Application Note

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

Industry	Food & beverage
Instrument	Automatic potentiometric titrator
Measurement method	Potentiometric titration/ Redox titration
Standards	GB/T 5009.49

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 an automatic potentiometric titrator (Note 2).

2. Post-measurement procedure

Seal the refill port for electrolyte of reference electrode by rubber septum so that electrolyte is prevented from leaking out or concentrating and store the electrode.

3. Apparatus

Main unit	Automatic potentiometric titrator (Preamplifier STD)
Electrode	Combined platinum electrode (Reference internal solution 1 mol/L Potassium chloride solution)

4. Reagents

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

5. Procedure

- 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 hydrogencarbonate (Note 3) and titrate with 0.01 mol/L iodine solution. (Note 4)

- 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 5).
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

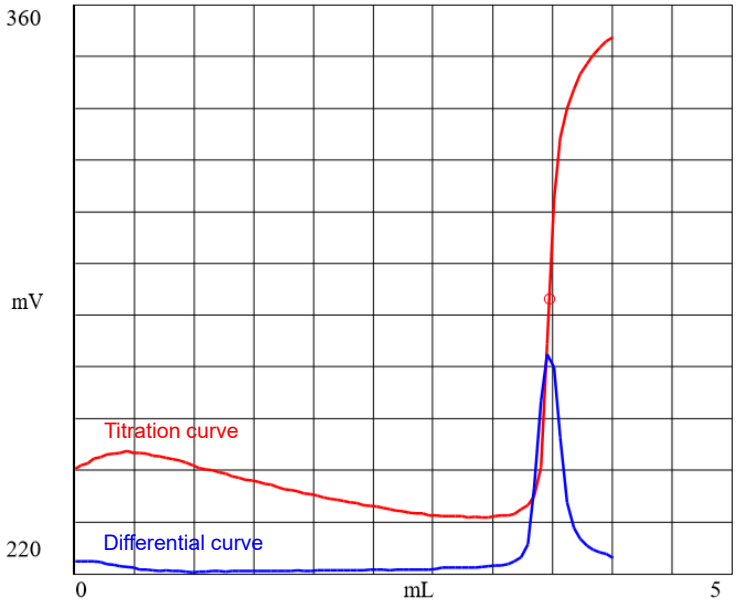
— Parameter —

<Titr. Mode>	Intermit
<Titr. Form>	EP Stop
<Titr. Para.>	
Max Volume	20.0 (mL)
Channel/Unit	Ch1, 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	1.0251	29.67	25	3.8987	112.85
2	25	1.0431	30.19	25	3.9533	114.43
3	25	1.0203	29.53	25	3.9359	113.93
Average	-	-	29.80	-	-	113.74
SD	-	-	0.35	-	-	0.81
RSD (%)	-	-	1.17	-	-	0.71

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	0.7299	21.13	25	3.6654	106.10
2	25	0.7506	21.73	25	3.6156	104.66
3	25	0.7286	21.09	25	3.6102	104.50
Average	-	-	21.32	-	-	105.09
SD	-	-	0.36	-	-	0.88
RSD (%)	-	-	1.69	-	-	0.84

8. Notes

Note 1) Sulfurous acid bonded with sugar, aldehyde, anthocyanin, etc., is called bound 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 1 L of the sample.

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

Note 3) Sodium hydrogencarbonate 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 excludes oxygen from the system and suppresses errors caused by air oxidation of sulfurous acid during titration.

Note 4) 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 5) The bound sulfurous acid reacts with the sodium hydroxide solution and decomposes into free sulfurous acid.