Benchmarking of ABV Analysis Instruments and Methods in Wine Applications

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Abstract: Alcohol By Volume, or ABV, measured as a percentage of volume of ethanol to wine, is an important parameter in wine analysis. The purpose of this study was to qualitatively assess any correlation among three common methods used for measuring ABV in wine: ebulliometry, chemical oxidation, and distillation. Based on single-test measurements (N=1), results show that the three methods differ by 0.24% to 0.37% ABV. Given that there were no test samples with known and exact ABV values that could be used as references, and given the possible ranges of theoretical ABV values of wine samples, no conclusion can be drawn as to which method measured ABV most accurately. More exhaustive testing with multiple tests performed for each sample and method would allow performing an analysis of experimental errors and accuracy of each method.

Key words: ABV, alcohol by volume, ebulliometry, hydrometry, distillation, titrimetric, dichromate

Introduction. Alcohol By Volume (ABV), measured as a percentage of volume of ethanol to wine, is an important parameter in wine analysis because: 1) alcohol has the most impact on wine body, i.e., generally, the higher the alcohol content, the more body; 2) higher alcohol content improves microbial stability, which requires less sulfite to adequately protect wine; and 3) alcohol content can affect how commercial wines are taxed if ABV exceeds prescribed limits; these can vary by winemaking region or jurisdiction.

In winemaking, the potential ABV, or PA, is estimated by measuring the amount of fermentable sugars in a juice sample using a hydrometer before the start of alcoholic fermentation. Hydrometer readings of sugar content are commonly reported in Brix degrees or Specific Gravity (SG) in North America.

Given the many dissolved substances, such as tannins, anthocyanins (color pigment molecules in red varieties), acids, and minerals, the hydrometer is really a measurement and estimation of total soluble solids (TSS), but which provides a good approximation of the amount of fermentable sugars.

The challenge in estimating PA is further complicated by fermentation biochemistry as different yeast strains convert sugars differently, which is further influenced by wine chemistry, e.g., nitrogen availability, pH, and temperature. This challenge is evidenced by the myriad of calculations used to convert Brix or SG readings into PA. Triple-scale (Brix, SG and PA) hydrometers use any one of these calculations on their scales.

Given the importance of ABV, winemakers and particularly commercial winery operators cannot rely on hydrometer readings to establish an actual ABV, hence a requirement to measure ABV using more accurate techniques.

There are three common methods used in small laboratories or by small-scale winemakers (commercial or amateur) for measuring ABV in wine: ebulliometry, chemical oxidation and distillation.

In the ebulliometry method, the boiling point (BP) of a wine sample is measured using an ebulliometer (or ebullioscope) and compared to the BP of pure or distilled water at constant atmospheric pressure. A nomogram (ebulliometer disk) is used to determine the ABV of the wine sample based on the relative BPs. Most accurate results are obtained when the difference in BPs is less than 4°C (7.2°F), which, for most wines, requires a fivefold dilution of test samples, although this is seldom done in practice (Ough and Amerine 1988) as the dilution step introduces error and it also increases analysis time. Ough and Amerine (1988) also recommend diluting samples so that the amount of residual sugar (RS) is below 2 g/L (0.2%) to obtain a theoretical error of about ±0.1% (in volume % alcohol read). In practice, a threshold of 4–5 g/L (0.4–0.5%) is used for dry wines, which avoids introducing dilution errors. Where dilution is used, measured ABV is multiplied by the dilution factor (DF) to determine the final ABV.

In the chemical oxidation method, also known as the titrimetric/dichromate method, ethanol from a wine sample is collected by distillation, for example, using a micro-Kjeldahl distillation apparatus (Zoecklein et al. 1999), or by heat-enabled vaporization though this is a slower process. The ethanol is allowed to react in a reaction bottle with acidified (sulfuric acid) dichromate of known molarity to form acetic acid. The amount of dichromate remaining after the reaction is determined by conversion to iodine and titration with sodium thiosulfate. A blank (distilled water) is also measured to establish a reference. ABV is then calculated from the amount of titrant used compared to that used for the blank. The accuracy of this method depends

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on the extent of ethanol vaporized and oxidized, the accuracy of instruments used for titrations, and titration techniques.

In the distillation method, a wine sample is distilled to separate volatile components from interfering substances, i.e., dissolved solids, to simplify measurement of ethanol (Ough and Amerine 1988). The ethanol-containing distillate is brought back to a known volume and then the ABV and temperature are measured using an alcohol hydrometer with a built-in thermometer. The measured ABV is adjusted to compensate for temperature if it is different from the alcohol hydrometer's calibration temperature. High amounts of free sulfur dioxide (SO_2) or acetic acid as well as compromised distillation execution efficacy (e.g. poor connections, insufficient cooling capacity) and poor equipment cleanliness can increase analysis error (Ough and Amerine 1988).

