APPLICATION NOTE

Sulfur dioxide in wine by manual ripper titration with a Platinum ORP Electrode

Key Words
Wine analysis, Ripper titration, sulfur dioxide, platinum ORP electrode, iodine titrant standardization, SO_2.

Goal

The following application note describes a simple way to analyze the sulfur dioxide in wine using a Thermo Scientific™ Orion™ 9778BNWP or 9678BNWP ORP Electrode and the Ripper titration method.

Introduction

SO_2 is widely used in wine production as a chemical antioxidant and inhibitor of microbial activity. SO_2 in wine is traditionally analyzed by Ripper titration using a color indicator. In this note, the same Ripper titration is performed by using an Orion platinum ORP electrode to signal the endpoint. The color and clarity of red wine does not interfere, thereby improving the results. This method provides a simple solution to SO_2 analysis in wine.

Basic Titration Workflow

Fill buret with titrant → Prepare sample in beaker → Insert electrode and stir → Titrate to inflection endpoint → Calculate results

Recommended Equipment

- Thermo Scientific™ Orion™ Versa Star Pro™ pH/mV meter, Thermo Scientific™ Orion Star™ A211 pH/mV meter, or equivalent Orion pH/mV meter
- Thermo Scientific Orion 9778BNWP Glass Combination Platinum ORP Electrode or Thermo Scientific™ Orion™ Sure-Flow™ 9678BNWP Platinum ORP Electrode
- Stirrer probe (Cat. No. 096019)
- Swing arm stand (Cat. No. 090043)
- Electrode polishing strip (Cat. No. 948201)
- 10 mL burette, burette clamp, ring stand

Required Reagents and Solutions

- Purchased or prepared Iodine (I_2) standard titrant solution, 0.01 M (0.02 N)
- Sodium hydroxide (NaOH), 1 N
- 25% sulfuric acid (1+3 H_2SO_4)
- Electrode filling solution for ORP electrode (Cat. No. 900011)
- Laboratory Reagent Water (LRW)

Optional:

- Standard sodium thiosulfate solution, 0.01 M (0.01 N)
- Sodium sulfite (Na_2SO_3)
- Sodium bicarbonate ($NaHCO_3$)

Meter Setup

Connect Orion electrode and the stirrer probe to the meter. In Setup, select the mV mode, set read type to continuous, and set the stirrer speed to 3. Refer to the Orion meter and electrode user guides for more details.

Titration Setup

Secure the burette on the clamp. Fill the burette with iodine titrant solution and adjust the level to the zero mark. Consider standardizing the titrant before titrating samples. See *Hints and Tips* on the following page.

Sample Preparation

Make sure the wine sample is at room temperature.

Total SO_2: Add 25.0 mL of wine and 25 mL of 1 N NaOH to a 100 mL beaker. Mix and allow 10 min for hydrolysis then proceed immediately to the Sample Titration.

Free SO_2: Add 25.0 mL of wine to a 100 mL beaker. Proceed immediately to the Sample Titration.

Sample Titration

The Ripper titration should be done relatively quickly to avoid loss of SO_2 to the air. Rinse the electrode and stirrer with LRW. Immerse the electrode and stirrer at least one inch below the liquid level in the beaker, with the stirrer just below the electrode. Turn on the stirrer. Stir gently so that a vortex is not created. Tap to release air bubbles trapped on the surface of the electrode.

Total SO_2: Add 10 mL of 25% sulfuric acid to the beaker.
Free SO_2: Add 5 mL of 25% sulfuric acid to the beaker.

Watching the mV reading, titrate at moderate speed with the iodine titrant. The mV values will not rise quickly, until near the endpoint (EP). The EP is considered the point where the largest mV change is observed per volume addition of titrant. See the example graph on the next page for a description of the EP. Depending on the ORP electrode, generally look for the EP to occur between 275 to 375 mV.

Record the volume of titrant used (V_t) at the EP. Repeat the titration as desired or required by your protocol. After each titration, rinse the electrode and stirrer with LRW and tap electrode to remove excess water droplets.

Quality Control (QC)

Recommended QC procedures may include: standardization of the iodine titrant*, analysis of SO_2 standard* or QC sample, and/or replicates.

*See Application Note #016: Standardization of Iodine Titrant for Ripper Titration of Wines.

Calculation of Free or Total SO_2

SO_2 (mg/L) = $V_I \times N_I \times 1280$

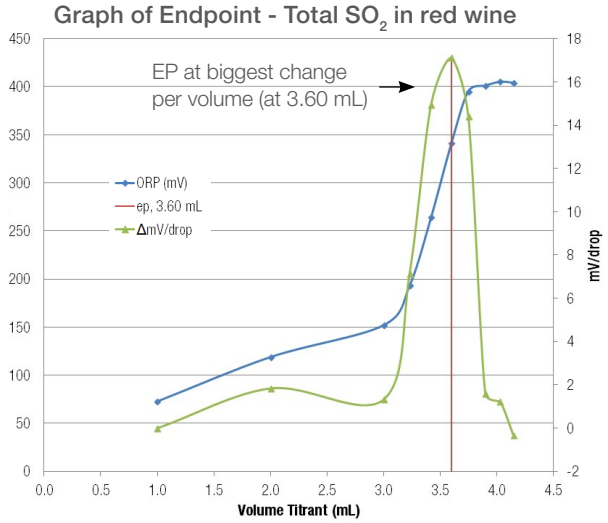
V_I = Volume of iodine titrant used at the endpoint of the titration (mL)
N_I = Normality of the iodine titrant (certified or standardized value)
1280 = (32g SO_2/equivalent × 1000 mg/g)/25 mL wine

