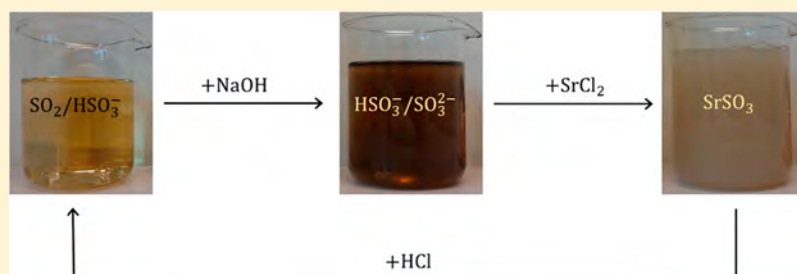


A Qualitative Analysis of Sulfite Ions in White Wine Based on Visible Color Changes

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S Supporting Information



ABSTRACT: In this demonstration, we show a qualitative analysis of sulfite ions in white wine with strontium ions. In base solution, a white precipitation occurs from strontium sulfite that disappears after a strong acid is added. This demonstration nicely illustrates chemical equilibrium in a school chemistry experiment.

KEYWORDS: High School/Introductory Chemistry, First-Year Undergraduate/General, Demonstrations, Equilibrium, Precipitation/Solubility, Qualitative Analysis

INTRODUCTION

Bottles of wine usually show the words “Contains Sulfites”, which is a general term for sulfur dioxide (SO_2) where sulfur has the oxidation state +IV. Therefore, understanding the chemistry of sulfites is necessary in viticulture and enology. Sulfites are widely used in winemaking as a preservative to protect wines from oxidation and microbial spoilage.¹ However, sulfites are controversial in winemaking as a small percentage of the population is sensitive to sulfites. This sensitivity can cause a wide range of reactions that range from mild to severe. Even though the population of sulfite-sensitive consumers is relatively small, the perception that sulfites may cause negative health effects appears to be more common. Some consumers report experiencing headaches and migraines after consuming small amounts of certain wines.² Therefore, the Food and Drug Administration (FDA) has required labeling of any food or beverage containing a sulfite concentration of more than 10 ppm.³

There are two internationally recognized methods for the quantification of sulfites in wine. The first method for the analysis of sulfites in wine is the Ripper method, which utilizes a direct titration of the wine with iodine using a starch indicator.⁴ Although rapid and convenient, the Ripper method is severely limited by poor precision and large systematic error.

In the Optimized Monier–Williams method (AOAC 990.28), the wine is acidified and aspirated into a hydrogen peroxide solution, whereby sulfur dioxide is oxidized to sulfuric acid. Sulfite content is directly related to the generated sulfuric acid, which is determined by titration with a sodium hydroxide

solution. In addition, sulfate can be precipitated with barium ions and measured gravimetrically.⁵ However, this procedure is time-consuming, labor-intensive, and reportedly shows false-positive responses.

Other techniques have also been developed to detect sulfites in wines. Electrochemical techniques, such as cyclic voltammetry or coulometric titrations, are based on the oxidation of sulfite, and a wide range of electrodes can be used. One of the problems associated with these techniques is the potential fouling of the electrodes, which results in a loss of sensitivity. Moreover, the large overpotential required can encounter significant interference, particularly from the oxidation of other components present in wine.⁶ However, these experiments illustrate a number of principles related to electroanalytical chemistry, such as Faraday’s law and the Nernst equation, which make them useful for challenging and empowering students.⁷

Various chromatographic techniques are available to analyze sulfites in wine. High-performance liquid chromatography (HPLC) with photometric or fluorescent detection give reliable results, and also ion chromatography with conductometric detection is well-suited for the determination of sulfites in wine.^{8,9} Sulfite content in white wine samples can also be determined during a quantitative spectrophotometric experiment using the discoloring reaction between sulfite and anthocyanin.¹⁰

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An enzymatic method for the determination of sulfites is based on the oxidation of sulfite ions to sulfate ions by oxygen in the presence of sulfite oxidase. Hydrogen peroxide formed in this reaction is reduced by reduced nicotinamide adenine dinucleotide (NADH) in the presence of NADH peroxidase. The NAD⁺ formed in this reaction is proportional to the sulfite concentration. Consumption of NADH can be measured spectrophotometrically at 340 nm.¹¹ Test kits are available, but the presence of L-ascorbic acid will slow the sulfite oxidase reaction and therefore should be removed during sample preparation.

All the quantitative approaches described above obviously require elaborate technical specification, specific instrumentation, user expertise, and can incur substantial running costs. Sulfite test strips have been suggested as a fast and efficient way to determine the presence of sulfite in food and beverage.¹² The reaction zone on the test strip is impregnated with sodium penta-cyanonitrosylferrate(II) (sodium nitroprusside), potassium hexacyanoferrate(II), and zinc sulfate. It turns pink to brick red depending on the concentration of sulfite ions present. The chemistry of this reaction is not yet fully understood, and these strips yield many false-negative and false-positive results with some types of food.