Materials and Methods

Test Procedure. This study measured the ABV content in a model solution, a dry red wine, a dry white wine, and a sweet white wine by ebulliometry, chemical oxidation using titration (dichromate) techniques, and distillation. "Dry wine" is interpreted here to mean a wine with less than 5 g/L (0.5%) RS.

This study qualitatively compares measured ABV values with "theoretical" ABV values for samples as measured during winemaking and as described in the next section. The term "theoretical" is used given the unknown accuracy of ABV values in the reference model solution and wine samples.

This study was not exhaustive as each sample was only analyzed and measured once (N=1) for each method to assess correlation among the three methods. Tests were not repeated to determine reproducibility or precision.

Model Solution and Wine Samples. Pure ethanol was not available to prepare a reference model solution with an exact alcohol concentration. A bottle of 94% alcohol (Alcool Global) was purchased from a liquor store and diluted in the required proportions with distilled water (34.6:250.0) to prepare a 13% ABV model solution with approximately 7 g/L total acidity (tartaric acid), 3.5 pH (potassium chloride), and no residual sugar, i.e., RS = 0 g/L. As no data on the accuracy of the 94% ABV declaration on the label was available, accuracy of the ABV of the model solution can only be assumed to be an approximation. Assuming an error of as much as 1.5% ABV, the 13% sample may have an ABV in the range 12.8–13.2%.

Wine samples comprised of a dry red wine (Cabernet Sauvignon) and a dry white wine (Sauvignon Blanc) both with RS < 5 g/L, and a sweet white wine prepared from the same dry white wine but with 20 g/L of *D*-glucose added to achieve an RS of approximately 25 g/L to allow a simple fivefold dilution where diluted samples were required.

Triple-scale (Brix, SG and PA) hydrometers were used during winemaking: a Herculometer hydrometer for the dry red wine and a Mosti Mondiale (MM) hydrometer for the dry white wine, both calibrated for SG at 60/60°F. During winemaking, Brix, SG and PA were read off specified hydrometers and recorded (Table 1). For both hydrometers, the SG scale had the greatest accuracy with ±0.002 and the PA scale the least with ±1% ABV; the Brix scale had an accuracy of ±0.5 Brix. In the PA range of table wines, the Herculometer uses a conversion of (Brix X 0.55) to estimate PA while the MM hydrometer uses a conversion of (Brix X 0.57 − 0.63). Zoecklein et al. (1999) provides yet a different calculation: (Brix X 0.55 − 0.63). Based on experimental data from the literature, Margalit (2004) states that PA was experimentally found to be in the range (Brix X 0.57±0.03), and so, a wine with 22.0 Brix could have a PA in the range 11.88–13.20%.

Wine	Brix	SG	PA (% ABV) Brix X 0.55 (Herculometer)	PA (% ABV) Brix X 0.57 – 0.63 (Mosti Mondiale)
	22.0	1.092	12.1	11.9
Dry Red	-1.0	0.995	-0.7	-0.7
	Estimated ABV (%) =		**12.8**	**12.6**
	21.5	1.087	11.8	11.6
Dry White	-1.5	0.994	-0.8	-0.8
	Estimated ABV (%) =		**12.6**	**12.4**

Table 1 Hydrometer readings measured during winemaking of a dry red wine using a Herculometer and a dry white wine using a Mosti Mondiale hydrometer. Shaded PA entries are the actual measurements while the PA entries with no shading represent calculations as if measurements were made with the alternate hydrometer. The shaded PA values are used as "theoretical" ABV for a qualitative comparison in this study.

Hydrometer readings and PA estimation inaccuracies notwithstanding, actual measured ABV values can often be lower than expected (from the theoretical) values due to alcohol losses due to evaporation during wine aging and due to dilution effects from the addition of processing aids during winemaking, for example, bentonite rehydration and sulfite dissolution in water. These losses and dilution effects were not measured although evaporative losses can be expected to be negligible as the dry red wine was made from a kit and in a very short timeframe, and the white wine was processed at cold temperature.

Test Equipment, Methodology and Accuracy. The ebulliometry method was tested using a traditional non-electric ebulliometer, Dujardin-Salleron model 160000 (https://www.dujardin-salleron.com/product_complete-traditional-ebulliometer-in-case_160000-.html) using both diluted (fivefold with distilled water) and undiluted samples to obtain test samples with less than 5% alcohol. Only the sweet-white-wine sample was diluted (fivefold with distilled water) to specifically get the RS below 5 g/L.

