# Measuring

# $SO_2$ in Wine

Find out all you need to know about measuring $SO_2$ in wine making

HANNA instruments

# Contents

# Introduction

Quantitative analysis is a vital input for winemakers at all stages of the process including harvest, fermentation, aging, blending, and bottling. In-house testing is growing in popularity due to cost and convenience.

Making sure that the data represents the actual condition of the wine or juice is vital to the success. The accuracy and consistency of results depend on proper sampling, appropriate method selection, and effective execution.

To help with this challenge, Hanna Instruments is putting together a series of ebooks to help winemakers improve their in-house testing programs. This eBook focuses on how to put in place an effective $SO_2$ testing program.

**We cover:**

- How $SO_2$ affects wine quality
- The necessary tools
- How to use these tools to get accurate results

# Why $SO_2$ Matters

## 1 What is Sulfur Dioxide?

Sulfur Dioxide ($SO_2$,) is a molecular compound that winemakers add to their product to in order to keep it stable. Sulfur dioxide is known by a variety of terms to winemakers, such as "$SO_2$" "metabisulfite", or "sulfite".

Sulfur dioxide is usually measured in parts per million, or ppm. This unit simply quantifies how many parts of sulfur dioxide there are per million parts of wine. Another equivalent unit is mg/L, which refers to how many milligrams of $SO_2$ there are in one liter of wine.

The benefits of $SO_2$ as a preservative were recognized as early on as the time of the Romans and Egyptians. It has since become one of the safest and most widely used preservatives not only in the wine industry, but throughout the entire food and beverage industry.

There are several very significant and specific benefits to adding sulfur dioxide to wine. These include:

- helping to reduce undesirable bacteria, molds, and yeasts
- acting as an antioxidant - slowing down the oxidation process
- maintaining wine's desirable characteristics such as taste, fruit flavoring, and aroma

# Why $SO_2$ Matters

$SO_2$ can also result in negative outcomes including:

- slowing and even preventing the fermentation process
- undesirable flavors and aromas

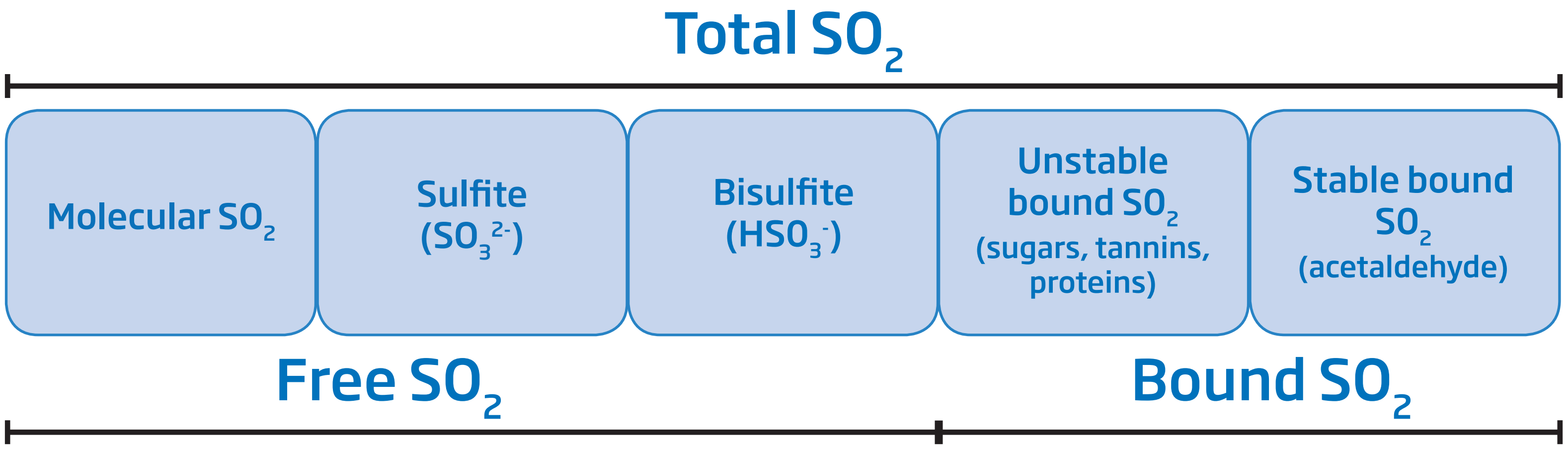
$SO_2$ is also a known allergen to many asthmatic individuals, so its concentration is regulated. The U.S. ATF requires that final products containing more than 10 ppm of total sulfur dioxide be labeled accordingly, and has set the maximum concentration for total sulfur dioxide in wine to be 350 ppm.

