SIRROMET

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Estimation of Alcohol Content of Wine by Ebulliometry

Chemical Concepts and Techniques:

Ebulliometry is based on the principle that the boiling point of wine is depressed in comparison to the boiling point of water as a consequence of, and relative to, the wine's alcohol content. The method is very accurate for simple mixtures of ethanol and water, and reasonably accurate for dry wine styles. Residual sugar content of greater than 5g/L is a significant interference. Other wine components such as acids, tannins and flavour compounds do affect the result slightly but can generally be ignored.

The analysis is based on **Raoult's Law** relationship of boiling point depression:

$$p = h * x_1$$

where p = vapour pressure of solution
h = proportionality constant
x_1 = mole fraction of solvent

The vapour pressure of ethanol in water will vary proportionally to its concentration.

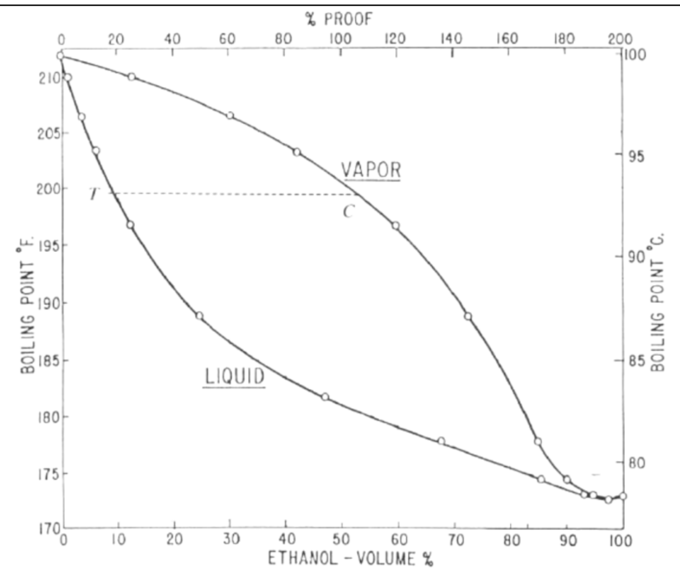
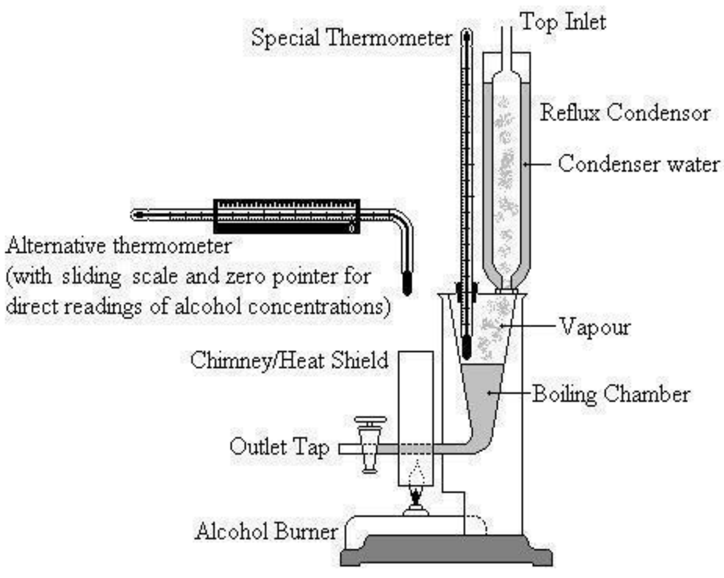


Fig. 2-7. Boiling point vs. composition for ethanol–water mixtures.

The above diagram illustrates the boiling point versus composition relationship for the water-ethanol system.
The lower curve represents the boiling point of various alcohol-water mixtures at constant pressure. The upper curve represents the composition of the vapour phase that exists in equilibrium with the boiling liquid phase.
Note the vapour phase contains proportionally more ethanol than the liquid phase due to the lower boiling point and vapour pressure of ethanol in comparison to water. Any loss of vapour from the system therefore takes with it a proportionately large amount of ethanol.
As the two systems are in equilibrium, this loss of vapour will affect the boiling point of the liquid phase, as ethanol is then removed from the liquid phase to reinstate the equilibrium. The boiling point of the liquid phase will increase.
From this, it can be seen that it is **critical that the system operates under total reflux to prevent loss of ethanol vapour**, for accurate determination of alcohol content to be made.
Ebulliometry, although a simple technique, is prone to some **interferences**, the most significant being the presence of **residual sugar** in the wine.
The presence of sugars might be expected to elevate the boiling point of wine, however in fact the opposite is observed. Sweet wines usually boil at a lower temperature than the equivalent dry wine, resulting in higher apparent alcohols. This behaviour is due to the effect of a sugar-water matrix 'squeezing out' the ethanol – increasing its vapour pressure. A calculation can be made to correct for the sugar content of sweet wines, however it is an approximation only and is not suitable for labelling analysis.

