11]

Oxidation state (formal)	**Typical chemical forms in foods**	**Stability in foods**
−2	Thiols (R–SH) and thioethers (R–S–R) — **cysteine, methionine, glutathione**	**Most abundant organic S** in proteins; relatively stable when bound in intact proteins but free thiols are easily oxidized on exposure to air/heat. Major dietary reservoir of S.[12]
−1 / per sulfide-like	Per sulfides, polysulfides (R–S–S–R, R–S–SH)	Present in Allium (garlic/onion) chemistry as polysulfides; biologically reactive and less stable — they form and break during processing and cooking.[13]
0	Elemental sulfur (S_8) and some zero-valent sulfur reservoirs (sulfane sulfur, S^0)	Rare as pure S_8 in foods; "sulfane" sulfur species are intermediates in metabolism and are reactive/transient.[14]
+2 (formal)	Sulfoxides and sulfenic acids — e.g. methionine sulfoxide	Formed by oxidation of thioethers/thiols during cooking/processing or enzymatic oxidation; often reversible (enzymes like methionine sulfoxide reductases reduce them). Not usually a major storage form in foods.[15]
+6	**Sulfate** (SO_4^{2-})	**Very stable**, common in foods, beverages and water; major inorganic form of dietary sulfur and the thermodynamically most oxidized, non-reactive reservoir.[16]

4. Behavior of sulphur as per changes in temperature

Temperature /range	**Behavior /change in sulphur**	**Observations**
Ambient (room T, ≈25 °C)	Solid — common orthorhombic α-S_8	Stable crystalline S_8 rings dominate; standard solid-state allotropy (many possible allotropes).[17]
~95-120 °C	α-S_8 → β-S_8 (solid → solid) then melting	Crystalline transition then melting at ~388 K (≈115

		°C)[18]
~120 °C (≈388 K)	Melting of sulfur (solid → liquid)	Formation of a liquid rich in S_8 rings initially [19]
~150-170 °C (≈423-443 K)	λ (lambda) transition / polymerization	Dramatic ring-opening: S_8 rings open to form diradical chain fragments → rapid increase in viscosity, changes in optical properties and heat-capacity anomalies (the so-called λ transition). Not a conventional first-order melt but an equilibrium ring↔chain transformation.[20]
~170–~400+ °C (higher T liquid)	Chain growth / changing polymer fraction	Increasing fraction of long Sn chains, higher viscosity (up to a max depending on kinetics), then eventual thermal fragmentation at still higher T; Raman/X-ray and MD studies show continuous compositional evolution. [21]
High temperature / vaporization (varies with pressure)	Gas-phase: mixture of Sn species (S_2, S_3, …)	Vapor consists of a temperature-dependent equilibrium mix of cyclic and open Sn units; composition shifts toward smaller fragments (S_2, S_3 etc.) at very high T — thermochemistry modeled in chemical-potential studies.[22]
High P or rapid	Liquid–liquid / pressure-induced	Under high pressure or fast

compression / glassy states	transitions; glass formation	compression, liquid sulfur can show a first-order-like liquid–liquid transition (low-density ↔ high-density liquid); rapid compression can trap chain/ glassy forms.[23]
Kinetic / specialized isolation conditions	Small/radical allotropes isolation	Lab methods (kinetic trapping, coordination networks) can isolate labile small allotropes (S_2, S_4, unusual cycles) that are otherwise transient at ambient. [24]

5. Changes in sulphur after shodhan

- Studies show that Śodhana, especially using media like Eclipta alba (Bhringraj) extract, cow's milk, or ghee, removes chemical impurities and volatile residues compared to unprocessed sulphur. Physical parameters such as odour, colour and transparency also change, indicating impurity removal.[25]
- When Gandhaka is subjected to melting and quenching steps (e.g., pouring molten sulphur into milk), ~**10 % weight loss** has been observed in transformed sulphur after Shodhana.[26]
- This loss is attributed to elimination of volatile substances, structural impurities, and mechanical losses during processing. [27]
- X-ray diffraction (XRD) and differential scanning calorimetry (DSC) analyses indicate that raw sulphur generally exists in the **orthorhombic form**, which transforms into the **monoclinic form** during Shodhana, and may revert to orthorhombic with further purification or drying.[28]

