



Free Sulphur Dioxide in Wine

Modified Ripper Method

Introduction

Sulphur dioxide is present in wines as free SO₂ and also bound to acetaldehyde. The sum gives "total" sulphur dioxide. Bound SO₂ is released by addition of NaOH 1M to the wine sample.

This application is dedicated to free SO₂ measurement.

As a rule, determination of SO₂ in wines by the modified Ripper method uses a coloured indicator to determine the equivalence point, but it is also possible to use a pre-set end point titration with imposed current potentiometry.

With this end point method, many chemical functions present in the wine can modify the electrode behaviour and the reaction kinetics.

This application note gives a modified procedure suitable for many wines (white, red or rosé). We have tested various different wines but not all those available worldwide. This method has not been tested on special types of wine such as sparkling or sweet wines.

Principle

SO₂ is determined by titration with iodine solution according to the reaction:



Free SO₂ is measured directly in acidic media.

The titration is run according to a pre-set end point titration with imposed current potentiometry and a double platinum wire electrode.

Results are expressed as SO₂ in mg/l.

Electrode and reagents

pM231Pt2 Metal Electrode, double platinum wire (part no. E32M001) with adapter part no. A94P801 or M241Pt2-8 Metal Electrode without adapter (part no. E32M002)

Iodine solution **0.01 mol/l** (0.02 eq/l)

25% v/v H₂SO₄ solution in distilled water

Dilute 250 ml of concentrated sulphuric acid in 750 ml of distilled water. This operation is highly exothermic so perform the dilution very slowly and respect laboratory safety regulations. Let the solution cool down to room temperature. This solution is approximately 9N or 4.5M.

KI 5%

Dilute 50 g of potassium iodide in 1000 ml of distilled water.

NaHCO₃ solid form (see notes and remarks)

End Point titration settings

Burette volume:	10 ml
Stirring speed:	400 rpm
Working mode:	mV with i = 1 µA (DC)
Number of end points:	1
End point:	100 mV
Stirring delay:	10 seconds
Minimum speed:	0.2 ml/min
Maximum speed:	5.0 ml/min
Proportional band:	3500 mV
End point delay:	5 seconds
Sample unit:	ml
Sample amount:	50ml for free SO ₂
Titration:	Decreasing potential
Result:	mg/l

Procedure

Free SO₂

Pipette 5 ml of H₂SO₄ solution 25% v/v into a low diameter beaker, add 10 ml of KI solution 5% and 50 ml of wine, and titrate quickly with 0.01M Iodine solution. Addition of NaHCO₃ indicated in some local procedures can be avoided if titration occurs quickly.

Results

Expressed as mg/l of SO₂ (MW of 64 g/mol)

Using as titrant unit: mol/l (M) In this case, as 1 mole of titrant reacts with 1 mole of SO₂ (or HSO₃⁻) in the sample:

$$R = V(\text{titr}) * C(\text{titr}) * 64 * 1000 / V(\text{smp})$$

-V(titr) = Total volume of titrant to reach the end point (in ml)

-C(titr) = Concentration of titrant in mol/l

64 = Molecular weight of SO₂ in g/mol

-V(smp) = sample volume in ml

For a result in mg/l with the Titration Manager

Enter the actual sample amount in the SAMPLE screen

The titrant concentration in the TITRANT screen (in mol/l)

1 Titrant and 1 Sample in the COEFFICIENTS display 64 as molecular weight

The Titration Manager gives a result according to the above formula.

Using as titrant unit eq/l and 64 for molecular weight of SO₂

Note that in this case, 2 eq. titrants (12 corresponds to 2l) react with 1 sample.

For a result in mg/l

Enter the actual sample amount in the SAMPLE screen

The titrant concentration in the TITRANT screen (in eq/l)

2 Titrants and 1 Sample in the COEFFICIENTS display 64 as molecular weight

The Titration Manager gives a result according to the above formula.

