

A Redox Titration to Determine the Ethanol Content of Wine (8A/RTE)

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Reported percentage of alcohol by volume (% ABV): 13 %

1 Titration Results and Calculation of % ABV of Wine

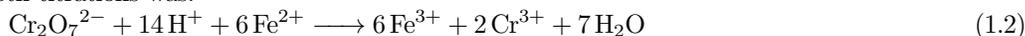
A mass of 7.7910 g of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 60 cm^3 of H_2SO_4 and made up to 200.00 cm^3 with deionised water in a volumetric flask. Each $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ molecule liberates one Fe^{2+} ion in solution, thus their concentrations in the solution are equal. The molar mass of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ is $392.139\text{ g mol}^{-1}$.¹

$$\text{Moles of Fe}^{2+} \text{ in } 200.00\text{ cm}^3 \text{ standard solution} = \frac{7.7910\text{ g}}{392.139\text{ g mol}^{-1}} = 0.019868\text{ mol}$$

Hence:

$$\text{Concentration of Fe}^{2+} \text{ in standard solution} = \frac{0.019868\text{ mol}}{200.00\text{ cm}^3 \times \left(\frac{1\text{ dm}}{10\text{ cm}}\right)^3} = \frac{0.019869\text{ mol}}{200.00 \times 10^{-3}\text{ dm}^3} = 0.099340\text{ mol dm}^{-3} \quad (1.1)$$

The reaction which occurred in both titrations was:



With sodium diphenylamine-4-sulphonate used as the indicator (colour change from green (due to Cr^{3+}) to purple at the end point).

Table 1: Results of titration between $\text{K}_2\text{Cr}_2\text{O}_7$ and standard solution of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$

Run	Start Volume / cm^3	End Volume / cm^3	Titre / cm^3
1	2.40	18.30	15.90
2	2.20	18.80	16.60
3	2.25	18.85	16.60

$$\text{Average titre} = \frac{16.60\text{ cm}^3 + 16.60\text{ cm}^3}{2} = 16.60\text{ cm}^3$$

$$\text{Using 1.1, moles of Fe}^{2+} \text{ in } 20.00\text{ cm}^3 \text{ aliquot} = 0.099340\text{ mol dm}^{-3} \times 20.00\text{ cm}^3 \times \frac{1\text{ dm}^3}{1000\text{ cm}^3} = 1.987 \times 10^{-3}\text{ mol}$$

From chemical equation 1.2 there is a 6:1 molar ratio between the Fe^{2+} and $\text{Cr}_2\text{O}_7^{2-}$.

$$\text{Concentration of Cr}_2\text{O}_7^{2-} = \frac{\frac{1}{6} \times 1.987 \times 10^{-3}\text{ mol}}{16.60\text{ cm}^3 \times \frac{1\text{ dm}^3}{1000\text{ cm}^3}} = \frac{3.311 \times 10^{-4}\text{ mol}}{16.60 \times 10^{-3}\text{ dm}^3} = 0.01995\text{ mol dm}^{-3} \quad (1.3)$$

During the reflux the ethanol from the sample of wine was oxidised by the $\text{Cr}_2\text{O}_7^{2-}$ ions to acetic acid as shown in this equation:



During this the solution changed colour from orange (due to the $\text{Cr}_2\text{O}_7^{2-}$) to dark green (due to the liberation of Cr^{3+}). A back titration was then performed with the standard solution of Fe^{2+} ions. The volumes used for this were half of those stated in the method since when the stated volumes were used the titre was very large and a maximum of two more titrations would have been possible before the reaction mixture was exhausted. This would have been problematic if these titres were not concordant since the completion of additional titrations would have been impossible.

Table 2: Results of titration between $\text{K}_2\text{Cr}_2\text{O}_7$ in product mixture and standard solution of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$

Run	Start Volume / cm^3	End Volume / cm^3	Titre / cm^3
1	2.20	18.40	16.20
2	18.90	35.25	16.35
3	3.10	19.50	16.40

$$\text{Average titre} = \frac{16.35\text{ cm}^3 + 16.40\text{ cm}^3}{2} = 16.38\text{ cm}^3$$

$$\text{Using 1.1, moles of Fe}^{2+} \text{ in } 5.00\text{ cm}^3 \text{ aliquot} = 0.099340\text{ mol dm}^{-3} \times 5.00\text{ cm}^3 \times \frac{1\text{ dm}^3}{1000\text{ cm}^3} = 4.97 \times 10^{-4}\text{ mol}$$

¹W. M. Haynes, ed. *CRC Handbook of Chemistry and Physics*. 97th ed. Boca Raton: CRC Press, 2016, Physical Constants of Inorganic Compounds, 4-46.

