



Demonstrating the efficiency of sulphur dioxide replacements in wine: A parameter review

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Sulphur dioxide seems indispensable in winemaking because of its properties. However, a current increasing concern about its allergies effects in food product has addressed the international research efforts on its replacement. This supposes a sufficient knowledge of its properties and conditions of use. Several studies compared SO₂ properties against new alternatives that are supposed to overcome SO₂ disadvantages. The question that lay on this review is how the efficiency of sulphur replacements in wine can be demonstrated. The *state of the art* and a deep revision of the parameters frequently determined in sulphur dioxide replacement studies in wine are summarized.

Introduction

The general use of sulphur dioxide (SO₂) for conservation dates back to the end of the 18th century. It is used nowadays in many food industries, especially in low pH foods, such as fruit juices and fermentable drinks (Ribereau-Gayon, Dubourdieu, Doneche, & Lonvaud, 2006). Traditionally, SO₂ has been used to control unwanted microorganisms and polyphenol oxidase activity during winemaking, being

added for examples to machine-harvested grapes and to wine after malolactic fermentation in red winemaking (Bartowsky, Costello, Villa, & Henschke, 2004; Oliveira, Ferreira, De Freitas, & Silva, 2011). In this way, it controls both, oxidative process and undesirable fermentations (Ribereau-Gayon *et al.*, 2006).

It is not easy to calculate the precise SO₂ quantities required because of the complex chemical equilibrium of this molecule in wine. It exists in different forms that possess different properties in media of different composition (Fig. 1). It exists either, bound to another compound with different equilibrium constant or in its free form as SO₂ which is the active form. The bound SO₂ is known as combined and together with the free SO₂ is measured as total SO₂. In addition, acid–basic equilibrium in wine must be considered as its concentration in the forms SO₂, HSO₃[−], or SO₄^{2−} depends directly on the pH (Ribereau-Gayon *et al.*, 2006). The concentration of SO₂ in wine is normally in levels of mg per litre (ppm).

The use of an excessive SO₂ doses must be avoided not only for health reasons but also because, from an oenological point of view, it can cause organoleptic alterations in the final product, neutralize the aroma and even produce characteristic aroma defects (Ribereau-Gayon *et al.*, 2006). Conversely, an insufficient concentration does not ensure the adequate stability of the wine against an excessive oxidation or microbial development, which can compromise its quality. Forbidding SO₂ as an antimicrobial agent without an alternative would increase the risk of wine spoiled by yeasts and bacteria (Du Toit & Pretorius, 2000). It is therefore important to continue the search for alternatives to SO₂ preservation to ensure a product that will comply with winemaker demands with no health related problems. Moreover, a free SO₂ wine is considered a wine more natural, healthier, more sustainable and genuine.

Actually, there is a great interest in the search for other preservatives and innovative technologies, harmless to health, that can replace or at least complement the action of SO₂, making possible to reduce its levels in wines. The replacement or reduction of SO₂ addition in the wine should be made by technologies that can ensure its microbiological safety while protecting against oxidation and maintaining its organoleptic properties.

The technologies described in the bibliography are not harmful for the health and present promising properties that allow considering them as alternative methods for

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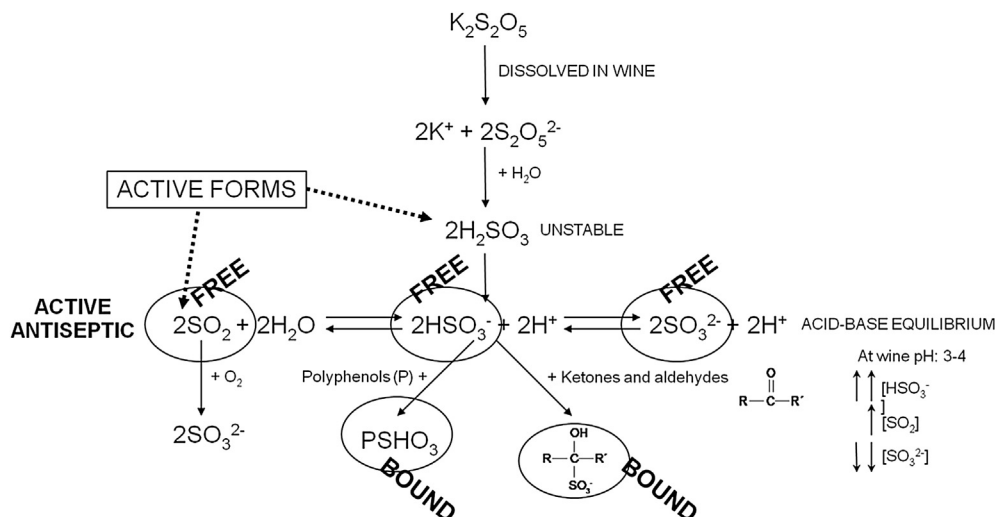