A sample of freshly purchased distilled water was analyzed to determine the reference boiling point (BP), which was locked on the ebulliometer disk. The BP for each sample was then measured and the ABV was determined by reading the value opposite the measured BP. A test of the sweet-white-wine sample without dilution was also performed to assess the impact of an appreciable amount (approximately 25 g/L) of sugar in the sample.

All tests were performed rapidly within a single session without re-measuring the BP of distilled water prior to each test sample; it is assumed that impacts due to any atmospheric changes were nil or negligible in this short test interval.

The ebulliometry method is expected to have a theoretical error of about ±0.1% (in volume % alcohol read) for samples diluted to less than 5% ABV and less than 2 g/L RS. Instructions for the Dujardin-Salleron ebulliometer recommend diluting samples when the RS is greater than 2%, although it is suspected that this is an error as the instruction text is similar to that of Ough and Amerine (1988).

The chemical oxidation (titrimetric/dichromate) method was tested using Vinmetrica's Alcohol By Volume (ABV) Kit (https://vinmetrica.com/product/abv/), which includes all necessary apparatus and reagents. 100-µL samples of distilled water (blank for use as a reference), the model solution, and wines were transferred to glass "buckets" and inserted and capped into reaction bottles containing 5.0 mL of acidified potassium dichromate solution. Reaction bottles were placed on a hot plate and allowed to react at temperatures of 45–60°C for 4–24 hours. The sweet white wine sample was tested both undiluted and diluted fivefold. Due to the limited number of reaction bottles (additional bottles are available from Vinmetrica), these tests were performed over 3 days; the blank was measured only once on the first day.

After the incubation period, the content of each reaction bottle was treated with approximately 2 mL of ABV Developer (iodide) and immediately titrated to a deep olive-green color with the ABV Titrant (sodium thiosulfate). Approximately 1 mL of Starch Indicator was added and the titration completed to a light-blue endpoint. The total volume (V_s) of ABV Titrant used was subtracted from that used for the distilled water sample (V_b) and the result multiplied by 2.88 to calculate the final ABV, i.e., $\%ABV = (V_b - V_s) \times 2.88$.

			Ebulliometry Method					
			without dilution		with dilution			
Sample	Theoretical ABV (%)	RS (g/L)	BP (°C)	Measured ABV (%)	BP (°C)	Measured ABV (%)	Dilution Factor	Calculated ABV (%)
Water	0.0	0	100.22	X	99.85	X	X	X
Model Solution	13.0	0	91.15	12.85	97.50	2.58	5	12.90
Dry Red Wine	12.8	<5	91.00	13.15	97.50	2.58	5	12.90
Dry White Wine	12.4	<5	91.30	12.54	97.60	2.46	5	12.30
Sweet White Wine	12.4	~25	91.38	12.40	97.65	2.40	5	12.00

Table 2 ABV test measurements and calculations by the ebulliometry method (N=1)

			Chemical Oxidation Method (Vinmetrica)				
Sample	Theoretical ABV (%)	RS (g/L)	Titration Volume (mL)	Measured ABV (%)	Dilution Factor	Calculated ABV (%)	Comments
Water	0.0	0	9.45	X	X	X	11 hrs @ 55°C
Model Solution	13.0	0	5.00	12.82	1	12.82	3.5 hrs @ 60°C
Dry Red Wine	12.8	<5	5.10	12.53	1	12.53	11 hrs @ 55°C
Dry White Wine	12.4	<5	5.12	12.47	1	12.47	3.5 hrs @ 60°C
Sweet White Wine	12.4	~25	5.55	11.23	1	11.23	3.5 hrs @ 60°C
			5.30	11.95	1	11.95	24 hrs @ 45°C
			8.60	2.45	5	12.24	4 hrs @ 45°C
			8.60	2.45	5	12.24	4 hrs @ 45°C

Table 3 ABV test measurements and calculations by Vinmetrica's chemical oxidation method (N=1)

			Distillation Method					
Sample	Theoretical ABV (%)	RS (g/L)	T (°C)	Apparent ABV (%)	Correction for Temperature	Corrected ABV (%)	Dilution Factor	Calculated ABV (%)
Water	0.0	0	X	X	X	X	X	X
Model Solution	13.0	0	22.0	13.00	-0.40	12.60	1	12.60
Dry Red Wine	12.8	<5	22.5	13.20	-0.55	12.65	1	12.65
Dry White Wine	12.4	<5	21.4	12.40	-0.30	12.10	1	12.10
Sweet White Wine	12.4	~25	22.0	12.40	-0.40	12.00	1	12.00

Table 4 ABV test measurements and calculations by the distillation method (N=1)

The Molarity of the acidified potassium dichromate solution was determined to be in the required range 0.197–0.203 using the method described in Vinmetrica's Alcohol By Volume (ABV) Kit User Manual (Version 1.4), and therefore, no corrections were necessary to the calculated ABV values.

