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# The Use of Sulfur in the Preparation of Chinese Herbs: Part 1

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*This is the first in a series of articles that are excerpted from my doctoral capstone from the American College of TCM. This first part describes the current use of sulfur dioxide to fumigate Chinese herbs. The second part will explain potential sources of confusion and the effects of sulfite additives on the environment, herb workers, wine, food, and patients. The third part will consider the effects of sulfites on Chinese herbs and herbal formulas. The third part will also explain the chemistry of sulfur fumigation and report on some analytical testing and research.*

Nearly everyone who practices Chinese herbal medicine has experienced patients that refuse Chinese herbs because they claim that they are allergic or that they have reactions to sulfur. Practitioners and students also frequently have questions about sulfur and express a general confusion about the use of sulfur on Chinese herbs. Many practitioners question whether or not the quality of the herbs has been affected. This issue is complex and there is a great deal that is still unknown. In this part, I explore the use of sulfur and sulfites, or more precisely sulfur dioxide ($SO_2$), to fumigate, bleach, and preserve Chinese herbs. I also report on relatively recent actions taken by the Chinese State Food and Drug Administration to regulate this practice.

A few words about nomenclature. The first thing to understand is that it is not precisely correct to say that herbs are sulfured, although this is a common way to describe the practice. Usually, sulfur is set afire under the herbs and the result is sulfur dioxide ($SO_2$) is created by the burning. The process is known as fumigation and it is also known as *smoking*. This gas ($SO_2$) is what perfuses the herbs and creates the effects. Technically, the use of sulfur dioxide is a sulfiting process and all of the sulfur-based products created by burning sulfur are known as sulfites, which are considered food additives. There is much more on sulfur dioxide chemistry in Part Two. Additionally, some dealers apply liquid sulfites or spray sulfites onto certain herbs that lend themselves to this form of application. The results are the same as fumigation—sulfites are added to the herbs.

## "SULFUR" TREATMENT OF HERBS

In contrast to most medicinal herbs used in Western countries, where herbs are used fresh or simply dried, Chinese herbs are, generally speaking, processed. After harvest, physical or chemical methods are employed to convert the raw materials into specific forms for the decocting process called *yinpian*, which are the medicinal forms of the herbs. Unprocessed herbs may not be medicinal or they may even be toxic. In 2012 *The Pharmacopeia of the People's Republic of China* (PPRC), fifteen processing methods applicable to herbs are defined and four acceptable drying methods are specified. According to TCM, Chinese herbs are processed to either increase the efficacy and/or reduce the toxicity of the herbs. Quite literally, processing changes the chemical finger print of the ingredients in the herbs, and this is done purposefully. In addition, processing may be used to improve the odor or flavor of the herb, enhance the solubility in water of specific components in the herb, reduce contaminants, and favor certain "active" ingredients over other chemicals that are present in the herb.

In the *PPRC*, the use of sulfur dioxide is not mentioned or defined as either a traditional or an acceptable preparation method for Chinese herbs. An extensive survey of texts of Chinese herbal medicine does not find any information regarding the use of sulfur, sulfur dioxide, or sulfites in the processing or preparation of herbs from China.

Primarily, financial concerns motivate herb dealers to treat the herbs in this manner. For many growers and gatherers, Chinese herbs are a significant source of income. To protect this valuable resource, steps must be taken to ensure the maximum yield and return on investment of both time and money. The use of sulfur, which is inexpensive and relatively easy to use, represents a crucial and an easy decision for dealers. Sulfur costs about 100¥ or nearly $16 for 50 kg of sulfur and 50 kg of sulfur blocks will treat a metric ton of herbs (See Figure 1).

Figure 1: Bricks of elemental sulfur to be used in preserving herbs

Otherwise, Chinese herbs are treated with sulfur dioxide or sulfites for four major, interrelated reasons.

***1. Fumigation/ Antimicrobial***

A major concern in the harvesting and storage of Chinese herbs is infestation by insects and other pests. Herb farmers and dealers report that it takes up to three months after harvesting and processing to sell herbs on the wholesale market. During this time, the herbs must be protected or significant loss in the quantity and quality of the herbs can occur. Although the herbs will eventually be dried, the growth of molds is a significant concern. Fumigation kills active insect activity and prevents infestation of mold and mildews after harvest. Sulfur dioxide prevents or slows down the rot and decay of the foods and herbs.

