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Role of Purifying Agents in Chemical Transformation of Sulphur: An Ayurvedic Perspective†

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Sulphur, one of the key ingredients in *Ayurvedic* formulations has been used as a single drug or in combination with metals to treat various diseases. Classical *Ayurvedic* texts describe purification techniques for sulphur as well for metals used in combination with sulphur. Butter is used to melt sulphur and the molten sulphur is quenched in milk to bring about an allotropic transformation. Elemental analysis revealed increase in calcium, potassium, phosphorus and sodium content in sulphur which gets incorporated from milk. A substantial increase in carbon, hydrogen and nitrogen content in the sulphur samples indicated incorporation of carbohydrate, protein and lactose content from milk. This was corroborated with decrease in protein and lactose content in the milk after quenching. The process of quenching with water did not result in an allotropic transformation, confirming that milk is responsible for this chemical change. The allotropic modification is necessary to facilitate further reactions of sulphur through mechanochemistry.

Keywords: Sulphur, Milk, Allotrope, Ayurveda.

INTRODUCTION

Sulphur has been used through ages as a panacea in the *Ayurvedic* system of medicine[1]. It has been used extensively in the preparation of drugs like *Rasasindura*[2], *Panchamrita parpati*[3], *Kajjali*[4], *Shila Sindoor*[5], *Swarna Makshika*[6] and many other *Ayurvedic* formulations. Mainly it is used to process mercury. It is believed that the toxic effects of mercury are avoided by combining with sulphur[4]. The mercury and sulphur are subjected to mechanical grinding in a mortar to obtain a black powder of β-HgS. This black powder is subjected to a controlled heating process to obtain *Rasasindura* (α-HgS). It is well known that sulphur forms covalent linkages to mercury[7]. This leads to formation of mercury sulphide, which is insoluble in the gastrointestinal tract and hence non-toxic[6]. According to *Ayurveda*, sulphur has to be purified before being used in combination with other formulations[8]. The purification process is carried out using butter/ghee and milk, resulting in certain chemical transformations and removal of impurities from raw sulphur. Thus far, there is no scientific evidence to prove this. This study was carried out to assess and scientifically validate the role of the purifying agents in the chemical transformation of sulphur.

EXPERIMENTAL

Sodium sulphate, copper sulphate, sodium tungstate, sodium potassium tartarate, phosphomolybdic acid were procured from Merck, India. Sulphur was procured from a local vendor of raw drugs. Cow's milk and butter were procured from Shanmugha Dairy Farm at the University campus.

General procedure: 20 g of butter was melted in a pan to which 300 g of sulphur was added. The mixture was heated gently till the sulphur melted and it was then poured through a muslin cloth into cow's milk (Fig. 1). The solidified sulphur was removed and again melted along with butter and quenched in cow's milk. This process was repeated 15 times to purify sulphur, which was then washed with water and dried under sunlight.

Elemental analysis: The quantitative analysis of the sample was performed using an X-ray fluorescence spectrometer (XRF, S8 Tiger, Bruker, Germany) using a 4 kW Rhodium anode X-ray tube. The carbon, hydrogen and nitrogen content of the samples were analyzed using a CHN auto analyzer (Perkin Elmer, USA).

Thermal analysis: The thermal analyses of the samples were carried out using thermogravimetry (SDT Q600, TA

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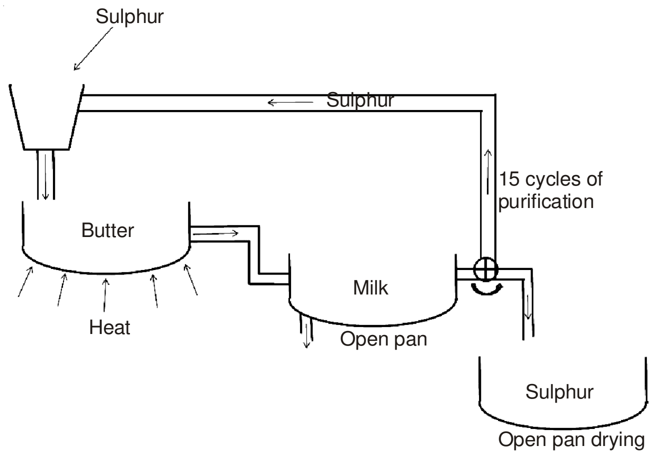

Fig. 1. Flow chart simulating the treatment process of sulphur

Instruments, USA). About 5 mg of the sample was taken in an alumina cup and heated gradually in nitrogen atmosphere at the rate of 10 °C/min.

