APPLICATION NOTE

Free and Total Sulfur Dioxide (SO_2) in wine (Ripper method) by automatic titration

Water Analysis Instruments,
Thermo Fisher Scientific

Key words
Sulfite, sulfurous acid, SO_2, juice, must, iodine, redox, Orion 9770BNWP, Orion Star T920, Orion Star T940, titrator.

Preprogrammed methods
T5 SO_2 Wine

Introduction
Free and Total sulfur dioxide in wine are determined using the preprogrammed method, T5 SO_2 Wine. To determine free sulfur dioxide, the sample is treated with appropriate reagents and titrated to the equivalence point using iodine/iodide titrant. To determine total sulfur dioxide, the sample is reacted with alkaline solution for a set period of time, then treated with appropriate reagents and titrated to the equivalence point using iodine/iodide titrant.

Recommended equipment
- Thermo Scientific™ Orion Star™ T920 Redox Titrator or T940 All-In-One Titrator or equivalent with a 20 mL burette
- Thermo Scientific™ Orion™ 9770BNWP platinum/iodide (chlorine) electrode or equivalent
- Glass pipette or graduated cylinder, 10 mL graduated
- 25 or 50 mL graduated cylinder
- 100 and 150 mL beakers

Required reagents and solutions
- Titrant: Purchased or prepared iodine/iodide titrant, 0.01M (0.02N)
- Standardizing Solution (optional): Purchased or prepared 0.01M (0.01N) standard sodium thiosulfate solution
- Reagent Solutions: Purchased or prepared 1N Sodium Hydroxide, purchased or prepared 25% Sulfuric Acid (1 + 3 H_2SO_4), prepared conditioning solution
- Solid Reagent: Sodium Bicarbonate
- Reagent grade water (RGW)

Use suitable Personal Protective Equipment (PPE) and ventilation as recommended by the Safety Data Sheets (SDS) for the chemicals utilized during this procedure.

ThermoFisher SCIENTIFIC

Titrator setup

Connect the electrode and the stirrer probe to the titrator. If not previously done, import the T5 SO_2 Wine preprogrammed method into the titrator from the Methods screen[1]. Rinse and fill the burette with titrant. See the titrator user manual for details on setting up the titrator.

If bubbles are visible in the tubing, dispense titrant (from the Burette screen) until the bubbles have been expelled. Tap the tubing to dislodge bubbles. Consider standardizing the titrant before titrating samples. See Titrant section below.

T5 SO_2 Wine method: Preprogrammed parameters

Electrode	Parameter
Electrode Type	Redox
Electrode Name	Edit as desired

Titrant	Parameter
Titrant Name	I2
Titrant ID	Edit as desired
Conc Input Mode	Standardization
Nominal Concentration	0.01 M[2]
Standardize Tech	Equivalence Pt.
Number of Endpoints	1
Results Units	M
Standardize Reaction Ratio	2
Standard Name	$Na_2S_2O_3$
Standard Amount	Fixed volume, 10 mL
Standard Concentration	0.010 M[3]
Pre-dose Titrant Volume	4 mL
Max total titrant volume	10 mL
Stand. Process Control	User defined
ΔE	10 mV
ΔVmin	0.02 mL
ΔVmax	0.100 mL
dE/dt	10
t min	2 seconds
t max	8 seconds
Threshold	250
Pre-stir Duration	5 sec
Stir Speed	Medium

Titration	Parameter
Titration Technique	Equivalence Pt.
Number of Endpoints	1
Titration Type	Direct
Blank Required	No
Result Units	mg/L
Reaction Ratio	1
Sample Amount	Fixed vol., 25 mL
Sample MW	64.07
Pre-dose Titrant Volume	0.1 mL
Max total titrant volume	10 mL

Titration (Contd.)	Parameter (Contd.)
Titration Process Control	User defined
ΔE	5 mV
ΔVmin	0.020 mL
ΔVmax	0.100 mL
dE/dt	10 mV/min
t min	2 seconds
t max	4 seconds
Threshold	250
Pre-stir Duration	10 sec
Stir Speed	Medium
Sample ID	Manual

Electrode preparation

Before the first titration of the day, place electrode into conditioning solution for 10 or 15 minutes. Rinse thoroughly with RGW before and between titrations. At the end of the day, clean any foreign materials from the platinum sensor by wiping with a moistened lint-free wiper. Thoroughly rinse the electrode with RGW and store the electrode dry.

Reagent solution preparation

Prepared 25% Sulfuric Acid: Place 750 mL of RGW in a large beaker or graduated cylinder. Add 250 mL of concentrated (98%) H_2SO_4. Mix and allow to cool. Store in a sealed container at room temperature.

Conditioning solution: Dispense 0.5 mL of titrant into a 150 mL beaker and add RGW to the 100 mL mark.

