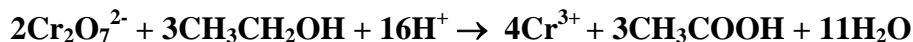


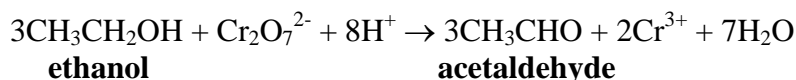
Estimation of Alcohol Content in Wine by Dichromate Oxidation followed by Redox Titration

Chemical Concepts and Techniques:

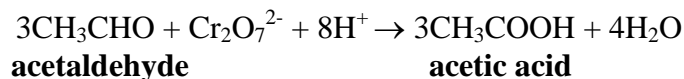
Potassium dichromate oxidises primary alcohols to the corresponding carboxylic acid. The intermediate product is the aldehyde. The reaction is critically dependent upon hydrogen ion concentration for the complete oxidation to occur, rather than to a mixture of aldehyde and acid. So in the case of ethanol the redox reaction is



taking place in two stepwise reactions:

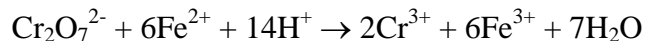


followed by



The reaction conditions most favourable to reaction completion are 60-65° C for a minimum of 30 minutes. Reduction of chromium from the [VI] oxidation state to the [III] oxidation state as a result of the oxidation reaction can be observed as the colour change from orange to green.

In addition to the strongly acidic conditions required, dichromate must be present in significant excess also, to allow sufficient residual dichromate for a back titration to be performed. The back titration that is usually recommended is with ferrous ammonium sulphate (FAS) with 1,10-Phenanthroline ferrous sulphate indicator:



For true accuracy, **this determination should be carried out on a sample of distillate following distillation of the wine**, as other components in wine could be expected to react to some extent with dichromate under the given conditions, particularly residual sugar. However an estimation of the alcohol content can be made on an 'as is' sample of dry wine without prior distillation.

Equipment Required:

1L and 50mL volumetric flasks (for reagent preparation)

50mL burette

100mL volumetric flask

25mL, 20mL and 5mL volumetric pipettes

50mL Schott™ reagent bottles or similar, with screw caps

Constant temperature water bath (can improvise with hot plate and saucepan)

250mL conical flasks for titrating

Halogen lamp for observing endpoint colour change (optional)

Reagent Preparation:

It is strongly advised that reagent solutions be prepared by laboratory technicians due to the hazardous nature of the acids and oxidising reagents used.

Standard Potassium Dichromate solution (acidified): Dissolve 33.768 (accurately weighed) potassium dichromate, $K_2Cr_2O_7$, in around 500mL of distilled water. Slowly and carefully, with stirring, add 325mL of concentrated sulphuric acid (*caution – solution will become very hot*). Addition of acid can be carried out while standing the solution vessel in an ice bath if desired. Allow the solution to cool to room temperature. Transfer volumetrically to a 1.0 L volumetric flask and make to volume with distilled water. Store in amber glass.

Caution: Potassium Dichromate is a strong oxidising agent. Chromium (VI) compounds are toxic and are known carcinogens. Avoid skin contact, ingestion or inhalation of solid particles.

Ferrous Ammonium Sulphate (acidified): Dissolve 135g of ferrous ammonium sulphate, $FeSO_4(NH_4)_2SO_4 \cdot 6H_2O$, in approximately 750mL of distilled water. Carefully and slowly add 25mL of concentrated sulphuric acid. Allow to cool and quantitatively transfer to a 1.0 litre volumetric flask. Dilute to volume with distilled water.

1,10-Phenanthroline Ferrous Sulphate indicator solution: Dissolve 0.348g ferrous sulphate ($FeSO_4 \cdot 7H_2O$) in approximately 25mL of distilled water. Add 0.743g of *o*-phenanthroline. Transfer solution quantitatively to a 50mL volumetric flask and dilute to volume with distilled water. Store in an eye-dropper bottle.

Method:

To perform the oxidation reaction:

1. Pipette 20.0mL of wine into a 100mL volumetric flask and dilute to volume with distilled water.
2. Pipette 5.0mL of the diluted wine into a 50mL Schott™ reagent bottle.
3. Stand the Schott™ bottle in a large plastic beaker of ice and water.

- Using a volumetric pipette, **very slowly** add 25.0mL of the potassium dichromate solution dropwise into the Schott™ bottle. The reaction will commence immediately, with generation of heat. **It is important that mixture remains cold during the addition of the dichromate and subsequent reaction, to prevent the loss of acetaldehyde vapour.**
- Screw the cap on the Schott™ bottle firmly.
- Place in a water bath at 60-65°C. Leave sample to react for at least 30 minutes.
- Perform a blank sample of 5.0mL of distilled water and 25.0mL dichromate solution. Place in water bath as for sample.
- Remove wine and blank samples and allow to cool.