Biochemical assay: The free lactose content in milk was determined by adding 5 mL of milk to a mixture of sodium sulphate and copper sulphate solutions followed by addition of sodium tungstate solution. The mixture was centrifuged at 1000 rpm and the supernatant was added to alkaline tartarate solution. Phosphomolybdic acid was added and the absorbance was measured at 660 nm using UV-visible spectrophotometer (Lambda 25, Perkin Elmer, USA). The protein content in the milk was determined by weighing the amount of protein precipitated after the addition of sodium tungstate.

RESULTS AND DISCUSSION

The first step in this process involved melting sulphur in butter (Fig. 1). Direct melting of sulphur generates sulphur dust and vapors, which are extremely inflammable[9]. The use of butter not only avoids generation of flame but also enables excellent energy management by causing a decrease in the melting point of sulphur. The melting of sulphur followed by its quenching in milk results in an allotropic transformation of sulphur from the orthorhombic to amorphous form (Fig. 2). The transformation from cyclic (orthorhombic) to a linear form (amorphous) enhances reaction with mercury in the subsequent stages and this treatment process adopts eco-friendly method to process sulphur by prevention of toxic sulphur fumes.

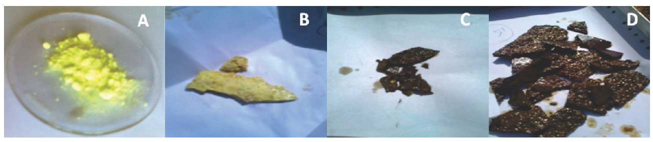

Fig. 2. Process of allotropic transformation of sulphur (A) Raw sulphur, (B) Sulphur after 1st cycle of quenching in milk, (C) Sulphur after 7th cycle of quenching in milk and (D) Sulphur after 15th cycle of quenching in milk

The thermogram of raw sulphur did not show any significant weight loss until 200 °C (Fig. 3). However, the DSC plot revealed endothermic peaks at 110, 125, 189 and 289 °C (Fig. 3). The endothermic peaks at 110 and 125 °C correspond to the removal of moisture and transformation of orthorhombic

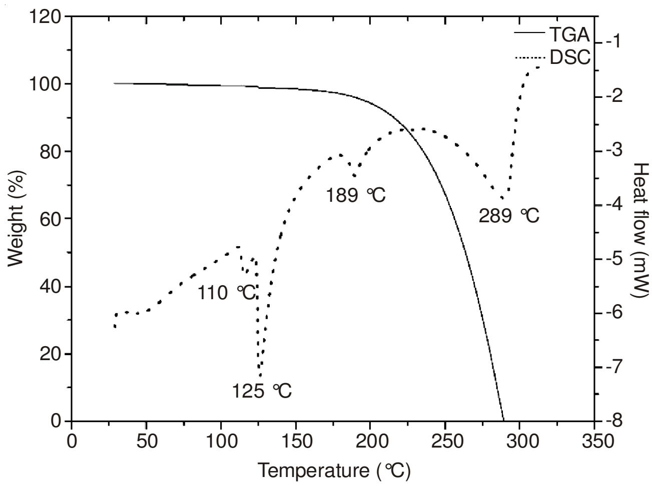

Fig. 3. TG-DSC pattern of raw sulphur

to monoclinic form of sulphur, respectively[10]. The orthorhombic form of sulphur is a cyclic structure containing eight sulphur atoms in a symmetrically puckered conformation[11]. On heating, it converts into β-sulphur (monoclinic form) and when quenched, gets transformed to amorphous sulphur where the cyclic rings are broken to form a polymeric chain of sulphur atoms with branches. Quenching can be carried out in water but it has a higher thermal conductivity than milk and can cause rapid cooling of sulphur, which results in formation of cracks. Presence of impurities both organic and inorganic, are known to influence the properties of the resultant allotrope[12]. Use of water alone is ineffective in removing organic impurities, whereas milk, which consists of a stable emulsion of water and fat-soluble constituents, aids better removal of all types of impurities. Analysis of milk before and after treatment with sulphur showed significant decrease in the free lactose content as well as in the protein content (Table-1).