In this demonstration, we describe a simple qualitative analysis of sulfites in wine that can be easily performed during classroom experiments. This demonstration is not expensive, and there is no need for special equipment, which makes it also very suitable for a student laboratory experiment. Moreover, it nicely illustrates precipitation reactions, acid–base reactions, and chemical equilibrium, which help students to understand this chemical terminology. We describe the chemistry of the sulfite precipitation reaction with strontium ions to strontium sulfite. Additionally, the chemical equilibrium of adding hydrogen chloride to the wine illustrates how the precipitate disappears again according to Le Châtelier's principle.

MATERIALS AND CHEMICALS

The materials and chemicals used during the demonstration are listed below.

- beaker
- pH indicator paper
- young white wine coming from a bottle stating “contains sulfites”
- NaOH solution
- HCl solution
- SrCl₂ 10% solution

The HCl and NaOH solutions should be handled with care, and contact with the skin should be avoided.

DISCUSSION

Theoretical Background

Sulfur dioxide is a gas, but it can readily dissolve in water:¹³



Once dissolved, a chemical equilibrium is established between sulfur dioxide and sulfurous acid according to the reaction



It should be pointed out that only a small part of the dissolved SO₂ is actually converted to H₂SO₃.

Sulfurous acid has two acid constants, which describe quantitatively its chemical equilibrium:¹⁴



To visualize this chemical equilibrium, fractional composition diagrams are instructive in studying which form will be the dominant species at a certain pH range. A derivation of the fractional composition equations for a polyprotic system can be found in the literature.¹⁵ For sulfurous acid, the relative fractions are described as

$$\begin{aligned} \alpha_{\text{H}_2\text{SO}_3} &= \frac{[\text{H}_2\text{SO}_3]}{[\text{H}_2\text{SO}_3] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}]} \\ &= \frac{[\text{H}^+]^2}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}} \end{aligned} \quad (5)$$

$$\begin{aligned} \alpha_{\text{HSO}_3^-} &= \frac{[\text{HSO}_3^-]}{[\text{H}_2\text{SO}_3] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}]} \\ &= \frac{K_{a1}[\text{H}^+]}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}} \end{aligned} \quad (6)$$

$$\begin{aligned} \alpha_{\text{SO}_3^{2-}} &= \frac{[\text{SO}_3^{2-}]}{[\text{H}_2\text{SO}_3] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}]} \\ &= \frac{K_{a1}K_{a2}}{[\text{H}^+]^2 + K_{a1}[\text{H}^+] + K_{a1}K_{a2}} \end{aligned} \quad (7)$$

By using these fractional composition eqs (5–7) including the acid constants from sulfurous acid, we obtained the fractional composition diagram shown in Figure 1.

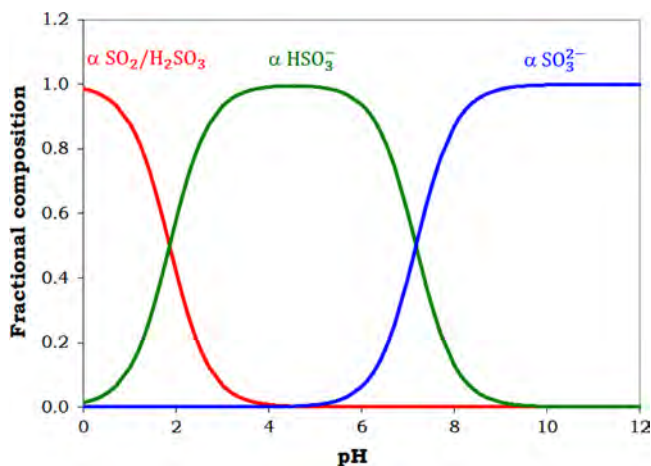


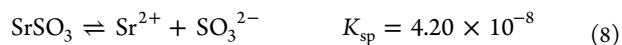
Figure 1. Fractional composition diagram of sulfurous acid. At low pH, SO₂/H₂SO₃ is dominant. In the pH range of white wine (3–4), HSO₃[−] is dominant, whereas at high pH, SO₃^{2−} dominates.

The weak acid SO₂/H₂SO₃ is the dominant species at low pH. The amphoteric hydrogen sulfite ions (HSO₃[−]) are present between pH 2 and 7, and the sulfite ions (SO₃^{2−}) are dominant in the more outspoken base region. The pH of white wine is commonly between 3 and 4, and white wines generally have a lower pH value than red wines. In this pH range, the white wine “sulfites” are present dominantly in the form of HSO₃[−] in equilibrium with the less dominant SO₂/H₂SO₃. Therefore, to

obtain SO_3^{2-} in white wine, the pH must increase by adding a base to the solution to shift the equilibrium according to Le Châtelier's principle. This theoretical background is necessary to understand the basic chemistry of sulfites in wine prior to the demonstration.

The reason to use strontium ions for a qualitative analysis of sulfite ions in wine is as follows.

