

Measuring SO₂ in Wine



Find out all you need to know about
measuring SO₂ in wine making

 **HANNA**[®]
instruments



Contents



Why SO₂ Matters

pg 4



What You Need

pg 13



How To Measure

pg 21



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 SO₂ Matters

1 What is Sulfur Dioxide?

Sulfur dioxide (SO₂) 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 "SO₂" "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 SO₂ there are in one liter of wine.

The benefits of SO₂ 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 SO₂ Matters

SO₂ can also result in negative outcomes including:

- Slowing and even preventing the fermentation process
- Undesirable flavors and aromas

SO₂ 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.

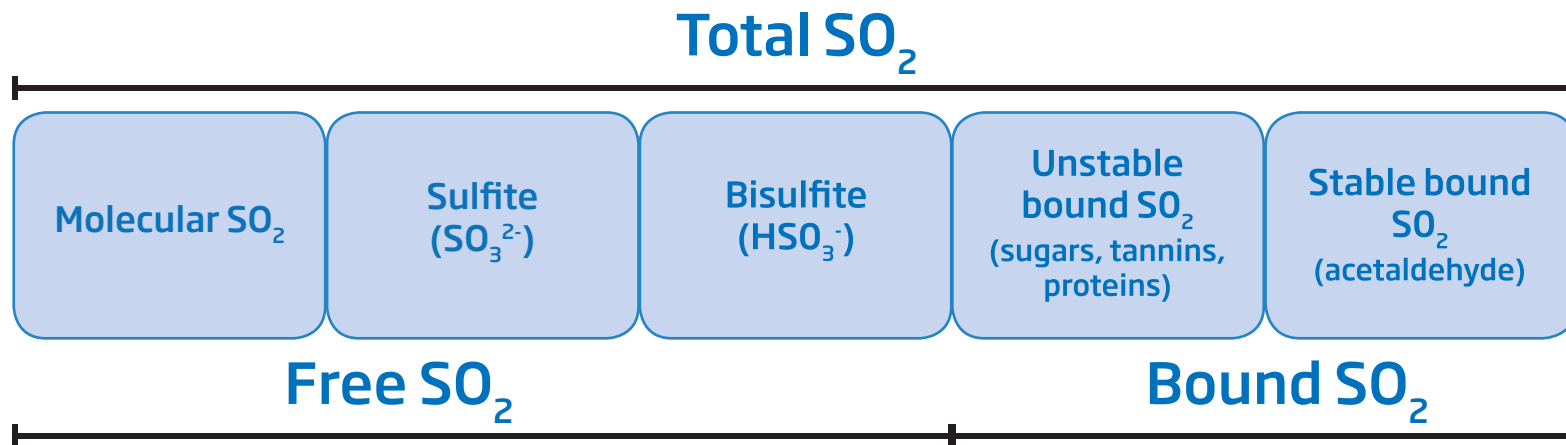


Why SO₂ Matters

2 Understanding SO₂

Before getting a handle on measuring the concentration of sulfur dioxide 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 SO₂ is called “free” SO₂ and is what is responsible for protecting the wine. The sum of the concentrations of both the bound and unbound portions of SO₂ are referred to as the “total sulfur dioxide”. The relationship between the amount of total SO₂ added and the amount of free SO₂ available to protect the wine is complex and will vary .





Why SO₂ Matters

As if this were not complicated enough, there are two main types of free sulfur dioxide in wine: molecular SO₂ and bisulfite (HSO₃⁻). The more abundant of the two forms, bisulfite, is virtually ineffective at protecting wine; the molecular SO₂ is what is going to act in a protective capacity. pH is a crucial determining factor in the amount of available molecular SO₂. The recommended amount of molecular SO₂ is a concentration of 0.825 ppm. This concentration should be maintained throughout the winemaking process to adequately protect the wine. The chart below shows how much free SO₂ is needed to maintain that ideal values of molecular SO₂ 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 SO₂ can be derived from the concentration of free SO₂ using the following formula: **Molecular SO₂ = (free SO₂)/(10^{pH-1.81} + 1)**



Why SO₂ Matters

3 Adding and Monitoring SO₂

It is critical in the winemaking process to know when and how much SO₂ to add to the wine. As stated previously, SO₂ can delay or prevent the fermentation of malolactic acid. Free SO₂ 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 SO₂ is made to kill any of the remaining yeast and bacteria and to halt all growth. During the first large-scale addition of SO₂, a lot of the free SO₂ is going to bind to various compounds in the wine, reducing the available free SO₂ by 30-50%.