# Why $SO_2$ Matters

## 2 Understanding $SO_2$

Before getting a handle on measuring the concentration of sulfur in wine. it is first important to understand what exactly is being measured and how sulfite is present in wine.

When sulfur dioxide is added to wine, a portion of this becomes immediately bound to the various compounds in the wine while the rest remains unbound.  This unbound $SO_2$ is called “free” $SO_2$ and is what is responsible for protecting the wine.  The sum of the concentrations of both the bound and unbound portions of $SO_2$ are referred to as the “total sulfur dioxide”.  The relationship between the amount of total $SO_2$ added and the amount of free $SO_2$ available to protect the wine is complex and will vary .



# Why $SO_2$ Matters

As if this were not complicated enough, there are two main types of free sulfur dioxide in wine: molecular $SO_2$ and bisulfite ($HSO_3^-$). The more abundant of the two forms, bisulfite, is virtually ineffective at protecting wine; the molecular $SO_2$ is what is going to act in a protective capacity. pH is a crucial determining factor in the amount of available molecular $SO_2$. The recommended amount of molecular $SO_2$ is a concentration of 0.825ppm. This concentration should be maintained throughout the winemaking process to adequately protect the wine. The chart below shows how much free $SO_2$ is needed to maintain that ideal values of molecular $SO_2$ at various pH level.

| pH | 3.0 | 3.1 | 3.2 | 3.3 | 3.4 | 3.5 | 3.6 | 3.7 | 3.8 | 3.9 |
|---|---|---|---|---|---|---|---|---|---|---|
| Free $SO_2$ | 14 | 18 | 22 | 28 | 35 | 44 | 55 | 69 | 87 | 109 |

The concentration of molecular $SO_2$ can be derived from the concentration of free $SO_2$ using the following formula: **Molecular $SO_2$ = (free $SO_2$)/( $10^{pH-1.81}$ + 1)**

## 3 Adding and Monitoring $SO_2$

It is critical in the winemaking process to know when and how much $SO_2$ to add to the wine. As stated previously, $SO_2$ can delay or prevent the fermentation of malolactic acid. Free $SO_2$ levels of just 5 to 8 mg/L are enough to interfere with fermentation. Care must be taken during initial additions to ensure that enough sulfur dioxide has been added to provide the benefits while still allowing the necessary steps of fermentation to take place.

After the fermentation process has been completed another addition of $SO_2$ is made to kill any of the remaining yeast and bacteria and to halt all growth. During the first large-scale addition of $SO_2$, a lot of the free $SO_2$ is going to bind to various compounds in the wine, reducing the available free $SO_2$ by 30-50%.

Usually a greater addition will be implemented to account for this. Free $SO_2$ levels should be analyzed every few days after this addition, allowing the time for the free $SO_2$ to react with the components of the wine.

| Situation | Molecular $SO_2$ (mg/L) |
|---|---|
| Storage | 0.5-0.8 |
| Market | 0.4-0.6 |
| Bactericidal effect | 0.6-0.82 |
| Bottling dry red wines | 0.3-0.6 |
| Bottling dry white wines | 0.4-0.8 |
| Bottling sweet wines | 0.8-1.2 |
| Sensory perception | 2.0 |

# Why $SO_2$ Matters

Most winemakers make supplemental additions of $SO_2$ to their wine right before bottling. This serves to protect the wine until the point of consumption. Free $SO_2$ readily reacts with oxygen. Because of the oxygen present the headspace in the bottle, less $SO_2$ is available to act in a protective capacity. Therefore, higher concentrations of sulfur dioxide are added during the bottling process to counteract this reaction.

Sulfur dioxide is added to wine in several ways.