Statistics

For 5 determinations with a white wine

Free SO₂

Mean:	35 mg/l SO ₂
Standard deviation:	0.7 mg/l SO ₂
Rel. standard deviation:	2%

Procedures for red and rose wines

With red wines, a secondary slow reactions between the iodine and tannin and other products can occur. Although addition of KI is not always necessary with white wines, it is compulsory for red and rosé wines. Addition of KI (potassium iodide) eliminates or reduces secondary slow reactions between iodine and reducing products present in red wine

Titrate immediately using the titration settings above

Results for free SO₂ in red or rosé wines

(4 tests on each kind of wine)

Grenache (red wine)

Mean:	23.1 mg/l
Stand dev.:	0.7 mg/l
Result (1):	21.7 mg/l

Merlot (red wine)

Mean:	15.2 mg/l
Stand dev.:	0.5 mg/l
Result (1):	16.0 mg/l

Syrah (red wine)

Mean:	16.9 mg/l
Stand dev.:	0.4 mg/l
Result (1):	15.6 mg/l

(Results verified free SO₂ determination measured by aspiration method)

(1) (Result for aspiration method)

Rosé wine

(3 determinations)

Mean:	20.3 mg/l
Stand dev.:	0.2 mg/l

Verification of the free SO₂ content by addition of Na₂SO₃ aqueous solution before titration

(The solution S1 contains 12.0 g/l of Na₂SO₃ or 6.2 mg/ml of SO₂)

50 ml Rosé wine	20.3 mg/l
50 ml Rosé wine + 0.2 ml of S1	42.0 mg/l
Theoretical 20 + 24 =	44 mg/l
50 ml of red wine 1	24.4 mg/l
50 ml of red wine 1 + 1 ml S1	126 mg/l
Theoretical 24.4 + 120 =	144 mg/l
50 ml of red wine 2	29.7 mg/l
50 ml of red wine 2 + 0.1 ml of S1	41 mg/l
Theoretical 29.7 + 12 =	42 mg/l
50 ml of red wine 2 + 0.2 ml of S1	51 mg/l
Theoretical 29.7 + 24 =	54 mg/l

Note that the recovery of added SO₂ is not 100% because the wine immediately binds part of this "SO₂".

Working range

For free SO₂ determination, using a 0.01 mol/l titrant and 50 ml for sample volume, 1 ml of titrant corresponds to 12.8 mg/l SO₂

Automation of the free SO₂ determination

Using a sample changer (SAC80 15 position), it is not recommended to add H₂SO₄ and KI for too long before the titration. The KI/H₂SO₄ mixture is not stable as in these conditions I⁻ is oxidised giving I₂.

Add the KI solution manually to the different beakers and use a peristaltic pump for H₂SO₄ addition.

Tests were run using a Watson- Marlow Alitea 400 (040.1501.D1E) peristaltic pump fitted with silicone tubing (ext. diameter 7 mm int. diameter 4 mm). With this tubing and a speed setting of 6, it takes 12 seconds to deliver 10 ml (typical value).

Fit the silicone tubing in the head of the pump.

Dip one end of the tubing in the H₂SO₄ solution bottle and fit the other with a glass delivery tip for example.

Set the pump (potentiometer in 6 position and in CW or clockwise)

Connect the pump to the mains and let it run until the air bubbles in the tubing are eliminated

Disconnect the pump.

Connect the pump to the 5 VTTL output

Black plug of the Titration Manager to pin 8 of the external command plug.

Red plug of the Titration Manager to pin 4 of the external command plug.

Set the pump

Potentiometer in position 6 and in CW (clockwise) position

Connect the pump to the mains

The pump does not start as it is controlled by the titration manager.

Titration Manager Settings

Use the above settings

Just add method parameters

Auxiliary output:	5 V
Aux. On for:	12 seconds

Note that use of twin head peristaltic pump allows simultaneous automatic addition of the two solutions at (H₂SO₄ 25% and KI 5%) the beginning of the titration.

Notes

This method, named Ripper's method, is less accurate than the aspiration method because part of the iodine can be consumed by reducing substances other than SO₂.

Using the aspiration method, SO₂ is removed from the sample by a stream of air through the acidified sample and oxidised in H₂SO₄.

Then H₂SO₄ is titrated by NaOH.

In some cases, the modified Ripper method can give higher results than expected with wines containing a significant amount of ascorbic acid because this acid (and some others) reacts quantitatively with iodine.

Adding NaHCO₃ forms a CO₂ blanket over the sample, which prevents oxygen interference during the titration. Addition should be avoided if the titration is run quickly in a covered beaker.

As it is easy to lose SO₂ during the preparation of the sample, make sure you titrate the sample immediately after preparation.

Imposed current values of 1 µA and 5 µA (DC) were tested without change in the results.

Titration concentrations corresponding to 0.01M and 0.05M were also tested without change in the titration speed reaction and in the results.

Bibliography

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AUSTRALIA