To perform the back titration:

- Quantitatively transfer the contents of the Schott™ bottle to a 250mL conical flask (using distilled water rinses).
- Rinse and fill the burette with ferrous ammonium sulphate solution.
- Perform the blank titration using the prepared blank sample. Titrate with ferrous ammonium sulphate until the solution turns to an emerald green.
- Add 5 drops of indicator solution.
- Continue the titration until the colour changes from blue-green to brown. The endpoint is sharp and distinct. A halogen lamp shone through the sample may assist in end-point detection.
- Record the blank titre V_B
- Perform the sample titration as for the blank titration.
- Record the sample titre V_A .

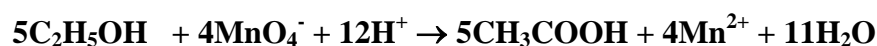
Calculate the alcohol content using the following formula:

$$\text{Ethanol (\% vol/vol)} = 25 - 25[V_A/V_B]$$

Points to Consider:

- The time and temperature of the incubation period are critical, both must be sufficient for the full oxidation of alcohol to acetic acid. The initial oxidation to acetaldehyde is the slowest reaction and is the rate determining step. Better results may be obtained by leaving the sample to incubate for longer.
- There is a significant risk of error if acetaldehyde vapour, generated by the heat of reaction during the dichromate addition, is allowed to escape prior to reacting further to produce acetic acid. The result of such an error would be a lower apparent alcohol content, as less of the dichromate is consumed.
- The reaction vessels must be tightly sealed during the incubation to prevent further escape of acetaldehyde by volatisation. It is best to maintain the temperature of the water bath at not more than 65° - this ensures completion of the oxidation to acetic acid, as well as minimising the oxidation of interfering (non-alcohol) substances.
- If using a saucepan of water and adjustable hotplate as a waterbath, experiment to determine the optimum hotplate setting to produce 60-65°C. Note that a kitchen hotplate will need to be on a very low setting. A laboratory hotplate is generally better for this purpose. Cover the saucepan with foil to prevent loss of water to evaporation.

- Glassware must be scrupulously clean, preferably soaked in dilute sulphuric acid and rinsed with distilled water prior to use.
- Dichromate has a significant expansion coefficient – when preparing, ensure solution is made to volume at 20°C. In addition all volumetric work should be carried out at a room temperature of 20°C.
- Note that it is not necessary to standardise the Ferrous Ammonium Sulphate solution for use in a back titration, as long as a blank titration is performed. The blank titration should be performed directly before the sample titration.
- Potassium dichromate is a primary standard, providing that the solution is prepared with accurately weighed salt, no standardisation is necessary.
- In order to familiarise themselves with the colour changes during the titration, it is advisable for students to prepare 2 blanks, and use one of them as a practice titration.
- For a very accurate analysis of alcohol content, the wine can be pre-distilled. See the method for alcohol by distillation.
- An alternative indicator for this titration is *sodium diphenylamine sulphonate and phosphoric acid*, however the endpoint is not as distinct and may require practice to detect accurately.
- Alternative procedures for the back titration are possible, including reduction of the excess dichromate by potassium iodide to stoichiometrically produce iodine, which is then titrated against standard thiosulphate with starch indicator. However the endpoint can be harder to detect using this method due to the green background of Cr³⁺ ions.
- The oxidation reaction could also be achieved by using **potassium permanganate** solution instead of potassium dichromate. In this case the reaction is



However there are several reasons why permanganate is less suitable than dichromate for this reaction:

1. Permanganate is a considerably **stronger oxidising agent** than dichromate, and therefore will be less specific for alcohol. Many compounds present naturally in wine such as tannins, phenolics, sulphites, sugars and some organic acids such as sorbic and succinic acids may be oxidised by permanganate under the conditions described. Therefore the associated error in determining alcohol will be larger when using permanganate, where a non-distilled wine sample is used.
2. The loss of acetaldehyde as vapour upon addition of the permanganate may be more difficult to avoid due to the stronger oxidising properties of permanganate and consequent faster reaction rate.
3. Permanganate titrations are generally considered to be self-indicating as the colour change is from purple to clear. However the colour of red wines is intensified under acidic conditions and may interfere with determining an accurate endpoint where the colour change is from purple-pink to clear (the solution will never turn completely clear because of the wine colour, so the endpoint becomes the point where the pink colour ceases to pale any further). As many white wines have a tendency to 'pink' when heated under strongly acidic conditions, white wine may cause similar problems.

4. Potassium permanganate is not a primary standard and requires careful preparation, standardisation and storage.
- However, some teachers may still prefer to use permanganate due to the hazardous properties of dichromate. Unfortunately no method was able to be sourced for substituting permanganate – some simple trials should help to fine tune reagent concentrations and quantities etc.

References: Zoecklein, Fugelsang, Gump & Nury, *Production Wine Analysis*, Van Nostrand Reinhold, 1990