Usually a greater addition will be implemented to account for this. Free SO₂ levels should be analyzed every few days after this addition, allowing the time for the free SO₂ 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 SO₂ Matters

Most winemakers make supplemental additions of SO₂ to their wine right before bottling. This serves to protect the wine until the point of consumption. Free SO₂ readily reacts with oxygen. Because of the oxygen present in the headspace in the bottle, less SO₂ 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 (K₂S₂O₅)
- Sodium metabisulfite (Na₂S₂O₅)
- SO₂ in a gaseous or liquid form

Typical additions using these methods are as follows:

- K₂S₂O₅: 0.044 g/L for a 25 ppm addition; 0.174 g/L for a 100 ppm addition
- Na₂S₂O₅: 0.037 g/L for a 25 ppm addition; 0.148 g/L for a 100 ppm addition
- SO₂: 0.025 g/L for a 25 ppm addition; or 0.1 g/L for a 100 ppm addition



Why SO₂ Matters

4 Analyzing SO₂

There are several methods for determining the concentration of SO₂ 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.

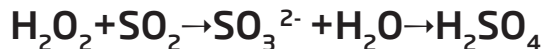
A titration is a technique where a solution of known concentration is used to determine the concentration of an unknown solution. The titrant, or known solution, is added to a known quantity of the analyte, or the unknown solution, until the endpoint is achieved. Knowing the volume of titrant added allows 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.



Why SO₂ Matters

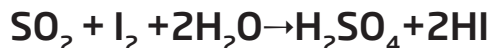
a. The Aeration-Oxidation method

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 SO₂ from an acidified sample solution is volatilized and distilled. The distillate is collected into a hydrogen peroxide solution. Here, the SO₂ is oxidized to sulfuric acid (H₂SO₄). The volume of standardized sodium hydroxide (NaOH) required to titrate the acid formed is then measured to calculate SO₂ levels. The reaction proceeds as follows:



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 SO₂ 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:





Why SO₂ Matters

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:



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 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.



What You Need

Titration Options in Wine Making

eBook focus

	Manual Titration with Color Indicator	Single-Parameter Titrator	Multiparameter Titrator
Parameters	SO ₂	SO ₂	SO ₂ , acidity, YAN, reducing sugars...
Detection method	Color change (visual)	Potentiometric (ORP electrode)	Potentiometric (ORP and pH electrodes)
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 SO₂ analysis built-in to test both free and total SO₂.

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: $\text{H}_2\text{SO}_3 + \text{I}_2 \rightarrow \text{H}_2\text{SO}_4 + 2\text{HI}$.

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.



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 Solutions:** A few drops of a storage solution should be added to the protective cap prior to storage to prevent the loss of electrolyte.

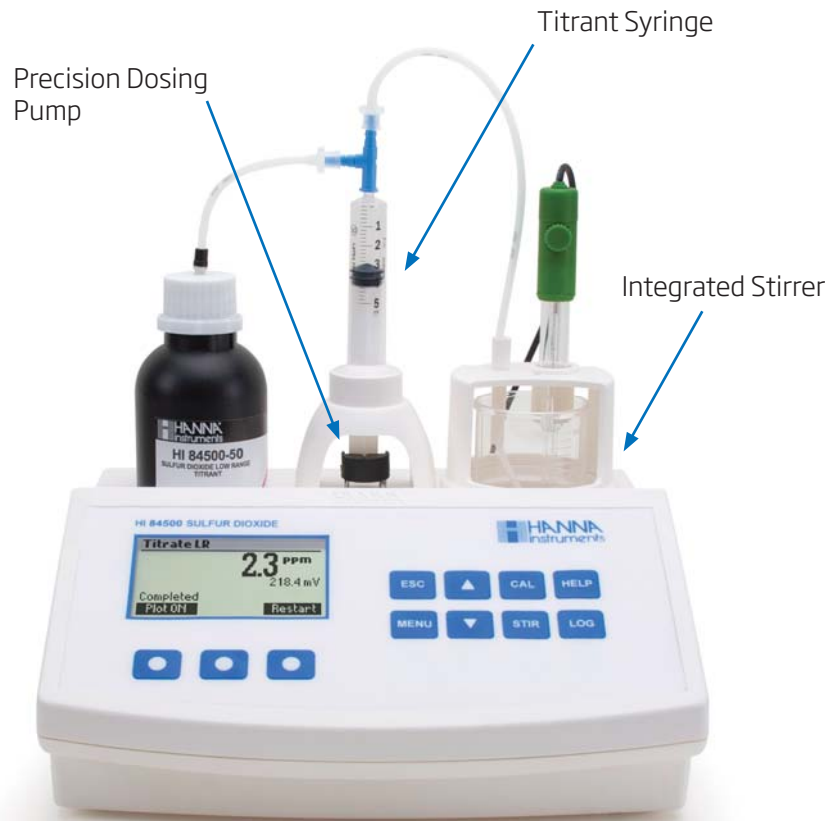
Labware: Beakers, volumetric pipettes.