TABLE-1
LACTOSE AND PROTEIN CONTENT IN RAW MILK BEFORE AND AFTER SULPHUR TREATMENT

Milk sample	Lactose content (mg/mL)	Protein (mg/mL)
Raw milk	0.727 ± 0.030	250 ± 25
After 1st cycle	0.357 ± 0.060	94 ± 11
After 7th cycle	0.309 ± 0.030	55 ± 4
After 15th cycle	0.268 ± 0.030	4 ± 1

The reduction in free lactose content was up to 63 % while the protein content decreased by 98 % after 15 cycles of treatment. This indicates that the lactose and protein were involved in the treatment process of sulphur. Amorphous sulphur is widely believed to have helical structure that imparts certain degree of elasticity[13] and the carbohydrate and protein molecules can occupy the interstices of this structure conveniently. This localization may result in keeping the chains of the amorphous sulphur from coming closer and forming a closed ring structure, a characteristic of the more stable orthorhombic form. Thus the constituents of milk may stabilize amorphous sulphur and prevent their reversion to orthorhombic state (Fig. 4). The amorphous form of sulphur can favour easier processing in the subsequent steps and hence the treatment with milk assumes significance in the traditional process.

TABLE-2
QUANTITATIVE ELEMENTAL ANALYSIS OF SULPHUR BEFORE AND AFTER TREATMENT

Element	Raw sulphur (mass %)	Sulphur after 1st cycle (mass %)	Sulphur after 7th cycle (mass %)	Sulphur after 15th cycle (mass %)
Sulphur	99.62 ± 0.03	99.35 ± 0.04	99.00 ± 0.04	99.03 ± 0.04
Aluminum	0.09 ± 0.00	0.02 ± 0.00	0.04 ± 0.00	0.02 ± 0.00
Calcium	0.07 ± 0.00	0.25 ± 0.00	0.30 ± 0.02	0.43 ± 0.00
Chlorine	0.08 ± 0.00	0.10 ± 0.02	0.24 ± 0.02	0.25 ± 0.01
Silicon	0.05 ± 0.00	0.05 ± 0.00	0.03 ± 0.00	0.02 ± 0.01
Iron	0.04 ± 0.00	0.03 ± 0.00	0.03 ± 0.00	0.02 ± 0.00
Potassium	0.02 ± 0.02	0.08 ± 0.00	0.06 ± 0.01	0.14 ± 0.00
Magnesium	0.01 ± 0.01	0.02 ± 0.00	0.02 ± 0.01	0.02 ± 0.01
Phosphorus	–	0.04 ± 0.00	0.02 ± 0.02	0.08 ± 0.00
Sodium	–	–	0.05 ± 0.00	0.07 ± 0.00

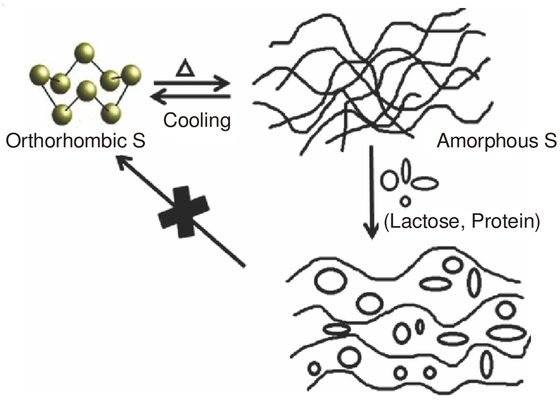

Fig. 4. Mechanism of irreversible allotropic transformation of sulphur

The elemental analysis of the sulphur after 15 cycles of treatment using X-ray fluorescence spectroscopy (XRF) shows the increase in calcium, chlorine, potassium, phosphorus and sodium content indicating that these ions have been transferred from milk to sulphur during the process (Table-2). This was further substantiated by CHN analysis of the sulphur samples, which indicated an increase in carbon, hydrogen and nitrogen content at the end of the 15th cycle of purification (Table-3).

TABLE-3
CHN ANALYSIS OF SULPHUR SAMPLES

Sample name	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Raw sulphur	0.00	0.00	0.00
Sulphur after 1st purification	0.59±0.08	0.02±0.01	0.00
Sulphur after 7th purification	2.03±0.92	0.25±0.09	0.00
Sulphur after 15th purification	9.37±0.52	0.39±0.10	0.81±0.05

Conclusion

The scientific rationale behind the ancient process, used in the treatment of sulphur has been systematically investigated. The results of our study demonstrate that the ancient processes that utilized naturally available products to treat sulphur had a strong scientific basis. Our study demonstrates the role of various purifying agents, signifying a scientific rationale that existed in the stringent purification procedures, which were followed. But whether these contribute to provide any therapeutic efficacy remains to be answered.

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