The most typical methods include:

- potassium metabisulfite ($K_2S_2O_5$)
- sodium metabisulfite ($Na_2S_2O_5$)
- $SO_2$ in a gaseous or liquid form

Typical additions using these methods are as follows:

- $K_2S_2O_5$: 0.044 g/L for a 25 ppm addition; 0.174 g/L for a 100 ppm addition
- $Na_2S_2O_5$: 0.037 g/L for a 25 ppm addition; 0.148 g/L for a 100 ppm addition
- $SO_2$: 0.025 g/L for a 25 ppm addition; or 0.1 g/L for a 100 ppm addition

## 4 Analyzing $SO_2$

There are several methods for determining the concentration of $SO_2$ in wine. Two of the most common methods are:

- the Aeration-Oxidation Method
- the Ripper Method

Both of these methods utilize a method of quantitative chemical analysis called titration.

A titration is a technique where a solution of known concentration is used to determine the concentration of an unknown solution. The titrant, or known solution, is added to a known quantity of the analyte, or the unknown solution, until the endpoint is achieved. Knowing the volume of titrant added allows the determination of the concentration of the unknown. An indicator is used to signal the endpoint of the reaction. This indicator may be a color change or a response from an electrode.

### a. The Aeration-Oxidation method

The Aeration-Oxidation method of sulfur dioxide analysis is an Association of Analytical Communities (AOAC) and Alcohol and Tobacco Tax and Trade Bureau (TTB) approved method in which free and total $SO_2$ from an acidified sample solution is volatilized and distilled. The distillate is collected into a hydrogen peroxide solution. Here, the $SO_2$ is oxidized to sulfuric acid ($H_2SO_4$). The volume of standardized sodium hydroxide (NaOH) required to titrate the acid formed is then measured to calculate $SO_2$ levels. The reaction proceeds as follows:

$$H_2O_2+SO_2 \rightarrow SO_3^{2-}+H_2O \rightarrow H_2SO_4$$

### b. The Ripper method

The Ripper method is another commonly used method for the analysis of both free and total sulfur dioxide in wine. In this method, standardized iodine is used to titrate free sulfur dioxide. The completion of this reaction is signaled by the blue-black color change produced by the starch indicator which results from the presence excess of iodine. An oxidation-reduction potential (ORP) electrode may also be used to indicate the endpoint. Total $SO_2$ can be determined by first treating the sample with sodium hydroxide to release the bound sulfur dioxide into solution. The reaction is represented by the equation:

$$SO_2 + I_2 + 2H_2O \rightarrow H_2SO_4 + 2HI$$

### c. The Ripper method with iodate (Modified Ripper)

There is a variation of the Ripper method that uses standardized iodate as the titrant rather than iodine. This is accomplished by adding potassium iodide (KI) to the sample to form iodine from iodate as it is added to the sample. This reaction occurs as follows:

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

Once the iodine is formed in the sample, the titration proceeds as the traditional Ripper method.

The advantage to forming iodine from iodate in the sample is that the iodate titrant is much more stable than iodine. Iodine is susceptible to breakdown from UV and heat, as well as volatilization over time and requires frequent standardization to verify that it is the correct concentration. Iodate will change less frequently over time.

This ebook will focus on the modified Ripper method since it is the most popular method with winemakers.

# What You Need

There are two ways of performing titrations, manually or using an automatic titrator.

## a. Manual Titration

In a manual titration an apparatus called a burette is used to slowly add the titrant to the sample. An indicator solution will usually produce a color change signifying the end point of the reaction. Using a known chemical equation specific to the titration, the volume of the titrant added to achieve the end point is used to determine the unknown concentration of the sample. Using a manual titration can be problematic as it is sometimes difficult to visually pinpoint the exact moment that the color change occurs. This especially difficult when testing red wines.

## b. Automatic titration

Automatic titration is done with instrumentation that delivers the titrant, determines the endpoint and calculates the concentration of the wine sample automatically. Automatic titrators offer increased accuracy and repeatability for two reasons. First an electrochemical indicator (i.e. ORP electrode) is used to determine the equivalence endpoint rather than a subjective color indicator. Secondly t the heart of any automatic titration system is a precision dosing pump. The volume of titrant that a dosing pump delivers is more exact than a burette used in a manual titration.

