

Determination of Alcohol Content of Wine by Distillation followed by Density Determination by Hydrometry

Chemical Concepts and Techniques:

Distillation is a method for **separating two or more liquid compounds on the basis of boiling-point differences**. As each component boils at a different temperature, it is theoretically possible to remove and discretely recondense the vapour of each component from a boiling solution of the mixture.

Distillation is a very important process in industrial chemistry, but can also be used analytically.

The physical chemistry of distillation is complicated by the fact that mixtures of compounds may behave rather differently from what might be expected from the physical properties of each individual compound – consider the following:

The **boiling point** of a liquid is the temperature at which the **vapor pressure of the liquid equals the pressure surrounding the liquid**. The normal boiling point of a liquid occurs when the vapor pressure of the liquid equals the ambient atmospheric pressure.

It is a common assumption that in a **liquid mixture** at a given pressure, each component boils at the boiling point corresponding to the given pressure and the vapors of each component will collect separately and purely. This, however, does not occur even in an idealized system. Idealized models of distillation are essentially governed by Raoult's Law and Dalton's Law.

Dalton's Law assumes that the total pressure exerted by a gaseous mixture is equal to the sum of the partial pressures of each individual component in a gas mixture.

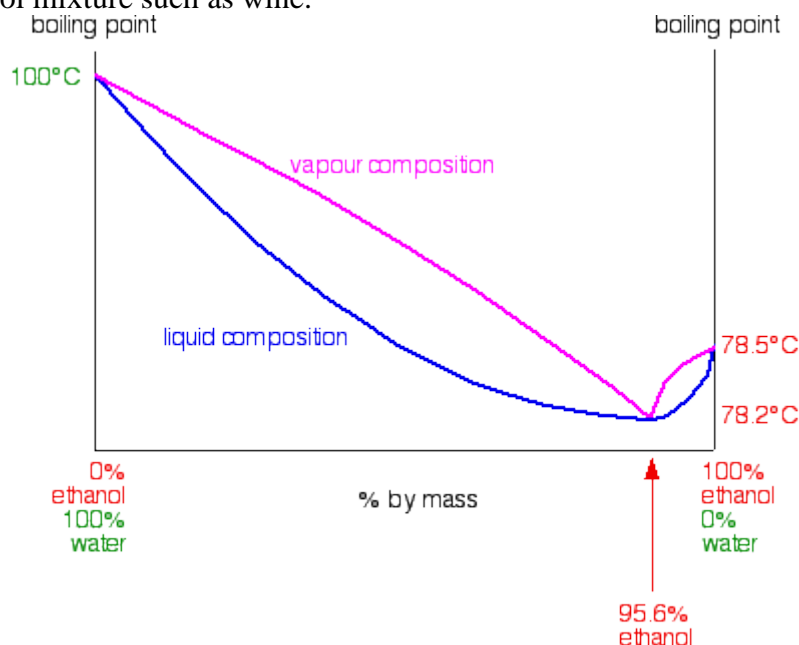
Raoult's Law assumes that a component contributes to the total vapor pressure of the mixture in proportion to its percentage of the mixture and its vapor pressure when pure. If one component changes another component's vapor pressure, or if the volatility of a component is dependent on its percentage in the mixture, Raoult's Law does not apply.

Interactions between the components of the mixture create boiling properties unique to the mixture. Such interactions can result in a constant-boiling **azeotrope** which behaves as if it were a **pure compound** (i.e., boils at a single temperature instead of a range). At an azeotrope, the mixture contains the given component in the same

proportion as the vapor, so that **evaporation does not change the purity, and distillation does not effect separation.**

In this case, ethanol and water form an azeotrope at 95.6% ethanol which boils at 78.1 °C. Note that the azeotrope has a **boiling temperature that is lower than the boiling temperature of each separate liquid.**

The following diagram shows a detailed view of the vapour phase behaviour of a water:alcohol mixture such as wine.