Equipment Required:

The diagram below shows a commercial **ebulliometer.**



The instrument is usually made of stainless steel and comes in kit form. It may be possible to construct a homemade version of an ebulliometer – the following are crucial requirements:
As discussed above, the boiling of the wine must be under **total reflux** conditions – an efficient condenser arrangement is essential.
A **thermometer** capable of accurate measurement (0.1 degree marked divisions) between 87°C and 101°C is required. Thermometers of this accuracy are extremely delicate and highly prone to cracking or breaking if subjected to thermal shock – sudden large changes in temperature.
Note: Commercial ebulliometer thermometers contain mercury and pose a considerable health hazard if broken due to the vaporisation of mercury.
A **spirit lamp or alcohol burner** is required for the heat source, these are readily available and inexpensive.

A special measuring cylinder for the wine and water aliquots is included with ebulliometer kits. However a **50mL measuring cylinder** can be used just as well to measure the volumes specified in the method.
A **scale or table of alcohol values** is required to calculate the alcohol content. A table is included in the method.
A **Baume hydrometer** is required if using the formula to correct for residual sugar levels in sweet wines.

Reagent Requirements:

Distilled or deionised water: For best results use distilled water. Do not use tap water.
Methylated spirit or ethanol: for spirit lamp
1% Sodium Hydroxide solution: for cleaning the boiling chamber periodically.

Method:

To measure the boiling point of water:

1. Rinse the boiling chamber carefully with distilled water.
2. Add approximately 20mL of distilled water to the boiling chamber.
3. Insert the thermometer.
4. Light the spirit lamp and place under the instrument in the position shown.
5. As the water boils, observe the thermometer. When the mercury level stabilises (>30 seconds) record the temperature reading, to the nearest 0.02°C if possible. This temperature is $\mathbf{T_1}$.
6. Allow the instrument to cool before removing the thermometer and draining.

To measure the boiling point of wine:

1. Rinse the boiling chamber with the wine.
2. Measure 50mL of wine and pour into the boiling chamber.
3. Insert the thermometer.
4. Fill the condenser chamber with **cold** water. (Colder the better, tap water ok).
5. Light the spirit lamp and place under the instrument in the position shown.
7. As the wine boils, observe the thermometer. When the mercury level stabilises (15-30 seconds) record the temperature reading, to the nearest 0.02°C if possible. Be sure to take the first stable (15-30 sec) reading. This temperature is $\mathbf{T_2}$.
8. Allow the instrument to cool before removing the thermometer and draining.

To calculate the alcohol content:

1. Calculate the value $\mathbf{\Delta T = T_1 - T_2}$
2. Determine the alcohol content from the table displayed on the final page, where ΔT is 'Ebull. Deg'.

Correction for sweet wines:

1. Calculate the Apparent Alcohol by following the above procedures.
2. Using the Baume hydrometer (0-10 scale), determine the Baume reading of the sweet wine **at 20°C**. The Baume must be >0.5° for the conversion to be applicable.
3. Calculate the True Alcohol by applying the following correction:

True Alcohol (% v/v) = Apparent Alcohol (% v/v) x [1-(°Baume x 0.015)]

Points to Consider:

- The boiling point of distilled water will vary considerably with atmospheric pressure. It is recommended that this measurement be repeated at regular intervals, particularly during periods of unstable weather.
- The **system must be under efficient reflux** during the boiling of the wine. This is best achieved by using ice-cold water in the condenser. The water in the condenser must be replaced with fresh, cold water for each successive analysis. At no time should the temperature of the water in the condenser exceed 35°C. As the condenser water warms, ethanol vapour is lost from the system, resulting in erroneously high boiling points and lower apparent alcohols.
- Samples must be of high clarity and free of suspended solids. Suspended solids tend to raise boiling points, resulting in erroneous results. Allow suspended solids to settle out of wine, or filter wine, prior to analysis.
- While a correction has been given for sweet wines, it should be noted that it can be difficult to obtain a stable boiling point for sweet wines due to the influence of the sugar. It is possible to dilute the wine to less than 2% residual sugar, however note that ebulliometry is generally less accurate on lower alcohol samples, and any error caused by sugar will generally be amplified when multiplying up to correct for dilution factor.
- Over time, debris will coat the inside walls of the boiling chamber. It is recommended that the chamber be cleaned regularly with a boiling solution of 1% NaOH. Rinse very well with distilled water following cleaning.