Sr. No.	Observed Parameter / Behavior	Reported Changes After Śodhana
1.	Physical Form	Crystalline → amorphous, fine, smooth yellow powder; loss of translucency.[29]
2.	Organoleptic properties (colour, odour, texture)	Brighter yellow colour, modified odour, softer texture [30]
3	Purity / Sulphur & heavy metals	Godugdha method yielded 99.47% sulphur, lowest arsenic (~2.03 ppm) [31]
4	Toxicity / Safety in chronic exposure	Gandhaka Rasayana showed safety in 180-day rat study, no significant toxicity at therapeutic doses [32]
5	Impact of Bhavana / processing method	Increasing number of *Bhavana* cycles influences particle size and structure [33]
6	Antimicrobial / antifungal activity	Gandhaka Rasayana showed inhibition of fungal / bacterial growth (e.g. *Candida albicans*) [34]
8.	Structural / surface chemistry changes	Differences in XPS, particle morphology, surface chemistry with or without Bhavana[35]

6. Form of sulphur found in different ingredients

Sulfur-containing amino acids (protein-bound sulphur): methionine & cysteine (and cystine, homocysteine, taurine).These are the principal nutritional forms of sulfur in animal and plant proteins (meat, eggs, dairy, legumes, cereals). Methionine and cysteine supply sulfur for protein synthesis and for glutathione and other metabolites. [36]

S-alk(en)yl-L-cysteine sulfoxides (precursors in Alliums — e.g., alliin, isoalliin). In fresh garlic/onion these nonvolatile sulfoxides (e.g., alliin in garlic, S-1-propenyl-L-cysteine sulfoxide in onion) are the stored forms that, when the tissue is cut/crushed, are converted enzymatically to volatile sulfur compounds (allicin, sulfenic acids).[37]

Thiosulfinates and thiosulfonates (e.g., allicin, ajoene) and lower allyl sulfides (diallyl sulfide, diallyl disulfide, diallyl trisulfide) — volatile organosulfur in garlic. Crushing garlic converts alliin via alliinase to allicin (a thiosulfinate) which rapidly decomposes to ajoene and allyl sulfides; these are responsible for garlic's odor and many bioactivities (antimicrobial, cardioprotective). Recent reviews and mechanistic papers summarize structures and biological actions. [38]

Sulfenic acids and the onion lachrymatory factor pathway (e.g., 1-propenesulfenic acid → (Z)-propenethial S-oxide). In onion, enzymatic cleavage produces sulfenic acids which are acted on by lachrymatory factor synthase (LFS) to form the lachrymatory factor (the "makes you cry" molecule). Structural and mechanistic studies of LFS and sulfenic acid intermediates document this pathway. [39]

Glucosinolates (sulfur-containing glycosides) and their hydrolysis products (isothiocyanates, nitriles) — cruciferous vegetables. Brassica vegetables store glucosinolates (sulfur-rich) that, upon tissue damage, are hydrolysed by myrosinase to yield isothiocyanates (e.g., sulforaphane), which are bioactive and widely studied for chemopreventive properties. Comprehensive reviews cover their distribution, metabolism and effects.[40]

Inorganic sulfate and sulfated conjugates (e.g., sulfate esters, sulfated polysaccharides) — minor dietary/intrinsic forms. Foods contain inorganic sulfate and molecules that are sulfated (e.g., in some plant polysaccharides/phenolics or as part of glycosaminoglycans in animal tissues). Sulfate is also a metabolic product and conjugating group in detoxification. Scoping reviews on sulfur in foods discuss these pools.[41]

Taurine (free sulfonic amino acid) — abundant in many marine foods. Taurine (2-aminoethanesulfonic acid), while not incorporated into proteins, is an important sulfur-containing free amino acid especially in fish and seafood; it has roles in osmoregulation and bile-acid conjugation. Reviews of sulfur nutrition list taurine among dietary sulfur compounds.[42]

Polysulfides and inorganic sulfides (in small amounts in some fermented or processed foods / environmental contamination).

