

Chemistry Internal Assessment

VERIFYING THE CONTENT OF ALCOHOL IN WINE

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1 Introduction

The idea for this investigation came from my personal need to establish the alcohol content of home-brewed beer. Home-brewers often utilise a hydrometer to compare the specific gravity before and after fermentation is complete (Flowers, 2014-07-15), but I forgot to do the former, which meant I had to establish the alcohol percentage based on the finished product alone. This need led me to my research question: **How can we determine the alcohol content of wine?**

Both wine and beer are produced through a similar process, and although I would speculate that the percentage of other compounds that may be oxidised (such as sulphites, tannins and sugar) is different, by distilling the wine we are able to separate alcohol and water from the other compounds – allowing us to deal with a possibly large source of error and any large differences in other compounds that may exist in the different alcoholic beverages.

The procedure is an extension of an experiment done in the classroom, which consisted of oxidising propanols in order to determine whether it was a primary or secondary alcohol. It became clear a similar experiment could be done with the alcohol in wine, ethanol – The distinction being that ethanol can only be a primary alcohol (Brown and Ford, 2014, pp.491-493). In short, the experiment consists of the alcohol's oxidation to aldehyde, which in turn is oxidised to a carboxylic acid, and finally back-titrated – thus determining the amount of alcohol that was oxidised.

Before describing the experiment in detail, a few considerations are really important regarding the motivation and safety of this experiment: Home distillation is illegal in many countries, thus the experiment will be conducted with both distilled and undistilled wine, as it may provide insight into what errors can be expected when replicating as a home-brewer. Furthermore, we will be dealing with strong oxidants and acids, so proper handling and safety equipment (gloves and glasses) is of the utmost importance. Although this may be easily replicable in one's home-brewery space, I cannot emphasise enough how much easier

and safer it is to utilise the standard, a hydrometer.

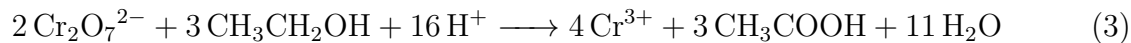
2 Background knowledge

The focus of the procedure is to measure the amount of oxidising agent (potassium dichromate) left in the solution after all of the ethanol has been converted to ethanoic acid. We are able to quantify this through a back-titration utilising ferrous ammonium sulphate as titrant. As will be seen below, both reactions require a large amount of available H^+ , hence both solutions are acidified with concentrated sulphuric acid (Walding, n.d.).

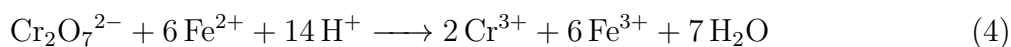
The two half-steps of the oxidation are as follows:



which result in the following complete equation:



And the back-titration is as follows:



Finally, throughout the calculations we will be using the standard letters to represent concepts followed by a subscript, such as concentration: c ; amount: n ; molar mass: M ; volume: V ; mass: m ; and so $m(\text{H}_2\text{O})$ would represent the mass of H_2O .

According to equation (2)

3 Procedure

3.1 Acidified Potassium Dichromate

In order to reduce the relative uncertainty, 1 litre of the solution was prepared, though a far smaller amount of it was used.

1. In a 1000.00 ml \pm 0.40 mL volumetric flask, 33.790 g \pm 0.001 g of Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) were added onto approximately 500ml of distilled water.
2. 325 ml of concentrated sulphuric acid were slowly added onto the volumetric flask. The solution very quickly became too hot to touch. Absolute precision is not necessary at this step, as the sulphuric acid only serves to provide H^+ to the reaction, which will be in excess.
3. The solution was allowed to cool down to room temperature, and the volumetric flask filled to its 1000 ml mark.

Thus we may calculate the concentration of the solution based on the molar mass of 294.18 g/mol:

$$c(\text{K}_2\text{CR}_2\text{O}_7) = \frac{n}{V} = \frac{m}{VM} = \frac{(33.790 \pm 0.001)\text{g}}{(294.18 \pm 0.01)\text{g/mol} \cdot (1000.00 \pm 0.40)\text{ml}} \quad (5)$$
$$\therefore c(\text{K}_2\text{CR}_2\text{O}_7) = (1.1486 \pm 0.0005) \cdot 10^{-4} \text{mol ml}^{-1}$$

The above calculation of the uncertainty in concentration (Δc) is done as follows:

$$\Delta c(\text{K}_2\text{CR}_2\text{O}_7) = c \cdot \left(\frac{0.001}{33.790} + \frac{0.01}{294.18} + \frac{0.40}{1000.00} \right)$$
$$\therefore \Delta c(\text{K}_2\text{CR}_2\text{O}_7) = 0.0005$$

3.2 Acidified Ferrous Ammonium Sulphate

The ferrous ammonium sulphate hexahydrate, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6 \text{H}_2\text{O}$ (FAS), for the back-titration was prepared as follows:

1. In a $250.00 \text{ ml} \pm 0.23 \text{ ml}$ volumetric flask, $36.450 \text{ g} \pm 0.001 \text{ g}$ of FAS was added to about 190 ml of distilled water.
2. 6.3 ml of concentrated sulphuric acid, H_2SO_4 , were added into the flask. (Same considerations regarding precision as the other solution)
3. The volumetric flask is filled with water to its 250 ml mark.