Results - Total SO_2 by Manual Ripper Titration with Orion Platinum ORP Electrode

Red Wine Sample	Endpoint Vol (mL)	Total SO_2 (mg/L)
1	3.80	80
2	3.60	76
3	3.65	77
Statistics	avg	78
	Stdev*	2.2
	RSD	2.8%

SO_2 QC Sample	Total SO_2 Result (mg/L)	Within ±7 mg/L?*
49 mg/L	43	Yes

*per Zoecklein et. el, anticipated error is ±7 mg/L



Endpoint Location – Platinum ORP Electrode

Note that at the EP, one drop of titrant will generally cause a mV change of >10 mV, while a mV change of >5 mV per drop generally means the EP is near, either quickly approaching or has just been passed. If another drop of titrant causes a smaller change than the last drop, the EP has passed, but if a larger change is observed, the EP is still approaching. Record the volume of titrant used (V_t) at the EP.

Hints and Tips for SO_2 Titration with Platinum ORP Electrode

- Per Zoecklein, consider using sodium bicarbonate to minimize loss of SO_2 during titration as follows: After the 10 minute hydrolysis (for total SO_2) and just before adding the 25% sulfuric acid, quickly add a pinch of sodium bicarbonate (0.5g or less) to the sample. The solution will fizzle forming a CO_2 atmosphere to minimize loss of SO_2.
- Iodine Titrant Standardization: Iodine titrant solution ages and changes concentration over time. For higher accuracy, standardize the titrant daily or weekly before titrating samples. See Application Note #016: Standardization of Iodine Titrant for Ripper Titration of Wines.
- Refer to the electrode user guide for details on cleaning, storage, and maintenance recommendations to keep the electrode performing well. Main points for electrode care are summarized as follows.

Daily Care	Weekly Care	As Needed
• Top up fill solution • Store electrode in 4M KCl or water	• Drain and refill the fill solution • Clean the electrode with 75% methanol or ethanol	• Clean the electrode with HCl or Orion 900023 • Measure mV of titrant to check electrode operation

- Filling solution - each day top up the filling solution in the electrode. On a weekly basis, drain and refill the electrode with filling solution, for best performance.
- Electrode Storage – store the electrode in 4M potassium chloride solution or store in water.
- Periodically clean the ORP electrode by stirring 1 minute in 75% methanol or alcohol. Wipe the platinum sensor gently with a lint free wiper afterwards.
- If periodic cleaning and refilling described above does not maintain or restore performance, clean with 0.1 to 1M HCl or Orion 900023 pH cleaning solution C. Follow directions (user guide or instruction sheet).
- To check the operation of the electrode, immerse the electrode in a portion of the 0.02N iodine titrant. Expect the mV reading to be near 410 mV (±30 mV) within 1-2 minutes. If not, polish the platinum sensor gently with a lint free wiper, then drain and refill the electrode to restore proper readings.

References

1. Zoecklein et al. *Wine Analysis and Production*, Chapman and Hall. 1995.
2. Napa Valley College. *Laboratory Analysis of Musts and Wines*, Viticulture and Enology Department. 2007. http://www.napavalley.edu/

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To purchase an Orion platinum ORP electrode, or other related products, please contact your local equipment distributor and reference the part numbers listed below.

Depending on your sample throughput needs and budget, we have developed application notes for both our electrochemistry meters for manual titrations and potentiometric titrators for automated titrations. Our automated titrators can help improve your titrations by simplifying your process and helping to deliver consistently reliable results. Just program it once and the titrator takes care of the rest - including addition of titrant, endpoint determination, results calculation, and data logging. Please visit **thermofisher.com/titrator** for more information.

Product	Description	Cat. No.
Meters	Thermo Scientific Orion Versa Star Pro pH Benchtop Meter	VSTAR10
	Thermo Scientific Orion Star A211 pH Benchtop Meter	STARA2110
	Thermo Scientific Orion Star A214 pH/ISE Benchtop Meter	STARA2140
Electrodes	Thermo Scientific™ Orion™ Combination Platinum ORP Electrode, Glass Body, BNC Waterproof Connector	9778BNWP
	Thermo Scientific™ Orion™ Sure-Flow™ Platinum ORP Electrode, Epoxy Body, BNC Waterproof Connector	9678BNWP
Solutions	Thermo Scientific Orion Electrode Filling Solution for ORP Electrode	900011
	Thermo Scientific Orion pH Electrode Storage Solution	910001
Accessories	Stirrer Probe	096019
	Electrode Storage Sleeve and Base	810017
	Swing Arm Stand	090043
	Thermo Scientific™ Orion™ ATC Temperature Probe with Steel Body	927007MD
Laboratory Reagent Water	Thermo Scientific™ Barnstead™ Water Purification Systems	Multiple

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