Foods or herbal ingredients subjected to fermentation or sulfur-containing processing can contain reduced inorganic sulfur species (sulfides, polysulfides); their levels are typically low compared with organic sulfur compounds but are chemically relevant for odor and reactivity. Scoping literature notes these minor pools.[43]

Methyl sulfonyl methane (MSM), sulfate salts and other supplemental sulphur species. Dietary supplements supply sulfur as MSM (an oxidized organic sulfur), or as sulfate salts (e.g., magnesium sulfate) used in some formulations; these are chemically distinct and are covered in reviews of therapeutic sulfur compounds.[44]

Bound sulfur in phytochemicals (sulfonyl, sulfonate, sulfoxide moieties) — in herbs and spices.

Many plant secondary metabolites include sulfoxide (e.g., S-alk(en)yl-cysteine sulfoxides), sulfone or sulfonate functional groups that influence reactivity and bioactivity; FTIR/LC-MS characterisations in plant chemistry literature identify these moieties.[45]

Sulphur containing therapeutic compounds

Form	Compound
1. Sulfonamides / sulfa antibiotics	Classic antibacterial drugs (eg. Sulfamethoxazole)[46]
2. Sulfones and sulfoxides	Eg. Dapsone (a sulfone antibiotic /anti leprosy drug); many sulfoxides / sulfones are in analgesics / anti inflammatory or other drug classes.[47]
3. Thioethers (sulfides) and thiols	Present in many drugs and metabolites ; some act as active pharmacophores or are metabolic intermediates.[48]
4. Sulfonium and sulfoxonium salts	Used as reactive intermediates and in some cases as drug motifs or delivery systems .[49]
5. Sulfated conjugates (eg. Sulfated steroids)	Endogenous or semi synthetic molecules with clinical relevance.[50]

7. Mode of action of Triterpenoid thiane as Apoptosis agonist [51]

Mechanism	Molecular Target / Pathway	Result / Effect on Cell
Reactive Oxygen Species (ROS) generation	Mitochondria	Induces oxidative stress and triggers mitochondrial apoptosis cascade
Cytochrome c release → Caspase-9 & -3 activation	Intrinsic apoptotic pathway	Execution phase of apoptosis (DNA fragmentation, cell death)

Mode of action of Gama lactone in inflammatory bowel disease treatment[52]

Mechanistic Step	Molecular Target / Effect	Outcome in IBD
Inhibition of NF-κB and MAPK signalling	Suppresses phosphorylation of NF-κB p65 and p38 MAPK in LPS-stimulated intestinal epithelial cells	↓ Expression of TNF-α, IL-6, IL-1β → reduced intestinal inflammation
Down-regulation of inflammatory mediators	Decreases mRNA/protein levels of COX-2, iNOS, IL-6, IL-8 in colon cell model	Reduces oxidative and nitrosative stress, protects mucosa
Attenuation of immune-cell infiltration	In vivo zebrafish gut-inflammation model: lowers neutrophil migration and MPO activity	Less epithelial injury and tissue damage

Mode of action of Triterpenoid thiane as antineoplastic action[53]

Mechanism	Description
Mitochondrial (intrinsic) apoptosis	Triterpenoids disrupt mitochondrial membrane potential → cytochrome-c release → caspase activation → apoptosis.
ROS (reactive oxygen species) induction / redox imbalance	Increase in intracellular ROS leading to oxidative damage and cell death.
Cell-cycle arrest	Triterpenoids modulate cyclins/CDKs, upregulate p21/p27 → block proliferation.
Anti-metastasis/angiogenesis	Downregulation of MMPs, VEGF, inhibition of migration/invasion/angiogenic processes.

DISCUSSION

Sulphur exhibits remarkable chemical versatility, which underlies its broad nutritional, biological and therapeutic relevance. The present review integrates information on sulphur sources, chemical forms, oxidation states, thermal behaviour and Ayurvedic processing (Śodhana) to provide a comprehensive understanding of its multifaceted role.

Animal-derived foods are the richest sources of sulphur as they contain high levels of **sulphur-containing amino acids (methionine and cysteine)**, where sulphur exists in a reduced, protein-bound and highly bioavailable form essential for protein synthesis and antioxidant defence. **Plant sources** provide sulphur mainly as **organosulphur phytochemicals**; Allium vegetables are characterized by reactive compounds such as allicin and ajoene with antimicrobial activity, while cruciferous vegetables contain sulphur-rich glucosinolates associated with chemoprotective effects.