Thus we may calculate the concentration based on the molar mass of 392.13g/mol:

$$\begin{aligned} c(\text{FAS}) &= \frac{(36.450 \pm 0.001)\text{g}}{(392.13 \pm 0.01)\text{g/mol} \cdot (250.00 \pm 0.23)\text{ml}} \\ \therefore c(\text{FAS}) &= (3.7181 \pm 0.0036) \cdot 10^{-4} \text{mol ml}^{-1} \end{aligned} \tag{6}$$

3.3 Preparation of Samples

For the distilled sample, $20.0 \pm 0.3 \text{ ml}$ were added to approximately 60 ml of water and distilled until about 40 ml of the ethanol + water solution were accumulated. The solution was moved to a 100.0 ml volumetric flask and filled with distilled water.

For the undistilled sample: In a 100.0 ml volumetric flask, 20.0 ml of wine were added, and then filled with distilled water.

In both cases, the same bottle of wine is used with 12% ABV(alcohol by volume).

3.4 Experiment

- In a 250 ml flask in an ice bath, $40.0 \text{ ml} \pm 0.1 \text{ ml}$ of the sample was pipetted, and then slowly $150.0 \text{ ml} \pm 0.1 \text{ ml}$ of the dichromate solution were added. The ice bath is meant

to prevent ethanal from escaping as a gas, however almost immediately there was a sweet smell in the air, indicating there had been some ethanal escaping. This was done for both samples.

- A cork was put on the flasks and both were placed in a water bath at 60 °C for 30 minutes, then allowed to cool.
- A burette was filled with FAS and 5.00 ml \pm 0.05 ml of the sample were prepared for titration with 5 drops of 1,10-Phenanthroline Ferrous Sulphate indicator.

I suspect the largest source of error in the experiment will come from the aldehyde not fully oxidizing, which would be noticeable in two different stages: 1) When the dichromate was poured onto the alcohol. As mentioned previously, the ice bath is used so that the ethanal remains in liquid state; and 2) after the thermostatic water bath, as the solution will be at 60 °C, any ethanal left will immediately escape when the cork is removed from the beaker.

4 Data

The following table describes our independent variable, the volume of FAS used in the titration:

	Distilled ml ± 0.1 ml	Undistilled ml ± 0.1 ml
	9.4	6.1
	9.0	7.3
	10.1	6.9
	10.2	6.2
	9.0	6.1
Average	9.5 ± 0.6	6.5 ± 0.6

Table 1: Volume of titrant used for distilled and undistilled wine.

5 Analysis

5.1 Calculations

By working from the back-titration backwards we are able to determine the initial conditions:

Titration Using V_S to represent the volume of Ferrous Ammonium Sulphate (FAS), and our previously determined values for the concentration of the prepared solutions, we can find the amount of titrant used, $n(\text{FAS})$:

$$\begin{aligned} n &= c \cdot V \\ \therefore n(\text{FAS}) &= (3.7181 \cdot V_S \pm 0.0040) \cdot 10^{-4} \text{ mol} \end{aligned} \tag{7}$$

The back-titration, as per (4), is a reaction between the ions $\text{Cr}_2\text{O}_7^{2-}$ and Fe^{2+} with ratio 1:6, respectively, so after the alcohol was oxidised there must have been $\frac{1}{6} \cdot n(\text{FAS})$ mol dichromate available for titration (n_f):

$$\begin{aligned} n_f(\text{Cr}_2\text{O}_7^{2-}) &= \frac{1}{6}n(\text{FAS}) \\ \therefore n_f(\text{Cr}_2\text{O}_7^{2-}) &= (0.61968V_S \pm 0.0006) \cdot 10^{-4} \text{ mol} \end{aligned} \tag{8}$$

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Analyte before titration A solution of 200ml of $\text{Cr}_2\text{O}_7^{2-}$ ($c = (1.1486 \pm 0.0006) \cdot 10^{-4} \text{ mol ml}^{-1}$, as found before) was mixed with 40ml of the wine + water solution. Then 10.0 ± 0.1 ml from it was used as analyte, thus the amount (n_0) of dichromate before the titration is:

$$\begin{aligned} n_0(\text{Cr}_2\text{O}_7^{2-}) &= \frac{(0.200 \pm 0.001) \text{ l} \cdot (0.11846 \pm 0.0006) \text{ mol l}^{-1}}{(240 \pm 1) \text{ ml}} \cdot (10.0 + 0.1) \text{ ml} \\ \therefore n_0(\text{Cr}_2\text{O}_7^{2-}) &= (9.8717 \pm 0.3) \cdot 10^{-4} \text{ mol} \end{aligned} \tag{9}$$

So the amount of dichromate used as oxidising agent to the alcohol is given by:

$$\begin{aligned} n(\text{Cr}_2\text{O}_7^{2-}) &= n_0(\text{Cr}_2\text{O}_7^{2-}) - n_f(\text{Cr}_2\text{O}_7^{2-}) \\ \therefore n(\text{Cr}_2\text{O}_7^{2-}) &= (9.8717 - 0.61967 \cdot V_S) \cdot 10^{-4} \text{ mol} \pm 0.3 \cdot 10^{-4} \text{ mol} \end{aligned} \quad (10)$$