The boiling point of pure water at one atmosphere is 100°C. The boiling point of ethanol at one atmosphere is 78.5°C. The boiling point of the ethanol : water azeotrope is 78.2°C.

The implications for separation by distillation are obvious. As the azeotrope boils at a lower temperature than either pure ethanol or pure water, **it is impossible to distil pure ethanol.** The best that can be achieved by simple distillation is 95.6% ethanol.

However, in terms of an analytical distillation, it is possible to fully remove all the ethanol from the wine mixture. The distillate in this case is a mixture of water and ethanol, containing all the ethanol that was in the aliquot of wine tested, plus water. The initial distillate would consist of 96.5% ethanol, with the proportion of water gradually increasing as distillation continued.

The final volume of the distillate should be the same as the initial portion of wine to ensure that the alcoholic content of the distillate is the same as it would have been in the wine.

The alcoholic content of the wine can then be determined by accurately measuring the density of the distillate. Using reference tables of water:ethanol mixture densities, the percentage alcohol can be calculated. Alcoholic content in wine is generally expressed as % v/v, or percentage volume per volume.

Equipment Required:

Quickfit™ **Distillation apparatus** as shown in the diagram below:

Round or Flat bottomed flask, 1L capacity (flat bottomed flask allows the use of a hot plate, Bunsen burner or heating mantle only for round-bottomed flask)

Distillation Splash Head

'Inland Revenue' Condenser (other condenser types are not adequate for distillation)

Receiver Adaptor (Quickfit™)

Retort stands and clamps appropriate to set up equipment as shown

250mL volumetric flask

Tubing to connect condenser to cold or iced water for condensing liquid

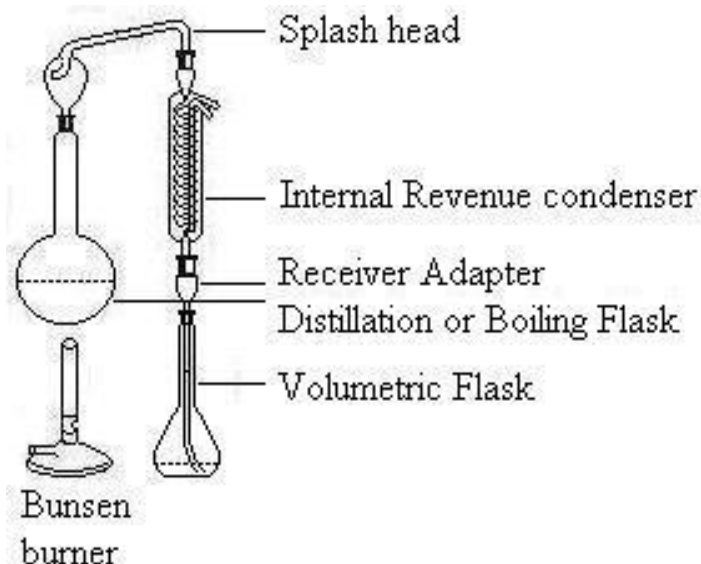
Pasteur pipettes

Alcohol Hydrometer (range 10-20 % vol/vol)

250mL hydrometer flask or suitable measuring cylinder

Heat source – Bunsen burner, hot plate or heating mantle

Controlled temperature bath at 20°C (or set air-conditioning to 20°C)



Reagent Requirements:

Ice (to make ice bath for receiving flask)

Distilled or deionised water

Boiling granules

2M Sodium Hydroxide: Use commercially available reagent, or prepare by adding 80g NaOH to 500mL water (caution – heat evolved). Mix well and dilute to 1L with distilled water. Accuracy not important.

Method:

Distilling wine sample:

1. Rinse volumetric flask with the wine being tested.
2. Carefully fill the volumetric flask with the wine to slightly over the mark.