References:

Zoeckein, Fugelsang, Gump & Nury, *Production Wine Analysis*, Van Nostrand Reinhold, 1990
Iland, Ewart, Sitters, Markides & Bruer, *Techniques for chemical analysis and quality monitoring during winemaking*, Patrick Iland Wine Promotions, 2000
http://www.monashscientific.com.au/AlcoholKeyWordPhrase.htm

Ebulliometer degree (wine) table by Churchward, (ACI J. & Proc. Jan. 1940)

Ebull Deg.	%v/v Alcohol	Ebull Deg.	%v/v Alcohol	Ebull Deg.	%v/v Alcohol	Ebull Deg.	%v/v Alcohol	Ebull Deg.	%v/v Alcohol
6.15	7.4	8.50	11.4	10.85	16.5	11.82	19.1	12.76	22.0
6.20	7.5	8.55	11.5	10.90	16.6	11.84	19.2	12.78	22.0
6.25	7.6	8.60	11.6	10.92	16.7	11.86	19.2	12.80	22.1
6.30	7.6	8.65	11.7	10.94	16.7	11.88	19.3	12.82	22.2
6.35	7.7	8.70	11.8	10.96	16.8	11.90	19.4	12.84	22.2
6.40	7.8	8.75	11.9	10.98	16.8	11.92	19.4	12.86	22.3
6.45	7.9	8.80	12.0	11.00	16.9	11.94	19.5	12.88	22.4
6.50	7.9	8.85	12.1	11.02	16.9	11.96	19.5	12.90	22.4
6.55	8.0	8.90	12.2	11.04	17.0	11.98	19.6	12.92	22.5
6.60	8.1	8.95	12.3	11.06	17.1	12.00	19.6	12.94	22.5
6.65	8.2	9.00	12.4	11.08	17.1	12.02	19.7	12.96	22.6
6.70	8.3	9.05	12.5	11.10	17.2	12.04	19.8	12.98	22.7
6.75	8.3	9.10	12.6	11.12	17.2	12.06	19.8	13.00	22.8
6.80	8.4	9.15	12.7	11.14	17.3	12.08	19.9	13.02	22.8
6.85	8.5	9.20	12.8	11.16	17.3	12.10	19.9	13.04	22.9
6.90	8.6	9.25	12.9	11.18	17.3	12.12	20.0	13.06	22.9
6.95	8.7	9.30	13.0	11.20	17.4	12.14	20.1	13.08	23.0
7.00	8.8	9.35	13.1	11.22	17.4	12.16	20.1	13.10	23.1
7.05	8.8	9.40	13.2	11.24	17.5	12.18	20.2	13.12	23.2
7.10	8.9	9.45	13.3	11.26	17.6	12.20	20.2	13.14	23.2
7.15	9.0	9.50	13.4	11.28	17.6	12.22	20.3	13.16	23.3
7.20	9.1	9.55	13.5	11.30	17.7	12.24	20.3	13.18	23.3
7.25	9.2	9.60	13.6	11.32	17.7	12.26	20.4	13.20	23.4
7.30	9.3	9.65	13.8	11.34	17.7	12.28	20.5	13.22	23.5
7.35	9.3	9.70	13.9	11.36	17.8	12.30	20.5	13.24	23.6
7.40	9.4	9.75	13.9	11.38	17.9	12.32	20.6	13.26	23.6
7.45	9.5	9.80	14.0	11.40	17.9	12.34	20.6	13.28	23.7
7.50	9.6	9.85	14.2	11.42	18.0	12.36	20.7	13.30	23.8
7.55	9.7	9.90	14.3	11.44	18.0	12.38	20.8	13.32	23.8
7.60	9.8	9.95	14.4	11.46	18.1	12.40	20.8	13.34	23.9
7.65	9.8	10.00	14.5	11.48	18.1	12.42	20.9	13.36	23.9
7.70	10.0	10.05	14.6	11.50	18.2	12.44	20.9	13.38	24.1
7.75	10.0	10.10	14.7	11.52	18.3	12.46	21.0	13.40	24.2
7.80	10.1	10.15	14.8	11.54	18.3	12.48	21.1	13.44	24.2
7.85	10.2	10.20	14.9	11.56	18.4	12.50	21.2	13.46	24.3
7.90	10.2	10.25	15.1	11.58	18.4	12.52	21.2	13.48	24.4
7.95	10.4	10.30	15.2	11.60	18.5	12.54	21.3	13.50	24.5
8.00	10.5	10.35	15.3	11.62	18.5	12.56	21.3	13.52	24.5
8.05	10.6	10.40	15.4	11.64	18.6	12.58	21.3	13.54	24.6
8.10	10.7	10.45	15.5	11.66	18.7	12.60	21.4	13.56	24.7
8.15	10.8	10.50	15.6	11.68	18.8	12.62	21.5	13.58	24.7
8.20	10.9	10.55	15.8	11.70	18.8	12.64	21.6	13.60	24.8
8.25	10.9	10.60	15.9	11.72	18.8	12.66	21.7	13.62	24.9
8.30	11.0	10.65	16.0	11.74	18.9	12.68	21.7	13.64	25.0
8.35	11.1	10.70	16.1	11.76	19.0	12.70	21.8	13.66	25.0
8.40	11.2	10.75	16.3	11.78	19.0	12.72	21.8	13.68	25.1
8.45	11.3	10.80	16.4	11.80	19.1	12.74	21.9		