Sample preparation

Free SO_2: Accurately add 25.0 mL of wine to a beaker. Add RGW to the 60 mL mark on the side of the beaker. Proceed to Sample Titration.

Total SO_2: Accurately add 25.0 mL of wine. Add 25 mL of 1 N NaOH to a beaker. Mix and allow 10 minutes reaction time. After 10 minutes, add RGW to the 60 mL mark on the side of the beaker. Proceed to Sample Titration.

Sample titration

1. Free SO_2
   a. From the Methods screen, select option to run the saved method T5 SO_2 Wine.
   b. Rinse the electrode, stirrer, and dispenser with RGW. Place the electrode, stirrer, and dispenser into the prepared sample in the beaker. Ensure that the dispenser tip is inserted below the surface of the sample. Ensure that the reference pellet on the side of the electrode is immersed.
   c. Add 5 mL of 25% sulfuric acid to the beaker. Start the titration immediately. When the stirrer starts to spin, immediately add about 1 g (¼ teaspoon) of solid

bicarbonate to the beaker. The sample will bubble and foam. Addition of the bicarbonate may be omitted if results are satisfactory without it.

d. Results are reported as mg/L SO_2.

2. Total SO_2

a. From the Methods screen, select option to run the saved method T5 SO_2 Wine.

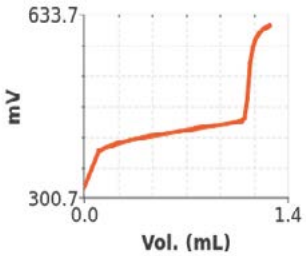
b. Rinse the electrode, stirrer, and dispenser with RGW. Place the electrode, stirrer, and dispenser into the prepared sample in the beaker. Ensure that the dispenser tip is inserted below the surface of the sample. Ensure that the reference pellet on the side of the electrode is immersed.

c. Add 10 mL of 25% sulfuric acid to the beaker. Start the titration immediately. When the stirrer starts to spin, immediately add about 1 g (¼ teaspoon) of solid bicarbonate to the beaker. The sample will bubble and foam. Addition of the bicarbonate may be omitted if results are satisfactory without it.

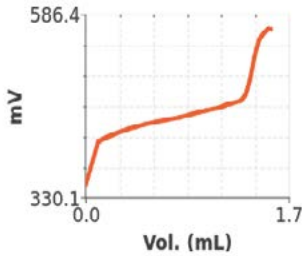
d. Results are reported as mg/L SO_2.

Results

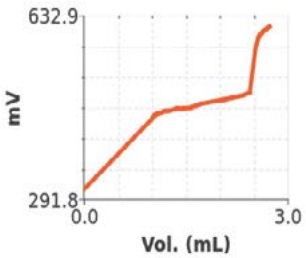
Parameter	Sample	Average (n = 3)	SD (mg/L)	Analysis Time
Free SO_2	White wine	26.3 mg/L FSO_2	0.6	02:39 minutes
Free SO_2	Red wine	29.9 mg/L FSO_2	0.7	03:03 minutes
Total SO_2	White wine	65.9 mg/L TSO_2	0.8	03:49 minutes[4]
Total SO_2	Red wine	51.8 mg/L TSO_2	0.9	02:51 minutes[5]



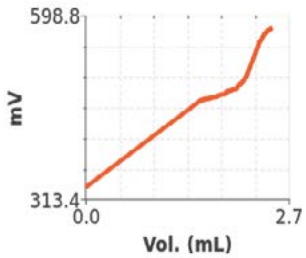
Free SO_2 in white wine



Free SO_2 in red wine



Total SO_2 in white wine



Total SO_2 in red wine

Range

This preprogrammed titration method covers a range of about 25 to 250 mg/L of SO_2, when using 0.01 M (0.02 N) Iodine/Iodide titrant and the prescribed volume of sample.

Method modifications

- For samples of a concentration less than 25 mg/L:
  - Double the sample volume tested, e.g., 50 mL.
  - Edit the method (SO_2 Wine), edit Titration, change Sample Amount to Variable Volume, and Save. When prompted by the titrator, enter 50 mL as the sample volume.
- For samples of a concentration of greater than 250 mg/L, choose one option:
  - Use a smaller sample volume, e.g., 15 mL. Edit the method (SO_2 Wine), edit Titration, change Sample Amount to Variable Volume, and Save. When prompted by the titrator, enter 15 mL as the sample volume.
- For shorter titrations:
  - Use a pre-dose to shorten the analysis time.
  - Edit the method (SO_2 Wine), edit Titration, change the Pre-dose Titrant Volume, and Save.
  - If desired, copy the method to create two methods: one method for free SO_2 and another method for total SO_2. Adjust the predose as desired for each method.
  - In general, a pre-dose that can be expected to work well will be a volume of about 1 mL less than the expected final volume of the titration.
  - For example, a sample with a concentration near 100 mg/L will take about 4 mL of titrant. To make the titration go faster, edit the method to use a predose of 3 mL.

