Application Note

Determination of sulfurous acid in wine by Ripper method (Polarization titration)

Industry	Food & beverage
Instrument	Automatic potentiometric titrator
Measurement method	Polarization titration / Redox titration
Standards	

1. Scope

Sulfurous acid is generally added to wine as an antiseptic agent. Sulfurous acids in wine are classified into bound sulfurous acid and free sulfurous acid (Note 1). The total amount of these two is called total sulfurous acid. During the wine-making process, the concentration of sulfurous acid needs to be monitored and adjusted. This Application Note introduces an example of the determination of free sulfurous acid and total sulfurous acid in wine by the Ripper method using a polarization titration at constant current (Note 2,3).

2. Apparatus

Main unit	Automatic potentiometric titrator (Preamplifier POT)
Electrode	Twin platinum electrode

3. Reagents

Titrant	0.01 mol/L Iodine solution
Additive reagents	25 % Sulfuric acid solution
	Sodium hydrogen carbonate
	1 mol/L Sodium hydroxide solution

4. Procedure

- Calibration -

1) Set the constant current value to 1 μA.
2) Immerse the twin platinum electrode in pure water.
3) Execute calibration after the current display value becomes stable.

- Free sulfurous acid -

1) Add exactly 25 mL of sample to a 100 mL tall beaker.
2) Add 5 mL of 25 % sulfuric acid solution.
3) Add 1 g of sodium hydrogen bicarbonate (Note 4) and titrate with 0.01 mol/L iodine solution. (Note 5)

- Total sulfurous acid -

1) Add exactly 25 mL of sample to a 100 mL tall beaker.
2) Add 25 mL of 1 mol/L sodium hydroxide solution (Note 6).
3) Cover the beaker with food wrap film and fix it with a rubber band.
4) Stand for 10 minutes.
5) Add 10 mL of 25 % sulfuric acid solution.
6) Add 1 g of sodium hydrogen carbonate and titrate with 0.01 mol/L iodine solution.

6. Calculation

SO_2 (mg/L) = EP1 × TF × C1 × K1/S

EP1	Titration amount (mL)
TF	Factor of titrant = 1.1307
C1	Concentration conversion coefficient = 0.64 (mg/mL)
K1	Unit conversion factor = 1000
S	Sample size (mL)

7. Example

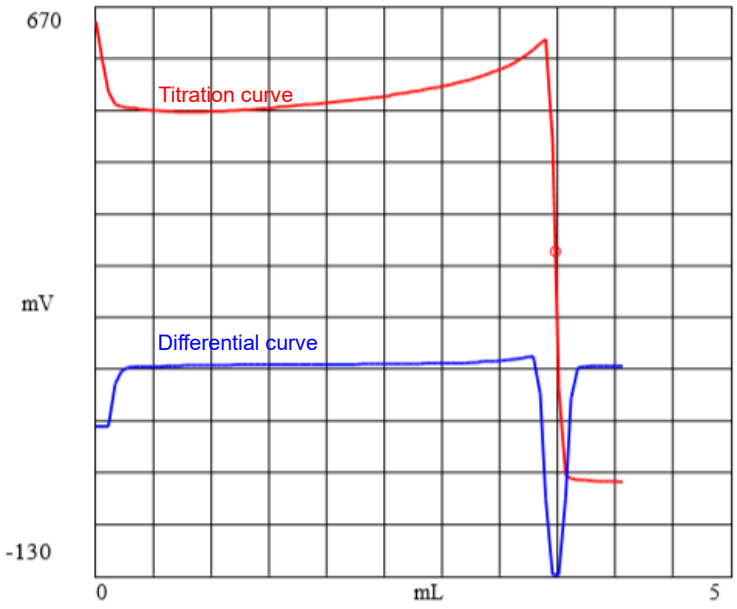
— Parameter —

<Titr. Mode>	Intermit
<Titr. Form>	EP Stop
<Titr. Para.>	
Max Volume	20.0 mL
Channel/Unit	Ch3, mV
Wait Time	0s
Dose Mode	off

<Ctrl. Para.>	
Number of EP	1
End Sense	Auto
Gain	2
Data Sampling	Set
Data sampling potential	999mV
Data sampling volume	0.05mL
Control Speed Mode	Set
Unit Volume	0.05mL
Cut-Off time	5s
Dispense Speed	1s/mL
Other Control	Standard
Stirrer Speed	4

（The above condition is an example. The setting condition depends on the model.）

— Example of titration curve —



— Measurement results —

Table 1 Measurement result of red wine

n	Free sulfurous acid			Total sulfurous acid		
	Sample (mL)	Titration (mL)	SO_2 (mg/L)	Sample (mL)	Titration (mL)	SO_2 (mg/L)
1	25	1.0977	31.77	25	3.9082	113.13
2	25	1.0695	30.96	25	3.9392	114.02
3	25	1.0495	30.38	25	3.9426	114.12
Average	-	-	31.04	-	-	113.76
SD	-	-	0.70	-	-	0.55
RSD (%)	-	-	2.26	-	-	0.48

Table 2 Measurement result of white wine

n	Free sulfurous acid			Total sulfurous acid		
	Sample (mL)	Titration (mL)	SO_2 (mg/L)	Sample (mL)	Titration (mL)	SO_2 (mg/L)
1	25	0.7138	20.66	25	3.6042	104.33
2	25	0.6981	20.21	25	3.6198	104.78
3	25	0.6950	20.12	25	3.6224	104.85
Average	-	-	20.33	-	-	104.65
SD	-	-	0.29	-	-	0.28
RSD (%)	-	-	1.43	-	-	0.27

8. Notes

Note 1) Sulfurous acid bonded with sugar, aldehyde, anthocyanin, etc. is called bond sulfurous acid. Unreacted sulfurous acid is called free sulfurous acid. The pH of wine is generally 3 to 4, and most of the free sulfurous acid exists as hydrogen sulfite ions (HSO_3^-). Sulfurous acid concentration is expressed as the mass (mg) of sulfur dioxide in 1L of the sample.

Note 2) The Ripper method is easy to operate and quick to measure. However, this method tends to show positive errors due to polyphenols. For this reason, it does not necessarily indicate the exact sulfurous acid concentration.

Note 3) The polarization voltage change between the twin platinum electrode during the titration is monitored. The voltage is high before the equivalence point, but it drops rapidly after the equivalence point due to excess iodine. This point is detected as the endpoint.

Note 4) Sodium hydrogen carbonate reacts with sulfuric acid to produce carbon dioxide.

$$H_2SO_4 + 2NaHCO_3 \longrightarrow Na_2SO_4 + 2H_2O + 2CO_2$$

The generation of carbon dioxide allows the system to be excluded from oxygen. As a result, it suppresses errors caused by air oxidation of sulfurous acid during titration.

Note 5) Under sulfuric acidic conditions, the equilibrium of the equation below shifts more to the left, and most of the sulfurous acid becomes sulfur dioxide (SO_2).

$$SO_2 + H_2O \rightleftharpoons H^+ + HSO_4^-$$

The titration reaction is shown below.

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

Note 6) The bound sulfurous acid reacts with sodium hydroxide solution and decomposes into free sulfurous acid.