From chemical equation 1.2 there is a 6:1 molar ratio between Fe^{2+} and $\text{Cr}_2\text{O}_7^{2-}$.

$$\text{Concentration of } \text{Cr}_2\text{O}_7^{2-} \text{ in product mixture} = \frac{\frac{1}{6} \times 4.97 \times 10^{-4} \text{ mol}}{16.38 \text{ cm}^3} = 5.05 \times 10^{-6} \text{ mol cm}^{-3}$$

$$\therefore \text{Moles of } \text{Cr}_2\text{O}_7^{2-} \text{ in } 126 \text{ cm}^3 \text{ product mixture} = 5.05 \times 10^{-6} \text{ mol cm}^{-3} \times 126 \text{ cm}^3 = 6.37 \times 10^{-4} \text{ mol}$$

Initially 100.00 cm^3 of $\text{Cr}_2\text{O}_7^{2-}$ of concentration $0.01995 \text{ mol dm}^{-3}$ (from 1.3) was in the reactant mixture.

$$\text{Initial moles of } \text{Cr}_2\text{O}_7^{2-} = 100.00 \text{ cm}^3 \times \frac{1 \text{ dm}^3}{1000 \text{ cm}^3} \times 0.01995 \text{ mol dm}^{-3} = 1.995 \times 10^{-3} \text{ mol}$$

$$\therefore \text{Moles of } \text{Cr}_2\text{O}_7^{2-} \text{ which reacted} = 1.995 \times 10^{-3} \text{ mol} - 6.37 \times 10^{-4} \text{ mol} = 1.36 \times 10^{-3} \text{ mol}$$

From chemical equation 1.4 molar ratio between $\text{Cr}_2\text{O}_7^{2-}$ and ethanol is 2:3. The molar mass of ethanol is $46.068 \text{ g mol}^{-1}$.²

$$\text{Moles of ethanol in } 1.00 \text{ cm}^3 \text{ sample} = \frac{1.36 \times 10^{-3} \text{ mol}}{2} \times 3 = 2.04 \times 10^{-3} \text{ mol}$$

$$\therefore \text{Mass of ethanol in } 1.00 \text{ cm}^3 = 2.04 \times 10^{-3} \text{ mol} \times 46.068 \text{ g mol}^{-1} = 0.0938 \text{ g}$$

The density of ethanol is 0.7893 g cm^{-3} .²

$$\% \text{ ABV of wine} = \frac{0.0938 \text{ g}}{0.7893 \text{ g cm}^{-3}} \times \frac{100 \%}{1.00 \text{ cm}^3} = 11.9 \%$$

2 Error Propagation

$$\delta[\text{Fe}^{2+}] = \pm 0.099340 \text{ mol dm}^{-3} \sqrt{\left(\frac{\pm 0.00005 \text{ g} \times 2}{7.7910 \text{ g}}\right)^2 + \left(\frac{\pm 0.001 \text{ g mol}^{-1}}{392.139 \text{ g mol}^{-1}}\right)^2 + \left(\frac{\pm 0.15 \text{ cm}^3}{200.00 \text{ cm}^3}\right)^2} = \pm 0.00007 \text{ mol dm}^{-3}$$

$$\delta[\text{Cr}_2\text{O}_7^{2-}] = \pm 0.01995 \text{ mol dm}^{-3} \sqrt{\left(\frac{\pm 0.00007 \text{ mol dm}^{-3}}{0.099340 \text{ mol dm}^{-3}}\right)^2 + \left(\frac{\pm 0.06 \text{ cm}^3}{20.00 \text{ cm}^3}\right)^2 + \left(\frac{\pm 0.1 \text{ cm}^3 \times 2}{16.60 \text{ cm}^3}\right)^2} = \pm 0.0002 \text{ mol dm}^{-3}$$