Titrant

Over time, standard titrant solutions age and can change concentration. For higher accuracy, determine the exact concentration by standardizing the titrant. It is common to standardize on a weekly basis, but other standardization frequencies may be suitable.

1. Standardizing titrant
   a. Pipet 10.0 mL standardizing solution, 0.01M (0.01N) standard sodium thiosulfate, into a clean 100 mL beaker. Add about 60 mL of RGW to the beaker.
   b. Select the SO_2 Wine method. At the pre-titration screen, select the standardize option.
   c. Add 2 drops of 25% sulfuric acid to the beaker (to lower the pH to < 5).
   d. Start the titration.
   e. The new standardized titrant concentration will automatically be saved and used for subsequent SO_2 Wine method titrations.
2. Certified standardized titrant solutions
   a. Some customers may prefer not to standardize their titrant, instead choosing to purchase and use certified standardized titration solutions. In this case, edit the Titrant section of the method and enter the certified concentration and titrant ID (i.e., lot number, if desired).

Titrator and electrode care

Refer to the titrator and electrode user manuals for details on cleaning, storage, and maintenance recommendations to keep the titrator and electrode performing well. Main points for care are summarized below.

Daily Care	Weekly or Biweekly Care	As Needed
• If bubbles are visible in the titrator tubing, dispense titrant until bubbles have been expelled. Tap tubing to dislodge bubbles that stick. • At the start of the testing, immerse the electrode in diluted titrant conditioning solution for 10 or 15 minutes. • Rinse electrode well with RGW before and between titrations. • Clean any foreign materials from the platinum sensor by wiping gently with a moistened lint-free wiper. • Storage: Thoroughly rinse the electrode with RGW and store the electrode dry.	• Consider standardizing the titrant on a weekly basis, or more frequently, as desired. • Prepare a small batch of conditioning solution for the week.	• For slow or drifty electrode response, soak 15 minutes in warm 1% laboratory detergent while stirring. Gently brush the platinum sensor and reference pellet with a *soft* toothbrush. Rinse well with RGW afterward. • If still slow or drifty, use Orion pH cleaning solution C, immersing only the platinum sensor. Do not immerse the reference pellet. Rinse well, then soak in conditioning solution solution 10 or 15 minutes before use. • See the electrode user manuals for maintenance details.

Notes

[1]Refer to the user manual for detailed instructions.

[2]If the concentration of the iodine titrant is listed in normality (N), divide by 2 to obtain the molarity (M). For example, 0.02N iodine ÷ 2 = 0.01M iodine.

[3]If the standardizing solution concentration is not 0.0100 M (0.0100 N), enter the true value.

[4]Using a predose of 1.0 mL. For a shorter run, try a predose of 1.5 or 2.0 mL.

[5]Using a predose of 1.5 mL.

thermo scientific

To purchase Thermo Scientific laboratory products, please contact your local equipment distributor and reference the part numbers listed below:

Product	Description	Cat. No.
Titrators	Thermo Scientific Orion Star T920 pH Titrator without electrode	START9200
	Thermo Scientific Orion Star T940 All-In-One Titrator without electrode	START9400
Electrodes	Thermo Scientific Orion Platinum/Iodide (chlorine) Electrode	9770BNWP
Accessories	100 and 150 mL beakers	
	25 or 50 mL graduated cylinder	
	10 mL graduated pipet	
Reagent Grade Water	Thermo Scientific™ Barnstead™ Smart2Pure™ 12 UV Water Purification System	50129890*
Reagents	0.01M (0.02N) iodine/iodide titrant	
	0.01M (0.01N) standard sodium thiosulfate solution	
	1M Sodium Hydroxide	
	Sulfuric Acid, 98% or 25%	
	Sodium Bicarbonate, solid	

*Please contact your local Thermo Scientific representative for support on ordering the best water purification system for your application. And visit our website at www.thermofisher.com/T900titratorseries.

References

Zoecklein et al. *Wine Analysis and Production*, Chapman and Hall. 1995.

Iland et al. *Chemical Analysis of Grapes and wine: techniques and concepts*. 2nd Edition, 2013.

Find out more at **thermofisher.com/T900titratorseries**

Australia: (613) 9757-4300 In Australia: (1300) 735-295 **China:** (86) 21-6865-4588
Germany: (49) 6184-90-6321 **India:** (91) 22-6716-2261/2247 **Japan:** (81) 045-453-9175
North America: 1-978-232-6000 Toll Free: 1-800-225-1480 **Singapore:** (65) 6778-6876

ThermoFisher SCIENTIFIC