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Ripper Titration for Determining Sulfur Dioxide Content in Wine

Chemical Concepts and Techniques:

This method is based on the redox reaction where sulfur dioxide, in the form of the bisulphite ion, reacts with iodine as follows:

$$HSO_3^- + I_3^- + H_2O \rightarrow SO_4^{=} + 3H^+ + 3I^-$$

Unreacted iodine forms a blue complex with starch indicator to signify the endpoint.
The addition of sodium bicarbonate prior to commencing the titration creates an inert blanket of carbon dioxide gas to prevent interference caused by oxygen in air.

Red wines may require decolourising with activated carbon prior to performing the titration in order for the endpoint colour change to be observed. Colour pigments in red wines may also interfere with the result, so this method is best suited to pale coloured or white wines only.

When determining total sulfur dioxide, the sample is pretreated with sodium hydroxide solution to adjust the pH. This causes chemically bound forms of sulfur dioxide to be released in solution as free sulphur dioxide.

It is essential to titrate to an endpoint where the blue colour persists for 30 seconds to ensure that all forms of sulfur dioxide in solution have reacted.

Equipment Required:

10ml or 25mL burette
50mL pipette
20mL pipette
250mL conical flask or beaker
desk lamp with halogen globe or other bright light source (optional)

Reagent Preparation:

It is strongly advised that solutions be prepared by laboratory technicians due to the corrosive nature of the acids and alkalis involved.

0.01M iodine solution: (Accurate) Prepare from commercially available ampoules as per the instructions provided. Standardise before use (method attached). Store in brown glass in the dark. Solution is stable for 3 months.
1M sodium hydroxide*:* (accuracy not necessary) Carefully and slowly add 40g of solid sodium hydroxide, with stirring, to a large beaker of around 800mL cold distilled water. Allow to cool and dilute to 1 litre with distilled water.. **Caution:** considerable heat is evolved from this dissolution.
25% v/v sulfuric acid*:* (accuracy not necessary) Measure 250mL of concentrated sulfuric acid in a graduated cylinder. Carefully and slowly, with constant stirring, add the acid to 750mL of cold distilled water. **Caution:** it may be necessary to stand the mixture in an ice bath during the addition and mixing operation, as considerable heat is involved with this dilution. Allow to cool completely and dilute to 1 litre with distilled water.
Vitex – Commercially available starch indicator

Method:

To determine free SO_2:

1. Pipette 50.0mL of wine into a 250mL conical flask
2. Add about 300mg Vitex (starch) to the flask
3. Add 5mL of 25% H_2SO_4. Mix.
4. Rinse and fill the burette with 0.01M iodine solution.
5. Add about 1g (approx. quarter teaspoon) of solid sodium bicarbonate to the flask and **commence the titration immediately.**
6. Titrate rapidly until the solution turns a blue colour which persists for 30 seconds.
7. Calculate the free SO_2 concentration in mg/L using the following equation:

$n(SO_2) = n(I_2)$
$m(SO_2 \text{ in grams})/M(SO_2) = C(I_2) \times V(I_2 \text{ in litres})$
$m(SO_2 \text{ in grams}) = C(I_2) \times V(I_2 \text{ in litres}) \times M(SO_2)$
$m(SO_2 \text{ in mg}) = C(I_2) \times V(I_2 \text{ in litres}) \times M(SO_2) \times 1000$
$m(SO_2 \text{ in mg})/V(\text{wine sample in L}) = (C(I_2) \times V(I_2 \text{ in L}) \times M(SO_2) \times 1000)/ V(\text{wine sample in L})$
$SO_2 \text{ (mg/L)} = (C(I_2) \times V(I_2 \text{ in mL}) \times M(SO_2) \times 1000)/ V(\text{wine sample in mL})$
$SO_2 \text{ (mg/L)} = (C(I_2) \times V(I_2 \text{ in mL}) \times 64 \times 1000)/ V(\text{wine sample in mL})$
NOTE: on the right hand side of the above equation the conversion from L to mL cancels out top and bottom. The final equation is:

$$\mathbf{SO_2 \text{ (mg/L)} = \frac{(\text{mL iodine}) * (\text{M iodine}) * (64) * (1000)}{\text{mL wine sample}}}$$

To determine total SO_2:

1. Pipette 20.0mL of wine into a 250mL conical flask.
2. Add 25mL of 1M sodium hydroxide solution.
3. Stopper the flask, mix well and allow to stand for 10 minutes.
4. Add about 300mg Vitex (starch) to the flask.
5. Add 10mL of 25% H_2SO_4. Mix.
6. Rinse and fill the burette with 0.01M iodine solution.
7. Add about 1g solid sodium bicarbonate to the flask and **commence the titration immediately.**
8. Titrate rapidly until the solution turns a blue colour which persists for 30 seconds.
9. Calculate the total SO_2 concentration in mg/L using the equation above.

Points to Consider:

- The addition of the sodium carbonate causes a reaction that releases carbon dioxide gas. The carbon dioxide acts as an inert blanket that prevents interference due to oxygen. The titration must be completed quickly before the carbon dioxide disperses to the atmosphere. It is advisable to do a few practice titrations first.
- At low pH (for example, once the acid addition step has occurred) a portion of the free sulphite is present in the volatile (SO_2 gas) form. To prevent erroneous results from the loss of SO_2 from volatilisation, it is essential that the titration is carried out as rapidly as possible.
- The colour change may be easier to detect if a strong light source is used to illuminate the solution.
- For best accuracy use a 10mL burette.
- The analysis for total SO_2 involves the addition of 1M NaOH to hydrolyse bisulphite addition compounds (bound SO_2). The completeness of this reaction is pH dependent. It has been determined that above pH 12 almost total dissociation of bound sulphites occurs. This is a timed reaction, allowing less or more time to elapse than instructed will introduce error.
- Ascorbic acid and other substances that react with iodine (including phenols, sugars and aldehydes) interfere with the determination. The result should therefore be treated as a good estimate of the amount of sulphites present. For a more accurate result the aspiration (Rankine) method should be used.

Appendix:

Method for standardising 0.01M iodine solution against standard sodium thiosulphate solution:

1. *Pipette 50mL of 0.01M sodium thiosulphate solution into a conical flask.*
2. *Add a few mg of Vitex indicator.*
3. *Titrate with iodine solution to a deep blue endpoint which persists for 30 seconds.*
4. *Reaction should be carried out under pH 5, a small addition of acid may be required prior to titration.*
5. *Molarity of iodine* = 0.25/(titre in mL)

References:

Iland, Ewart, Sitters, Markides & Bruer, Techinques for Chemical Analysis and Quality Monitoring during Winemaking, 2000
Zoeckein, Fugelsang, Gump & Nury, Production Wine Analysis,1990