3. Place in controlled temperature bath at 20°C (if available) or allow to equilibrate to 20°C.
4. Using a Pasteur pipette, remove the appropriate amount of wine so that the flask volume is exactly 250mL.
5. Pour wine into the distillation flask. Rinse volumetric flask several times with distilled water and add rinsing water to the distillation flask. The final volume of the wine plus rinses should be at least 400mL to prevent the distillation flask from boiling dry.
6. If the wine has a volatile acidity of >1g/L and/or a level of SO₂ of >200mg/L, neutralise the contents of the distillation flask to pH 8.2 with 2M NaOH.
7. Add boiling chips to the flask and connect to the distillation assembly. Check that all ground glass joints are secure.
8. Ensure that cold or iced water is flowing through the condenser. Place the 250mL volumetric flask in a large plastic beaker or bowl containing ice and place under the distillation apparatus as per the diagram. The adaptor tubing should reach well into the flask.
9. Apply heat to the distillation flask to commence boiling.
10. Once distillation commences, observe that efficient condensation of vapour is being achieved.
11. Collect 200-220mL of distillate before removing the volumetric flask. The best way to estimate this is to remove the volumetric flask when the level of distillate is just below the base of the flask neck.
12. Stopper the flask and place in a controlled temperature bath at 20°C (if available) or allow to equilibrate to 20°C.
13. Dilute to volume with distilled water. Mix well.

Determining alcohol content on distillate by hydrometry:

1. Rinse a hydrometer cylinder or suitable measuring cylinder with a small portion of the distillate. Discard the rinse liquid.
2. Transfer the remaining distillate to the cylinder.
3. Rinse the alcohol hydrometer with a small portion of the distillate.
4. Gently lower the hydrometer into the distillate, while gently 'spinning' the hydrometer stem. Ensure the hydrometer is floating freely in the distillate.
5. Record the density of the wine (or the alcohol content if hydrometer gives direct alcohol reading) at the point corresponding to the base of the meniscus.
6. Record the temperature of the distillate – ideally hydrometer readings should be taken at 20°C, however a temperature adjustment calculation can be made if necessary.

Points to Consider:

- This method is still the internationally accepted standard for alcohol determination. Sugar, which interferes in so many other methods for determining alcoholic strength, is not distillable and has no effect on the composition of the distillate.
- There are a few minor interferences however, high levels of either volatile acidity or sulphur dioxide may volatilise and potentially affect the density of the distillate.
- Levels of VA >1.0g/L as acetic acid, or SO₂ levels >200mg/L can cause significant interference.

- Generally the effect of high VA or SO₂ is to increase the density of the distillate, therefore producing lower apparent alcohols.
- **Neutralisation of the wine** prior to distillation (use NaOH solution) will negate the interfering effects of volatile acidity and sulphur dioxide.
- Alcohol hydrometers in the range suitable for wine distillate testing have a very large bulb. This is to allow the density scale corresponding to alcohol content to be sensitive enough for an accurate result with sufficient significant figures to be obtained (generally 0.1% vol/vol graduations).
- Alcohol hydrometers are very fragile and must be handled with care.
- The cylinder used in the density measurement must be wide enough for the hydrometer to float freely without touching the sides.
- For lower alcohol wines it may be required to distil 500mL and use a larger cylinder, in order to obtain the depth of solution required for the hydrometer to float.
- The use of smaller SG hydrometers and attempting to convert to % alcohol by calculation is not recommended as the S.G scale is not fine enough to convert to an accurate, precise result. (The entire range of wine alcohols may be covered in an S.G. range of only 0.005, for example)
- As with all methods involving densitometry, temperature is critical. Only a very small range of density values correspond to the range of alcohol content in wine, therefore in this case **it is critical to work at the correct temperatures to avoid volumetric error**. When measuring the initial volume of the wine to be distilled, and when diluting the distillate to volume prior to measuring density, it is imperative that the **working temperature is 20°C**, as this is the temperature that the volumetric glassware is calibrated at. Even slight variations in temperature can alter the volume enough to cause a significant density measurement error.
- Hydrometers may vary as to which temperature they are calibrated at. In every case, if measuring density at a temperature that differs from that at which the hydrometer was calibrated will require a temperature correction calculation.

References:

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