Particularly in southern areas of China, where pest problems can occur with greater frequency, aluminum phosphide fumigation may also be used. Aluminum phosphide, when it reacts with water or water vapor, is the source of phosphine gas which is deadly to all living organisms. Most sources of aluminum phosphide also contain ammonium carbamate which releases ammonia and carbon dioxide, two gases which are non-flammable and are added to prevent an explosion of the aluminum phosphide. However, even if subsequently treated with aluminum phosphide, fumigation with sulfur dioxide is commonly used all over China. Dealers report that if herbs are not "smoked" with sulfur dioxide, they do not sell.

Sulfur dioxide is a broad-spectrum antimicrobial agent that has an inhibitory effect on a wide variety of microorganisms. Chinese herbs can carry a heavy microbial load which is demonstrated by measuring Total Plate Count, a standard microbiology test. Herbs are subjected to bacteria, fungi, yeasts, and protozoa naturally found in soil, microbes present in organic fertilizers and composts, air borne bacteria and yeasts, and handling by humans. The level of sulfur dioxide at which the microbe, either yeast or bacteria, is affected varies widely by species. It has been understood since the early 1900s that only the free forms of sulfur dioxide (and not the bound) have an antimicrobial effect. It was further discovered in the 1960s that molecular $SO_2$ was several hundred times more effective than bisulfite. The mechanism for sulfur dioxide's antimicrobial effect works by the sulfur dioxide gas entering the microbe and disrupting the activity of the enzymes and proteins of the cell. Since only the molecular form of sulfur dioxide can enter through the cell membrane, it is the concentration of molecular sulfur dioxide that controls microbial growth.

***2. Shelf Life***

The second reason is to increase the shelf life of the herbs. The supply timeline from harvesting of herbs, processing, preparation, transportation within and to China, warehousing, packaging, shipping overseas, warehousing in the US, and distribution to practitioners and retailers, who sell them to patients and consumers is, conservatively speaking, 3-8 years. For some lesser-used herbs, it can be as long as 10-15 years.

Drying food and herbs is a popular and effective preserving method since most bacteria and fungus require moisture to grow. Foods such as fruits, vegetables and meats were often dried for preservation. However, many foods with high moisture content, such as dates and apricots, do not lend themselves to drying as much as would be necessary to prevent molds and bacteria from quickly rotting the food. This was remedied by the discovery that sulfur could help preserve those foods with high moisture content. The use of sulfur as an additive in the preservation of food and herbs dates back to the ancient cultures of Egypt, Greece, China, et al.

Herb dealers in China report that when herbs are fumigated or "smoked" with burning sulfur, then their shelf life is extended by 2-3 years. When a longer shelf life is anticipated or needed, the herbs are fumigated a second time.

***3. Shen***

The third reason that herbs are exposed to sulfur dioxide is to project a false sense of "freshness". Traditionally, the quality of herbs is based on their *shen* or spirit, which is manifested in their appearance. Herbs are graded by their color shape, size, and conformity to a standard particular to that herb. However, the *shen* that appears after herbs have been treated with sulfur dioxide, is not true *shen*, but "*false shen*". When herbs are treated with $SO_2$, their color is kept artificially bright. The sulfites also act as a bleaching agent. (It is also a common practice to use actual chlorine bleach on "white" herbs to make their *shen* brighter. See Figure 2).

Figure 2: Shan yao in bleaching solution

***4. Antioxidant property***

Because of sulfur dioxide's ability to bind with the precursors and the products of oxidation, it can be used as both a preventative and a treatment. The added sulfites protect the herb's color and taste from oxidation. Oxygen from the air attacks the double bond in the carbonyl groups (C=O), which are found in the ketones, aldehydes, fatty acids and other bio-chemicals that are naturally occurring in the herbs. This will be discussed in more detail in the paragraphs regarding "Sulfur Chemistry" in Part Three. Oxygen also attacks the carbon-carbon (C=C) double bond found in unsaturated fats, including Essential Fatty Acids. This oxidation is what makes foods give off the odor and taste associated with rancidity. Visually, this oxidation results in browning or graying of the color of the herbs.

THE PROCESS OF FUMIGATING CHINESE HERBS

The way that this preservation process is accomplished is that the herbs are cleaned and washed, and as noted above, white herbs are often bleached. Then the herbs are placed on a pallet rack or screen. Workers ignite waste paper in a metal pan to burn small chunks of sulfur brick. The pans are placed under the pallet racks. The herbs are covered with a tarp and are "smoked" for at least five hours and often, overnight. Since sulfur dioxide is more than twice as dense as air, the tenting of the herbs provides for a long exposure to the sulfur dioxide. Figures 3-6 illustrate the steps involved in fumigation.