$$\delta V_{\text{reaction mixture}} = \pm \sqrt{(\pm 0.015 \text{ cm}^3)^2 + (\pm 0.15 \text{ cm}^3)^2 + (\pm 0.06 \text{ cm}^3)^2} = \pm 0.2 \text{ cm}^3$$

$$\delta n_{\text{initial } \text{Cr}_2\text{O}_7^{2-}} = \pm 1.995 \times 10^{-3} \text{ mol} \sqrt{\left(\frac{\pm 0.15 \text{ cm}^3}{100.00 \text{ cm}^3}\right)^2 + \left(\frac{\pm 0.0002 \text{ mol dm}^{-3}}{0.01995 \text{ mol dm}^{-3}}\right)^2} = \pm 0.02 \times 10^{-3} \text{ mol}$$

$$\delta n_{\text{final } \text{Cr}_2\text{O}_7^{2-}} = \pm 6.37 \times 10^{-4} \text{ mol} \sqrt{\left(\frac{\pm 0.00007 \text{ mol dm}^{-3}}{0.099340 \text{ mol dm}^{-3}}\right)^2 + \left(\frac{\pm 0.03 \text{ cm}^3}{5.00 \text{ cm}^3}\right)^2 + \left(\frac{\pm 0.1 \text{ cm}^3 \times 2}{16.38 \text{ cm}^3}\right)^2 + \left(\frac{\pm 0.2 \text{ cm}^3}{126 \text{ cm}^3}\right)^2}$$

$$= \pm 0.09 \times 10^{-4} \text{ mol}$$

$$\delta n_{\text{ethanol}} = \sqrt{(\pm 0.02 \times 10^{-3} \text{ mol})^2 + (\pm 0.09 \times 10^{-4} \text{ mol})^2} = \pm 0.03 \times 10^{-3} \text{ mol}$$

$$\delta \% \text{ ABV} = \pm 11.9 \% \sqrt{\left(\frac{\pm 0.03 \times 10^{-3} \text{ mol}}{2.04 \times 10^{-3} \text{ mol}}\right)^2 + \left(\frac{\pm 0.0001 \text{ g cm}^{-3}}{0.7893 \text{ g cm}^{-3}}\right)^2 + \left(\frac{\pm 0.001 \text{ g mol}^{-1}}{46.068 \text{ g mol}^{-1}}\right)^2} = \pm 0.2 \%$$

Hence the % ABV of ethanol of the wine was found to be $11.9 \pm 0.2\%$.

3 Analysis of Results

The reported % ABV value of the wine is greater than that determined by experiment, however the reported % ABV value of wine is only required to be accurate within $\pm 1\%$ ³, hence there is a slight overlap between the possible error in the reported value and that of the determined value from 12.0–12.1%. Despite this systematic errors are likely to have influenced the % ABV determined since this is at the extreme end of the uncertainty in the reported value, hence it is unlikely that the true % ABV value lies within this range.

A possible error is that the ethanol might not have been fully oxidised to acetic acid hence reducing the amount of $\text{Cr}_2\text{O}_7^{2-}$ which reacted and thus the % ABV value determined. To minimise this error the reaction mixture could be refluxed for longer (e.g. 2 hours). There may have also been a loss of ethanol and ethanal vapour while the reactants were being transferred into the round bottomed flask. To minimise this the flask could have been cooled in an ice bath until the condenser was added, hence reducing losses due to evaporation. There was also uncertainty about the end point for the second titration since the indicator colour change was not very distinct. To minimise this an alternative indicator such as 1,10-phenanthroline ferrous sulphate solution could be used which would have more distinct colour change from blue-green to brown at the end point.⁴

²Haynes, see n. 1, Physical Constants of Organic Compounds, 3-246.

³Official Journal of the European Union. Regulation (EU) No 1169/2011 of the European Parliament and of the Council of 25 October 2011. 22nd Nov. 2011. URL: <http://eur-lex.europa.eu/legal-content/EN/TXT/HTML/?uri=CELEX:30211R1169> (visited on 08/12/2017), Annex XII.

⁴Sirromet Wines Pty Ltd. Estimation of Alcohol Content in Wine by Dichromate Oxidation followed by Redox Titration. URL: <http://seniorchem.com/4.%20Alcohol-Content-bu-Dichromate-Oxidation-and-Redox-Titration.pdf> (visited on 09/12/2017), pp. 3.