**Hanna Note**

- **Using an ORP electrode / meter to determine the end point with a manual titration is a more accurate alternative to the visual indicator.**

# Titration Options in Wine Making

ebook focus

| | Manual Titration with Color Indicator | Single-Parameter Titrator | Multiparameter Titrator |
|---|---|---|---|
| Parameters | $SO_2$ | $SO_2$ | SO2, acidity, YAN, reducing sugars... |
| Detection method | Color change (visual) | Potentiometric (ORP electrode) | Potentiometric (ORP electrode) |
| Dosing Accuracy | Low | High | Very high |
| Time | Time-Consuming | Rapid | Rapid |
| Calculations | Manual | Automatic, fixed | Automatic, adjustable |
| Measuring modes | Titration | Titration, ORP | Titration, ORP, pH, ISE |
| Real-time Graphing | No | Yes | Yes |
| Equipment Cost | $25-100 | $800 | $8-10k |
| Automation | None | 1 Sample | Autosampler Compatible (available) |

# What You Need

Here's what to look for when choosing a automatic titrator, electrode and solutions.

**Titrator:**

*Must have* – Automatic titrator with the Ripper Method of $SO_2$ analysis built-in to test both free and total $SO_2$.

*Good to have* - A precision dosing pump to determine the volume of titrant used to reduce effort and improve accuracy. On-screen features such as real-time graphing so you can follow the titration progress on the screen. The ability to log data and export it to computer for record keeping.

**Electrode:**

*Must have* - An ORP electrode to monitor the redox reaction: $\mathbf{H_2SO_3 + I_2 \rightarrow H_2SO_4 + 2HI}$

*Good to have* - The ORP electrode should have clogging prevention system (CPS) technology. This technology prevents the clogging of the reference junction from the solids found in wine must and juice.

**Hanna Note**

- **The equivalence point of the titration should be determined using an algorithm.**

# What You Need

## Solutions

- **Titration Solutions:** Standardized titrant is crucial to ensure accurate determination of $SO_2$
- **Titration Reagents:** All chemicals used for titration should be reagent-grade. These include 25% sulfuric acid, potassium iodide, and stabilized iodine (iodate).
- **Cleaning solutions:** Clogged reference junctions are the number one reason for poor performance in $SO_2$ measurement. This is particularly apparent in wine because wine samples (must, juice etc.) leave residues on the junction of the ORP electrode. A dirty or clogged junction will result in noisy, slow responses and/or excessive drift. Cleaning solutions ensure that the electrode is free from wine deposits.
- **Storage solution:** A few drops of a storage solution should be added to the protective cap prior to storage to prevent the loss of electrolyte.

**Labware:** Beakers, volumetric pipettes

**Hanna Note**

Some titration systems come with pre-measured and pre-standardized chemicals for ease of use. In this case, simply add the reagents and titrate there is no need for an analytical balance or glassware.