Figure 3: Shan yao on pallet ready to be "smoked" with $SO_2$

Figure 4: Workers igniting sulfur

Figure 5: Shan yao being treated with sulfur dioxide

Figure 6: Covering shan yao with plastic tarp to hold in smoke

RECENT INFORMATION ABOUT SULFUR FUMIGATION

Most Chinese herbs are "sulfured", and somewhat heavily. A survey from Hangzhou Food and Drug Administration reported in Oct 2011 that 60% -70% of the roots and herbs currently on the market have been processed by "smoking" with sulfur. Other estimates from dealers at Chinese medicine markets reported that more than 90% of herbs have been fumigated.

Although the sulfuring of certain foods has ancient roots, the widespread and ubiquitous usage of this procedure on Chinese herbs is of recent origin; as is the sheer amount of sulfites being added to the herbs. Concern over the health effects on patients and the decrease in the quality of the herbs led the People's Republic of China (PRC) to ban the use of sulfur fumigation beginning in 2005. Nonetheless, the practice has continued unabated, primarily due to market needs and financial concerns. Implementation of this ban was delayed because there was no agreed upon method for determining sulfite levels and the lack of published standards for acceptable sulfite levels.

In 2007, the PRC State Food and Drug Administration (SFDA) floated an interim rule and in 2011, announced draft recommendations in which 11 TCM herbs, are allowed to be processed by sulfur fumigation, but should have a sulfur

dioxide residual amount less than 400 ppm (400 mg/kg). These herbs are:

Achyranthis Bidentatae Radix (Niu Xi, *Achyranthes bidentata* Bl.)
Asparagi Radix (Tian Dong, *Asparagus cochinchinensis* [Lour.] Merr.)
Atractylodis Macrocephalae Rhizoma (Bai Zhu, *Atractylodes macrocephala* Koidz.)
Bletillae Rhizoma (Bai Ji, *Bletilla striata* (Thunb.) Reichb. f.)
Codonopsis Radix (Dang Shen, *Codonopsis pilosula* (Franch.) Nannf.)
Dioscoreae Rhizoma (Shan Yao, *Dioscorea opposita* Thumb.)
Gastrodiae Rhizoma (Tian Ma, *Gastrodia elata* Bl.)
Kansui Radix (Gan Sui, *Euphorbia kansui* T.N. liou ex T.P. Wang)
Paeoniae Radix Alba (Bai Shao, *Paeonia lactiflora* Pall.)
Puerariae *Thomsonii* Radix (Ge Gen, *Pueraria thomsonii* Benth.)
Trichosanthis Radix (Tian Hua Fen, *Trichosanthes kirilowii* Maxim.)

This same rule allowed a residue limit of 150 ppm (150 mg/kg) for all other TCM herbs with sulfur fumigation of these remaining herbs being "prohibited".

Additionally, in 2010, *The Pharmacopeia of the People's Republic of China* (PPRC) set forth a method for determining total $SO_2$ levels. So, at this time, there is both a method for testing for $SO_2$ levels and a standard for the limits of total $SO_2$ in the PRC.

However, these official residue limits are far above those in the US and California that require the herbs, as with any food or beverage (such as wine), to bear a label "Contains Sulfites", when the level is above 10 ppm (mg/kg). A survey of the Certificates of Analysis of Mayway's Plum Flower herbs, which have not been treated with sulfur dioxide, reveals that most herbs test for total sulfur dioxide at <10 ppm and all Plum Flower herbs yield results below 40ppm (due to naturally occurring sulfites). Certainly, allowing a residue limit of 150 ppm seems inadequate to curtail the fumigation of the herbs that are prohibited to be treated with $SO_2$.

According to the World Health Organization, the tolerable maximum amount of sulfur dioxide that a human body can take in one day is 0.7 mg per kg, which means that an adult of 60 kg should not take in more than 42 mg of sulfur dioxide a day. Additionally, these official limits are above the legal limits for wine in both the US and EU in which the addition of sulfites plays a crucial role not only in the production of wine, but also in maintaining its quality. Whether or not the setting of these limits is sufficient to protect the quality and efficacy of the herbs or the health of patients remains to be seen. Much more research seems to be called for.

Next time, in Part Two, I will report the effects of sulfite additives on the environment, herb workers, wine, food, and patients. These concerns are what prompted the PRC SFDA to regulate sulfur fumigation.

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