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APPLICATION NOTE

No. 017

Sulfur dioxide in wine by enhanced manual ripper titration with platinum and iodide electrode

Key Words

Wine analysis, sulfur dioxide, Ripper titration, platinum and iodide electrode, mV endpoint titration, SO_2.

Goal

The following application note explains how to analyze sulfur dioxide in wine using a Ripper titration with a Thermo Scientific™ Orion™ 9770BNWP Platinum and Iodide Electrode.

Introduction

Sulfur dioxide (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 using an Orion 9770BNWP Platinum and Iodide Electrode to signal the endpoint at a known mV value. The color and clarity of red wine does not interfere, thereby improving the results. The Orion 9770BNWP Electrode is fast, low maintenance, requires no fill solution, and is long-lasting. The mV endpoint titration is comparable to a Titratable Acidity (TA) determination to pH 8.2. This method provides a simple solution to SO_2 analysis in wine.

Basic Titration Workflow

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
- Orion 9770BNWP Platinum and Iodide Electrode (residual chlorine ISE)
- Stirrer Probe (Cat. No. 096019)
- Swing Arm Stand (Cat. No. 090043)
- Electrode Polishing Strip (Cat. No. 948201)
- 10 mL burette, burette clamp, ring stand

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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)
- Laboratory Reagent Water (LRW)

Optional:

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

Meter Setup

Connect the 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* section 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. After 10 minute, 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 the electrode 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. Expect the endpoint (EP) to occur near 555 mV (±35 mV) when titrating red wine. The mV values will not rise quickly, until near the 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.

Record the volume of titrant used (V_t) at the EP and the mV reading at the EP. For subsequent titrations of this wine today, titrate to this mV value. Repeat the titration as desired or required by user's 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.

*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 and Iodide Electrode (9770BNWP)

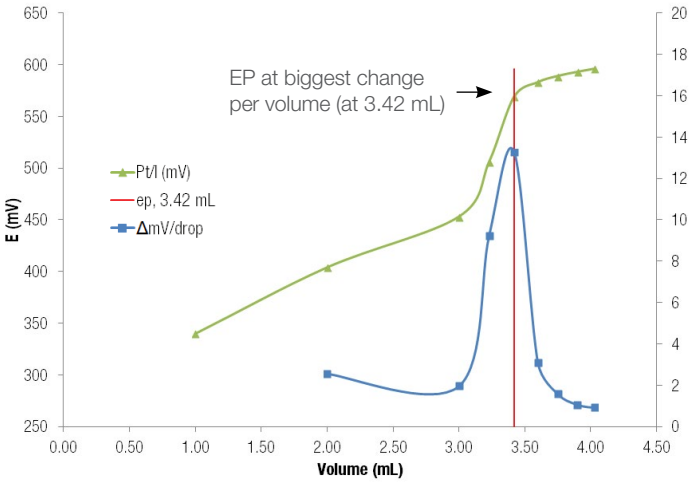
Red Wine Sample	Endpoint Vol (mL)	Total SO_2 (mg/L)
1	3.53	75
2	3.42	73
3	3.65	78
Statistics	avg	75
	Stdev*	2.4

SO_2 QC Sample	Total SO_2 Result (mg/L)	Within ±7 mg/L?*
68 mg/L	63	Yes

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

Endpoint Location – Platinum and Iodide Electrode

Graph of Endpoint - Total SO_2 in red wine



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 and the mV reading at the EP. For subsequent titrations of this wine today, titrate to this mV value.

Hints and Tips for SO_2 Titration with Platinum and Iodide 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 (0.5 g 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
• Store electrode dry	• Clean the electrode with 75% methanol or ethanol	• Gently polish sensor • Measure mV of titrant to check electrode operation

- Electrode storage - Thoroughly rinse the electrode with LRW water and store the electrode dry.

- Periodically clean the 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 by gently polishing the platinum sensor with an Orion 948201 polishing strip. See electrode user guide for details.

- To check the operation of the platinum and iodide (9770BNWP) electrode, immerse the electrode in a portion of the 0.02N iodine titrant. Expect the mV reading to be near 670 mV (±20 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.

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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.

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/

To purchase an Orion Platinum and Iodide Electrode, or other related products, please contact your local equipment distributor and reference the part numbers listed below.

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™ Platinum and Iodide Electrode (Residual Chlorine ISE)	9770BNWP
Accessories	Stirrer Probe	096019
	Electrode Polishing Strip	948201
	Swing Arm Stand	090043
Laboratory Reagent Water	Thermo Scientific™ Barnstead™ Water Purification Systems	Multiple

Thermo Scientific Orion Versa Star Pro pH Benchtop Meters

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