# What You Need


**Features of the ideal single parameter mini titrator**

**Easy to use, accurate, and fast:**

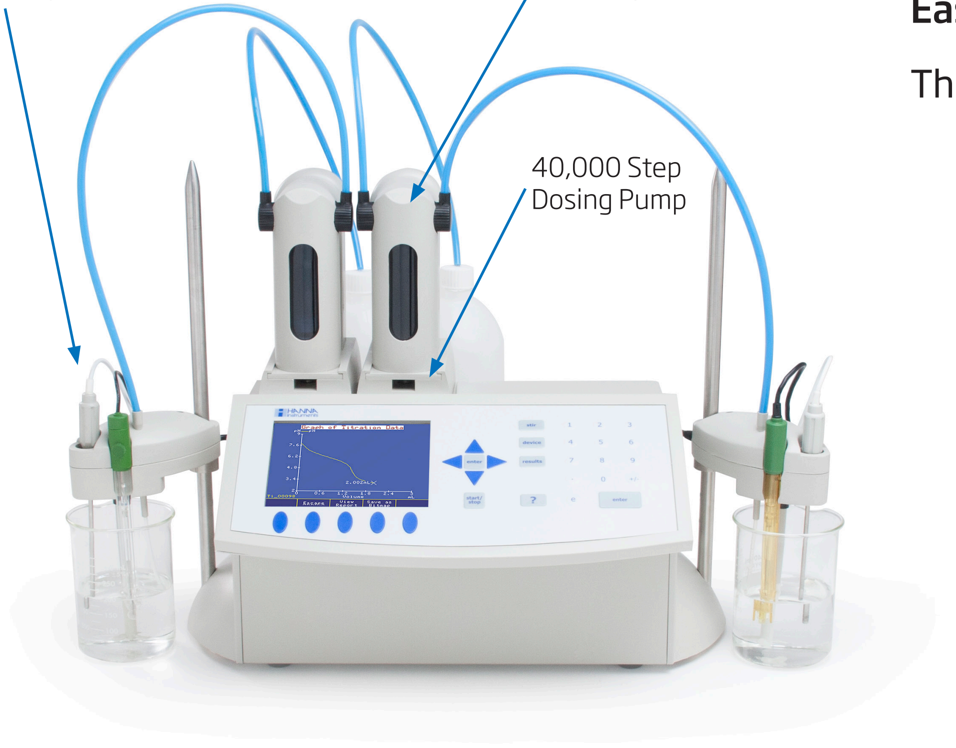
The mini titrator should have:

- an pre-programmed method of analysis with an algorithm that determines the equivalence endpoint of the titration.
- a precision piston-style dosing pump that adjusts titrant addition based on a voltage response.

This mini titrator dispenses the titrant, detects the endpoint, and performs all necessary calculations automatically in a fraction of the time as compared to a manual titration. As found in Triage for Basic Wine/Grape Lab by Richard Carey, "the mini-titrator by Hanna reduces the time for an individual analysis by 75%".

**Affordable:** Single-parameter titrators should cost in the $800 range.

# What You Need




**Features of the ideal multiparameter titrator**

**Easy to use, accurate, fast and versatile.**

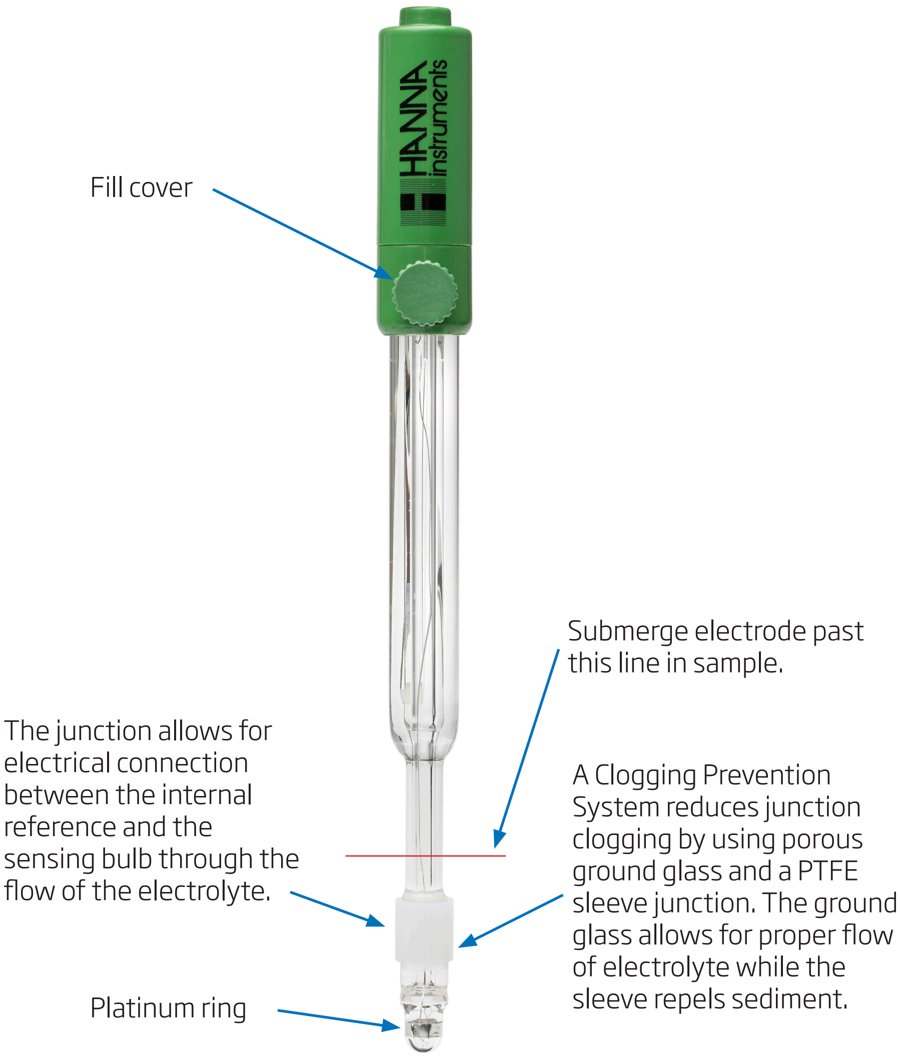
The multiparameter titrator should have:

- Offer the capability to incorporate multiple parameters in one unit.
- Full configuration capabilities to accommodate custom calculations and dosing preferences.
- Multiple measurement modes, enabling them to be used to determine pH, ORP, or ion concentrations depending on the type of electrode connected.

**Hanna Note**

**These units are ideal for an all-in-one solution to measure acidity, $SO_2$, reducing sugars, and yeast assimilable nitrogen(YAN).**

# What You Need




## Features of the Ideal ORP Electrode

**The ideal ORP electrode should be designed for wine.**

Conventional electrodes may clog quickly in wine with a high suspended solids content.

The ideal electrode should have a **Clogging Prevention System** (CPS). This means that electrode utilizes a ground glass/PTFE sleeve junction which permits a steady, predictable flow of electrolyte solution, while keeping the junction open. The hydrophobic properties of PTFE also repels wetness and wine deposits.

# What You Need

## Features of Ideal Solutions

**Solutions should be certified and wine specific.**

**Electrode cleaning solutions:** Specially designed cleaning solutions remove wine, juice, and must stains and deposits without damaging the electrode.

**Electrode storage solution:** A storage solution is designed to keep the electrode hydrated and ensure optimum performance. Properly stored electrodes exhibit higher accuracy and have a longer lifespan.

**ORP Test Solution:** A 240 mV ORP test solution is designed for testing the performance of ORP electrodes. When the ORP electrode is placed in the test solution, the reading obtained should be within +/- 20 mV stated value at 25°C. This solution is a diagnostic tool users can use to determine if the ORP electrode needs to be cleaned or the fill solution needs to be replaced.


**Hanna Note**

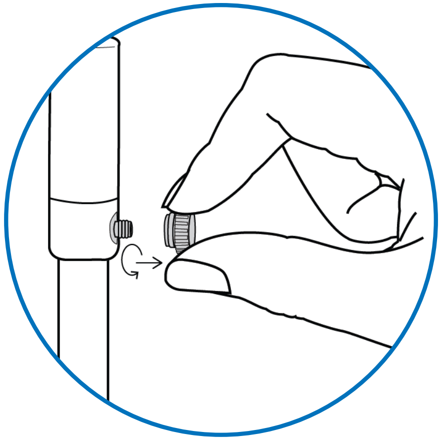
- **Use only fresh solutions and reagents and replace ones have been opened for more than six months.**
- **Always keep the electrode fill solution topped off.**

Each titrator has a different procedure and set up . The general approach and recommendations outlined in this eBook are useful for all similar titrators using the Ripper Method with iodate. Consult the manual for specific instructions on the operation of individual titration systems.

## 1 Prepare and Calibrate

### a. Preparing the ORP electrode

- Remove the protective cap from the probe.
- “Shake down” the probe as you would a thermometer to rid the glass bulb of any air bubbles that may have accumulated.
- Ensure that the fill hole screw cap is removed.