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

Overhead Stirrer
Assembly

Clip Lock
Exchangeable Burettes

40,000 Step
Dosing Pump

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).



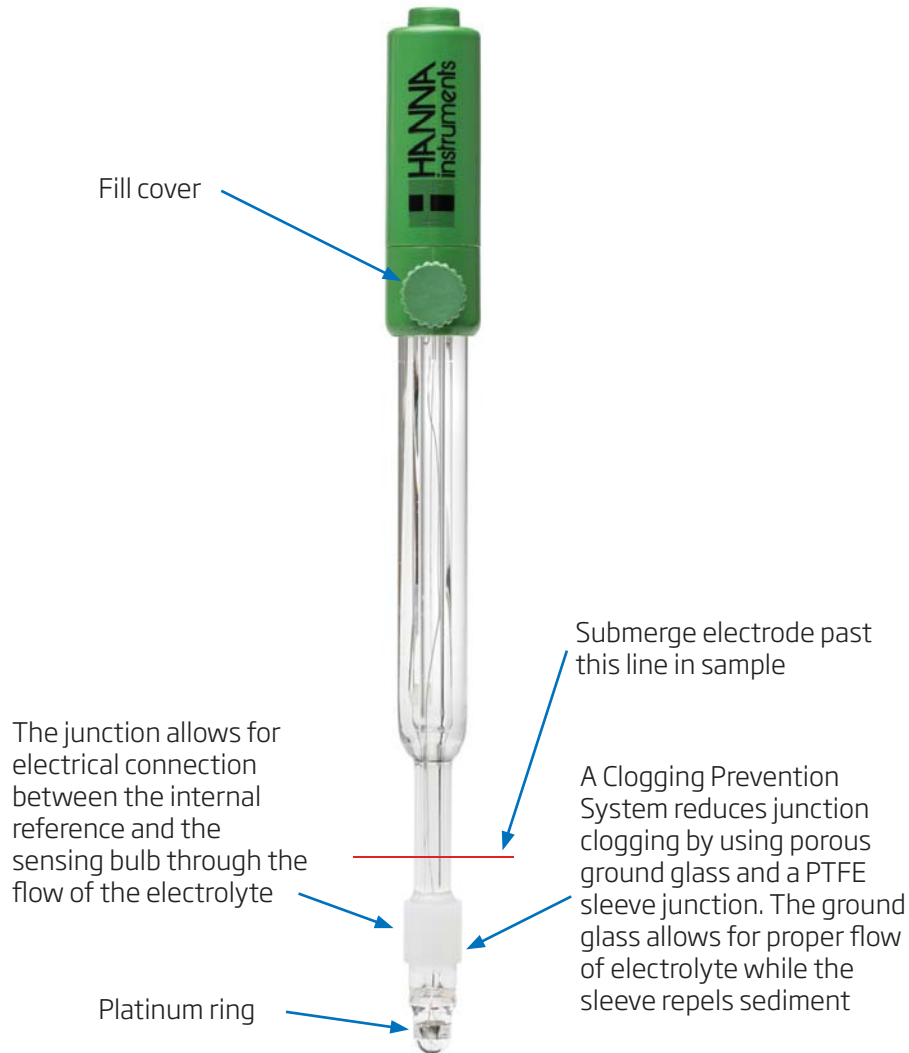
What You Need

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 Solutions: 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 Solutions: 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 that have been opened for more than six months.
- Always keep the electrode fill solution topped off.