Sulfite and sulfate ions both form a white precipitation with strontium ions. The solubility products for these two precipitations are¹⁶



The addition of a strong acid, such as a hydrogen chloride (HCl) solution, to both of these precipitations will lead to a complete dissolution of the precipitated SrSO_3 , whereas the SrSO_4 precipitation will remain almost completely because the strong acid H_2SO_4 cannot be formed, and HSO_4^- will be in equilibrium with SO_4^{2-} , according to¹⁵



The fractions of HSO_4^- and SO_4^{2-} at a given pH can be calculated similarly as described above. With $K_{\text{a1}} = 98$ for H_2SO_4 , we obtain a fractional composition diagram for sulfate species as shown in Figure 2.

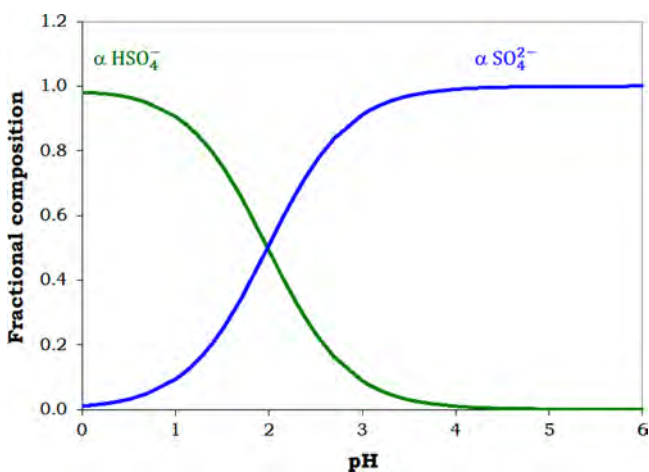


Figure 2. Fractional composition diagram for the $\text{HSO}_4^-/\text{SO}_4^{2-}$ system with $\text{p}K_{\text{a2}} = 1.99$. Below pH 1.99, HSO_4^- is the dominant form, and above this pH, SO_4^{2-} dominates.

In the pH range of white wine, sulfate, if present, is the dominant species. Therefore, strontium ions are useful for a qualitative analysis of sulfite ions and sulfate ions in both white and red wine.

Experiments and Demonstration

During the demonstration, we start by measuring the pH value of the white wine. Step-by-step instructions are available in the Supporting Information. Generally, white wine has a pH value around 3.3. However, a pH value of around 3–4 is usually observed when using pH indicator paper. In this pH range, according to the fractional composition diagrams in Figure 1 and Figure 2, sulfite ions will be dominantly present in the form of hydrogen sulfite ions (HSO_3^-) and sulfate ions in the form of SO_4^{2-} .

In a first experiment, we added a solution of 10% SrCl_2 to the white wine to see if a precipitation occurs. However, the addition of strontium ions did not result in a white SrSO_4 precipitation as would be expected when sulfate ions are present. Moreover, addition of a small amount of potassium sulfate to the SrCl_2 enriched white wine resulted immediately in a white precipitation of SrSO_4 . Hence, we can conclude that sulfate is barely present in the young white wine we used. If old white wines are used, little precipitation of SrSO_4 may occur since sulfite can be oxidized to sulfate during aging.

To demonstrate the presence of sulfite ions in white wine with strontium ions, the pH must be increased to shift the equilibrium from HSO_3^- to SO_3^{2-} . Therefore, we added in a second experiment a sodium hydroxide (NaOH) solution to the wine so the solution becomes basic. According to Le Châtelier's principle, the position of the equilibrium reaction is moved to the right, and the white wine sulfites will now be dominantly present as SO_3^{2-} .

The addition of a base to the white wine also results in a specific color change due to several phenolic components found in grapes and wine as shown in Figure 3.



Figure 3. Color change after addition of NaOH solution to white wine.

This phenomenon can be useful in visualizing a pH difference, and therefore a pH indicator paper is not really necessary during this demonstration. Then, a solution of 10% SrCl_2 is added to the wine solution. Almost immediately, a white precipitation is observed (Figure 4).

The sulfite ions react with the strontium ions to form a SrSO_3 precipitation. This demonstrates clearly the presence of



Figure 4. After addition of strontium chloride to a base wine solution, a SrSO_3 precipitation is formed.

sulfites in wine. Moreover, this qualitative analysis might be expanded to a gravimetric quantification of the SrSO_3 precipitation.

To demonstrate that the precipitation will disappear again according to the fractional composition scheme (Figure 1) and Le Châtelier's principle, we added HCl to make the white wine solution acidic (Figure 5).



Figure 5. SrSO_3 precipitation disappears after addition of HCl to the wine solution.

The chemical equilibrium shifts from strontium sulfites to the hydrogen sulfite ions and strontium ions in solution. At even lower pH, sulfur dioxide gas is formed as the dominant species escaping from the white wine solution.

CONCLUSIONS

A qualitative analysis of sulfites in white wine is discussed. Understanding of the chemistry of sulfites is necessary in viticulture and enology. This qualitative analysis of sulfites is an easy demonstration for classroom chemistry that illustrates chemical equilibrium using acid–base and precipitation reactions.

ASSOCIATED CONTENT

Supporting Information

Step-by-step instructions to perform the demonstration during a classroom experiment or for large audiences. This material is available via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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