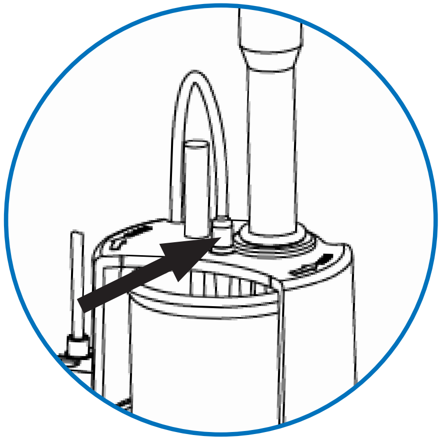
**Hanna Note**

- Caliabrate electrode after extended storage, cleaning or before use.

Each titrator has a different procedure and set up . The general approach and recommendations outlined in this eBook are useful for all similar titrators using the Ripper method with iodate. Consult the manual for specific instructions on the operation of individual titration systems.

### b. Prime the Pump

- In order to properly use the automatic titrator, the burette and tubing should be filled with titrant.
- Before beginning the process of priming the pump, the aspiration tube should be in the titrant bottle and the dosing tip should be placed over a rinse beaker.



**Hanna Note**

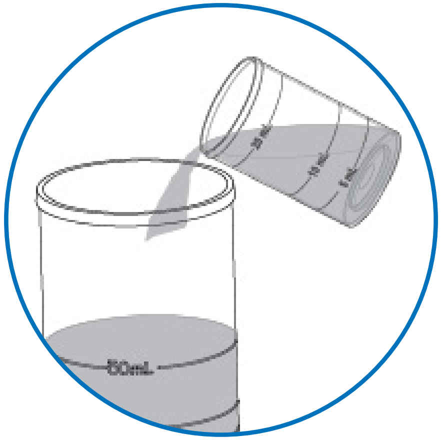
**The prime cycle should be performed:**

- **If there is no titrant in the tip.**
- **Whenever the dosing system tubes are replaced.**
- **Whenever a new bottle of titrant is used.**
- **Before starting a pump calibration (if applicable).**
- **Before starting a series of titrations.**

### c. Pump Calibration and Titrant Standardization

For a dedicated $SO_2$ titrator a pump calibration is performed while for a multi-parameter titrator a titrant standardization is performed.

- Precisely add pump calibration standard or titrant standard to a clean beaker.
- Add 5 mL of the acid reagent to the sample.
- Add potassium iodide to the sample beaker.
- Rinse the ORP electrode with deionized water and immerse into the sample until the reference junction is completely submerged. Be sure that the tip of the electrode the stirrer.
- Insert the dosing tip into the sample, making sure that the tip is submerged approximately 0.1" into the sample.
- Begin titrating immediately with iodate.



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## 2 Measure

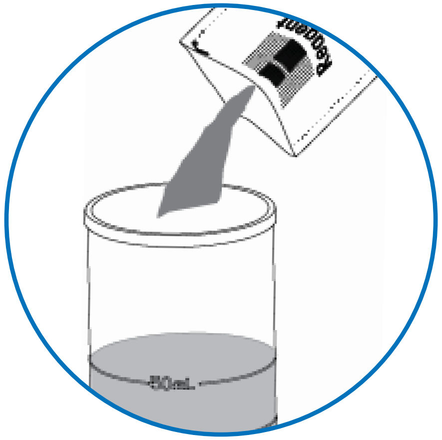
### Measuring Free and Total $SO_2$

- Use a clean pipette to precisely add 50 mL of wine to a clean 100 mL beaker.

**For Total $SO_2$ (only)**

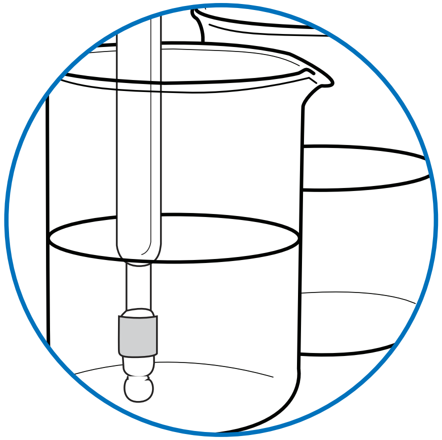
- Add 5 mL of alkaline reagent, cover the beaker and swirl. Allow the sample to sit for approximately 20 minutes.