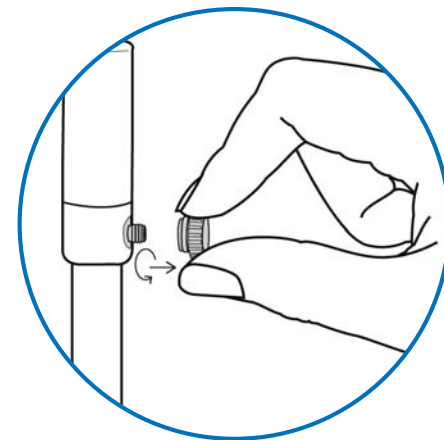
How to Measure SO₂

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

a. Preparing the ORP electrode

- Remove the protective cap from the probe.
- Ensure that the fill hole screw cap is removed.
- Make sure that the probe has sufficient fill solution.
- Reads correctly in the ORP test solution.

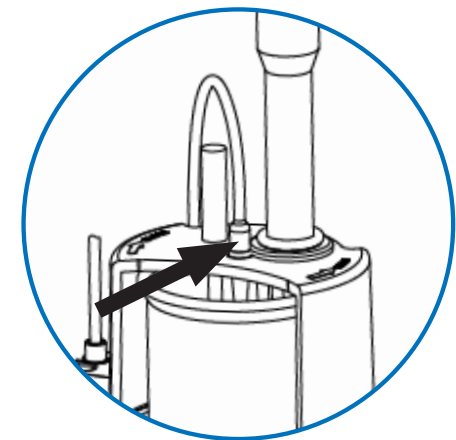




How to Measure SO₂

b. Prime the Burette

- 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.

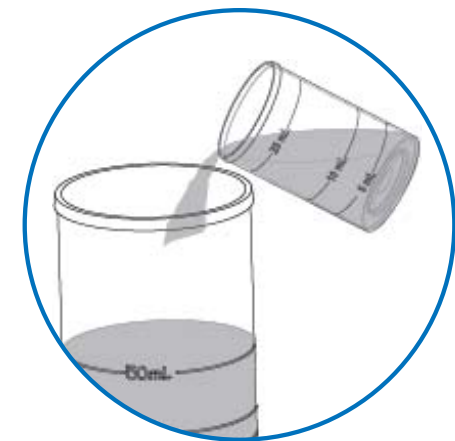


How to Measure SO₂

c. Pump Calibration and Titrant Standardization

For a dedicated SO₂ 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.





How to Measure SO₂

2 Measure

Measuring Free and Total SO₂

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

For Total SO₂ (only)

- Add 5 mL of alkaline reagent, cover the beaker and swirl. Allow the sample to sit for approximately 10 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.

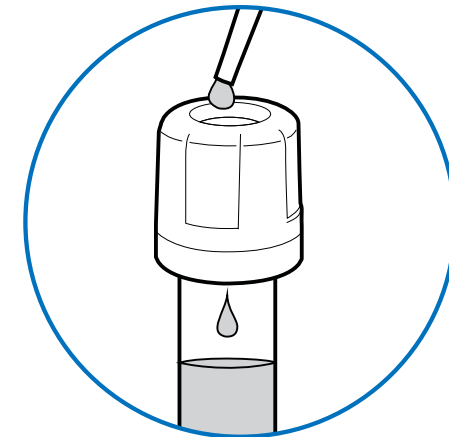
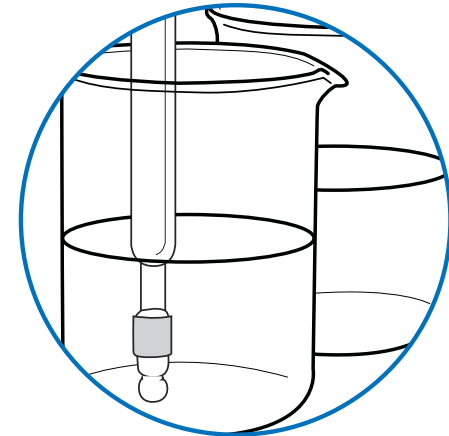




How to Measure SO₂

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 5 to 15 minutes. 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.



THANKS FOR READING!

Our experts are here to help you.

Visit us at
wine.hannainst.com

Email us at
wine@hannainst.com

Call us at
1 (877) MY-HANNA