Fig. 1. Chemical equilibrium of SO_2 when added as potassium metabisulphite ($\text{K}_2\text{S}_2\text{O}_5$) in wine.

wine conservation in substitution of SO_2 . A few reviewed studies compared SO_2 properties at same conditions against its new alternatives. Instead, most of them have not compared its properties with SO_2 . Others have been tested in other food products rather than wine or grape, or have studied its own antioxidant, antimicrobial or dissolving properties, and then recommended as SO_2 alternative for wine. What is common to them is that different analytical methodologies have been used to prove either, that these replacement technologies are suitable as an alternative or they can reduce SO_2 addition in wine.

This paper is a review of the current analytical parameters that resulted useful to compare SO_2 addition with new technologies that have been so far studied to substitute or reduce the use of SO_2 in winemaking. It advances the parameters that must be measured to claim that new alternatives complies the same SO_2 properties in wine.

SO_2 in winemaking: a current problem

Sulphur dioxide properties in winemaking

The action of SO_2 in wine is multitasking. It protects against oxidation; selects yeast; selects between yeast and bacteria; has a dissolving power; and has negative effects on taste and health (Table 1).

Protection against oxidation

Many constituents of wine, including phenolics, certain metals, tyrosine and aldehydes, are susceptible to oxidation during the winemaking process and lead to undesirable products that adversely affect its sensory and nutritional value. These oxidative processes can be classified in enzymatic and non-enzymatic. The enzymatic process occurs in grape must (having also consequences on wine quality), while the non-enzymatic oxidation occurs in grape, must and wine. As far as enzymatic oxidation is concerned, *polyphenol oxidase* is the most important *oxidoreductase* responsible for browning during grape processing, followed

by *laccase* and *peroxidase* (Li, Guo, & Wang, 2008; Oliveira *et al.*, 2011). SO_2 plays an important role against oxidation in wine (Li *et al.*, 2008) and prevents browning by inactivation of enzymes, and also by inhibition of Maillard reactions (Garde-Cerdán, Marsellés-Fontanet, Arias-Gil, Ancín-Azpilicueta, & Martín-Belloso, 2008; Ribereau-Gayon *et al.*, 2006). As antioxidant, SO_2 acts in three different ways: by direct oxygen scavenging; by reacting with hydrogen peroxide; and by reducing the quinones formed during the oxidation process back to their phenol form (Oliveira *et al.*, 2011).

Inhibition, activation and selection of yeasts and bacteria

SO_2 inhibits the development of microorganisms such as yeasts, lactic acid bacteria (LAB) and, to a lesser extent, acetic acid bacteria. Its action prevents yeast haze formation, undesirable secondary fermentation, *Brettanomyces* growth, the development of mycodermic yeasts, and various types of bacterial spoilage (Santos, Nunes, Saraiva, & Coimbra, 2012). The antimicrobial activity of SO_2 decreases as wine pH becomes higher (Fig. 1), making it more difficult to microbiologically stabilize wines with low acidity.

SO_2 is the additive most frequently employed to control LAB growth and malolactic fermentation (MLF) development during winemaking, because of its selective antimicrobial properties, especially against LAB (Ough & Crowell, 1987). The three main genera of LAB associated with the winemaking process are *Oenococcus*, *Pediococcus* and *Lactobacillus*. *Oenococcus oeni* is the specie best adapted to growing in the difficult conditions imposed during winemaking (low pH and high ethanol concentration) and, therefore, the main species to develop MLF in wine. The main influence of other LAB species such as *Lactobacillus hilgardii* and *Pediococcus pentosaceus* on wine quality is to cause alterations to the wine, including the so-called “lactic disease”, and the production of off-flavour compounds

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