Inorganic sulphur, present predominantly as **sulfate**, represents a fully oxidized and chemically stable form commonly found in water, beverages and food additives, contributing mainly to detoxification and conjugation pathways rather than direct bioactivity. **Environmental and geological sources**, including volcanic emissions, sedimentary sulphides and naturally occurring elemental sulphur deposits, are characterized by diverse oxidation states and low direct bioavailability, but they serve as important natural reservoirs in the global sulphur cycle. In Ayurveda, mineral sulphur (Gandhaka) derived from geological sources becomes therapeutically relevant only after **Śodhana**, which improves purity, safety and biological compatibility. Overall, the characteristics of sulphur are strongly source-dependent and governed by its chemical form and oxidation state.

Dietary and natural sources of sulphur supply the element predominantly in **organic reduced forms**, mainly as sulphur-containing amino acids (methionine, cysteine) and organosulphur compounds present in garlic, onion and cruciferous vegetables. These reduced forms (oxidation state approximately −2) are **biologically stable within proteins** and act as the primary nutritional reservoir of sulphur, supporting protein synthesis, antioxidant defence (glutathione) and redox homeostasis. In contrast, inorganic sulphur occurs mainly as **sulfate (+6 oxidation state)**, which represents the most oxidized and thermodynamically stable form, serving as a non-reactive pool involved in detoxification and conjugation pathways.

Oxidation state plays a critical role in determining sulphur's **chemical reactivity and biological function**. Reduced sulphur species (thiols, sulfides, polysulfides) are highly reactive and responsible for antioxidant, antimicrobial and signalling activities, whereas oxidized forms such as sulfate are chemically stable but biologically less reactive. Intermediate oxidation states, including thiosulfate (with sulphur present in both +5 and −1 states), sulfoxides and sulfones, act as transitional or functional forms that bridge redox transformations in biological and pharmaceutical systems. Thus, the biological activity of sulphur-containing compounds is closely linked to their oxidation state and molecular environment.

Temperature-dependent behaviour further influences sulphur stability and transformation. Elemental sulphur (S_8), the most stable allotrope at room temperature, undergoes reversible phase transitions and polymerization upon heating, leading to changes in viscosity, molecular structure and reactivity. These physicochemical transformations are particularly relevant in Ayurvedic pharmaceutics, where controlled melting and quenching steps are employed during Śodhana. Such processes facilitate removal of volatile impurities and induce structural modifications that may alter bioavailability and safety.

Ayurvedic Śodhana of Gandhaka represents a traditional yet scientifically meaningful intervention that correlates well with modern physicochemical principles. Studies have demonstrated that Śodhana leads to changes in crystalline form, particle size, surface chemistry and purity, with significant reduction in toxic impurities such as arsenic. These modifications transform raw elemental sulphur into a **pharmaceutically safer and biologically acceptable form**, aligning elemental sulphur with physiological sulphur metabolism and therapeutic use. The observed enhancement in antimicrobial and antifungal activity of processed Gandhaka further supports the functional relevance of these transformations.

The therapeutic relevance of sulphur is also reflected in naturally occurring sulphur-containing bioactive compounds. Organosulphur molecules such as allicin and ajoene exhibit antimicrobial activity due to their reactive sulphur centres, while sulphur-substituted triterpenoids and related compounds demonstrate antineoplastic effects through redox imbalance, mitochondrial dysfunction and apoptosis induction. These pharmacological actions further emphasize the central role of sulphur chemistry—particularly oxidation state and molecular stability—in determining biological outcomes.

CONCLUSION

Sulphur demonstrates complex chemical behaviour, vital biological roles, and diverse therapeutic potentials. Its presence in both organic and inorganic forms contributes to nutrition and pharmacology. Purification through Śodhana enhances sulphur's safety and bioactivity. Naturally occurring sulphur compounds, including triterpenoid thiane and gamma lactone, display significant apoptotic and anti-inflammatory activities, suggesting potential in modern drug discovery.

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