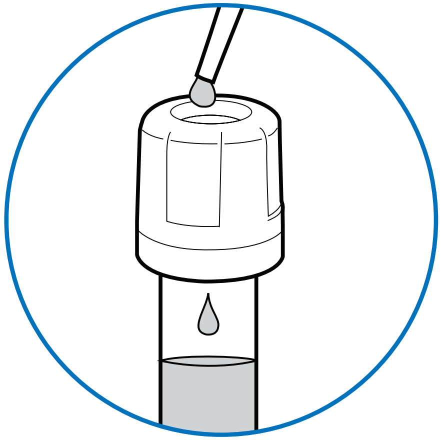
- Using the 20 mL beaker, add 5 mL of the acid reagent to the sample.
- Add one packet of the potassium iodide to the sample beaker.
- Rinse the ORP electrode with deionized water and immerse into the sample until the reference junction is completely submerged. Be sure that the tip of the electrode is not hitting the stir bar.
- Insert the dosing tip into the sample, making sure that the tip is submerged approximately 0.1” into the sample.
- Begin titrating immediately with iodate.



## 3 Clean and Store

- Once you are finished titrating your samples, remove the ORP electrode from the electrode holder and rinse it with water until all wine stains are removed.
- Examine the ORP electrode to determine if it needs to be refilled with fill solution (the level of the internal solution is less than ½ inch from the fill hole).
- If wine/must is present inside the ORP electrode (easier to spot with red wines because you see the red stains inside), then empty, rinse, and refill the electrode with fill solution. Close the fill hole with the cap.
- Fill a small beaker with cleaning solution for wine deposits or wine stains
- Immerse the ORP electrode for 2 to 3 hours. Make sure the junction is covered.
- Fill the storage cap of the ORP electrode to the half point with storage solution and replace the storage cap on the electrode. Make sure there is enough storage solution in the cap to cover the junction of the ORP electrode.





# How to Measure $SO_2$

## 1 Prepare and Calibrate

- ☐ Remove the protective cap from the probe.
- ☐ "Shake down" the probe like a thermometer to rid the glass bulb of any air bubbles.
- ☐ Remove the fill hole screw cap.
- ☐ Ensure that the burette and tubing are primed with titrant. Use a waste beaker to collect dispensed titrant as it is priming
- ☐ Precisely add pump calibration standard or titrant standard to a clean beaker.
- ☐ Add 5 mL of the acid reagent to the beaker.
- ☐ Add potassium iodide to the sample beaker.
- ☐ Rinse the ORP electrode with deionized water and immerse into the sample until the reference junction is completely submerged.
- ☐ Insert the dosing tip into the sample, until submerged approximately 0.1".
- ☐ Begin titrating immediately with iodate.
- ☐ Update the titrator with the calibration value.

## 2 Measure

**Free $SO_2$**

- ☐ Use a clean pipette to precisely add 50 mL of wine to a clean 100 mL beaker.

**Total $SO_2$ (only)**

- ☐ Add 5 mL of alkaline reagent, cover the beaker and swirl. Allow the sample to sit for approximately 20 minutes.
- ☐ Using the 20 mL beaker, add 5 mL of the acid reagent to the sample.
- ☐ Add potassium iodide to the sample beaker.
- ☐ Rinse the ORP electrode with deionized water and immerse into the sample until the reference junction is completely submerged. Be sure that the tip of the electrode is not hitting the stir bar.
- ☐ Begin titrating immediately with iodate.

## 3 Clean and Store

- ☐ After measuring samples, unclip the ORP electrode from holder and rinse
- ☐ Ensure all wine stains are removed
- ☐ Examine the ORP electrode - refill if the level of the internal solution is less than ½ inch from the fill hole
- ☐ Empty, rinse, and refill the electrode with fill solution if wine/must is present inside the ORP electrode
- ☐ Fill a small beaker with cleaning solution for wine deposits or wine stains
- ☐ Immerse the ORP electrode for 2-3 hours with junction covered
- ☐ Fill the storage cap of the ORP electrode to the halfway point with storage solution
- ☐ Replace the storage cap on the electrode
- ☐ Make sure there is enough storage solution in the cap to cover the junction of the ORP electrode