Alcohol before oxidation As per equation (3), the ratio of $\text{Cr}_2\text{O}_7^{2-} : \text{C}_2\text{H}_5\text{OH}$ is 2:3, therefore:

$$\begin{aligned} n(\text{C}_2\text{H}_5\text{OH}) &= \frac{3}{2} \cdot (9.8717 - 0.61967 \cdot V_S) \cdot 10^{-4} \text{ mol} \pm 0.3 \cdot 10^{-4} \text{ mol} \\ \therefore n(\text{C}_2\text{H}_5\text{OH}) &= (14.808 - 0.92951 \cdot V_S) \cdot 10^{-4} \text{ mol} \pm 0.5 \cdot 10^{-4} \text{ mol} \end{aligned} \quad (11)$$

Now we find the volume of ethanol in the analyte based on the density ($\rho(\text{C}_2\text{H}_5\text{OH})$) of 0.789 g/ml (disregarding the uncertainty on molar mass and density):

$$\begin{aligned} V &= \frac{M}{\rho} n \\ V(\text{C}_2\text{H}_5\text{OH}) &= \frac{46.068 \text{ g/mol}}{0.789 \text{ g/ml}} (14.808 - 0.92951 \cdot V_S) \cdot 10^{-4} \text{ mol} \\ \therefore V(\text{C}_2\text{H}_5\text{OH}) &= (8.6461 - 0.54272 \cdot V_S) \cdot 10^{-2} \text{ ml} \pm 0.1 \cdot 10^{-2} \text{ ml} \end{aligned} \quad (12)$$

We must find the volume of wine ($V(\text{wine})$) in the dichromate-alcohol solution so we can find the Ethanol/Wine percentage. We originally had 20.0 ml of wine, which was dilluted by a factor of 5, forming 100.0 ml ± 0.1 of water+wine. Out of which, 40.0ml ± 0.3 ml went in to form the 240.0 ml solution with the dichromate. Finally, the analyte consisted of 10 ml of the dichromate-alcohol solution:

$$\begin{aligned} V(\text{wine}) &= \frac{20 \text{ ml}}{100 \text{ ml}} \cdot \frac{40 \text{ ml}}{240 \text{ ml}} \cdot 10 \text{ ml} \\ \therefore V(\text{wine}) &= 0.333 \text{ 33 ml} \pm 0.003 \text{ ml} \end{aligned} \quad (13)$$

So the percentage of ethanol in wine can be given by the following formula based on the

volume of the titrant (V_S) in ml:

$$\begin{aligned}\frac{V(\text{C}_2\text{H}_5\text{OH})}{V(\text{wine})} &= \frac{0.086\,461\text{ ml}}{0.333\,33\text{ ml}} - \frac{0.0054272 \cdot V_S\text{ ml}}{0.333\,33\text{ ml}} \\ \therefore \frac{V(\text{C}_2\text{H}_5\text{OH})}{V(\text{wine})} &= (0.25939 - 0.016282 \cdot V_S) \pm 0.004\end{aligned}\tag{14}$$

or more appropriately, considering our degree of confidence:

$$\frac{V(\text{C}_2\text{H}_5\text{OH})}{V(\text{wine})} = (0.260 - 0.0160 \cdot V_S) \pm 0.004\tag{15}$$

Finally, by replacing V_S for our average values from Table 1 we can find the percentage of alcohol in both our distilled and undistilled samples:

- Undistilled: $(15.6 \pm 2.0)\%$
- Distilled: $(10.8 \pm 1.0)\%$

6 Conclusion and reflection

This paper aimed to estimate the alcohol content of two samples of a bottle of wine with 12% ABV: one distilled and another undistilled. The values found were $(10.8 \pm 1.0)\%$ and $(15.6 \pm 2.0)\%$ respectively – reasonably close to what I expected, considering the qualitative uncertainties in the process.

We speculated that a couple of situations in which ethanal could leak and consequently increase our uncertainty, and this would be noticed by a sweet, fruity smell. The smell was noticed both when dichromate was added to the alcohol and upon leaving the water bath. Furthermore, assessing the colour of the solution during titration presented a larger challenge than expected. This random uncertainty is reflected on our raw data, through the variance in the titrants, and is responsible for about half of our approximately 10% uncertainty. This was in part tackled during the experiment by changing to a beaker with smaller diameter and by diluting the titrate, however neither of them were good enough. A possible improvement would be to combine the methods used with a halogen lamp (Walding, n.d.).

The purpose of performing this experiment with undistilled wine was to find out how much impurity we could expect when utilising the same method as a homebrewer. Obviously we can't affirm that all homemade wine or beer will have about 5% of other oxidisable compounds, but this is a really good starting point as to what to expect. Reflecting after the experiment, the same results could have more reliably been achieved by oxidising what was left-over from the distillation, as we would be dealing with far less volatile compounds than ethanal.

References

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