Vinmetrica's stated sensitivity for their implementation of the chemical oxidation method is below 1% ABV with an accuracy of 0.3%.

The distillation method was tested using a Vinoquant 3 from Kübler-Alfermi (https://shop.leo-kuebler.de/shopware/distillery-equipment/determination-of-alcohol-value/225/vinoquant-3-alcohol-determination). For each of the model solution and wines, a 100-mL sample was distilled from a distillation flask heated on a hot plate. 80–90 mL of distillate was collected in a 100-mL volumetric flask, and then topped up to 100.0 mL with distilled water. The 100-mL distillate was then transferred to a glass cylinder. An alcohol hydrometer calibrated at 20°C with incorporated thermometer and with an ABV range of 8.5–14.5% was used to measure the "apparent" ABV. The "apparent" ABV and temperature measurements were then transferred and mapped onto an alcohol–temperature compensation nomogram to determine the adjustment value and final ABV.

The manufacturer does not provide any data on precision or accuracy of their implementation of this method.

Results and Discussion

Tables 2, 3 and 4 show the results of this study for the three methods used to measure ABV in test samples. With some exceptions, tests were performed once only (N=1) for each method.

For the model solution, containing only tartaric acid and potassium chloride and therefore considered to have very low total soluble solids compared to wine, the ebulliometer and Vinmetrica kit measured similar ABV values (within 0.08% ABV) and correlate well to the theoretical ABV of 13%, while the distillation method measured a lower value of 0.22%–0.30% ABV compared to the other two methods. Non-dilution was not considered a factor for the model solution with both undiluted and diluted samples measuring similar ABV values in the ebulliometry method.

For all three wine samples, measured ABV values by ebulliometry were lower in the diluted samples. This may be due to dilution error or, more likely, achieving more accurate measurements with diluted samples (assuming accurate dilution techniques) as BPs were within 4°C (7.2°F) as recommended by Ough and Amerine (1988). As expected, the sweet white wine had a slightly higher BP than the same but dry white wine given the higher RS. A very small BP increase of 0.05°C (0.09°F) resulted in a 0.30% ABV decrease although it should be considered that the accuracy of the thermometer is 0.1°C (1.8°F).

For the red wine sample, considering only the ABV measured using the diluted sample for the ebulliometry method, the three methods measured ABV values within 0.37% with the ebulliometer measuring closest to the theoretical ABV of 12.8% using the Brix conversion factor of the Herculometer. There is no strong correlation except that the Vinmetrica and distillation methods measured ABV values within 0.12% ABV. If the ABV value calculated using the alternate Brix-to-PA calculation, i.e., as if the measurements were made with the MM hydrometer, the Vinmetrica and distillation methods are closest to the theoretical value of 12.6%.

For the white wine sample, the three methods measured ABV values also within 0.37% with no strong correlation among the methods with the ebulliometry and Vinmetrica methods closest (within 0.10% and 0.05% ABV, respectively) to the theoretical ABV of 12.4%. The differences increase with the alternate Brix-to-PA calculations, i.e., with the Herculometer, when comparing to the theoretical ABV of 12.6%.

For the sweet white wine, no differences in ABV compared to the dry white wine measurement were expected. The three methods measured ABV values within 0.24%. The ebulliometer measured 12.00% compared to 12.30% for the dry version of the same wine, but, as described above, this may be due to the accuracy of the thermometer although the method by distillation too measured 12.00%, close to the 12.10% value of the dry white wine. The Vinmetrica method measured a higher ABV, 12.24%, but closer to the theoretical value of 12.4% and within 0.23% of the ABV of the dry white wine. Short-duration (3.5 hours at 60°C) and a long-duration (24 hours at 45°C) incubations of undiluted sweet white wine samples resulted in lower ABV values (Vinmetrica method); the higher RS may be impacting alcohol vaporization. An ABV value closer to the theoretical value of 12.4% and closer to the measured ABV of 12.47% for the dry white wine suggest that samples should preferably be diluted for non-dry wines in the Vinmetrica method. As the incubation period in the Vinmetrica method was determined not to be a factor beyond the prescribed minimum number of hours, results may reflect the difficulty in establishing the first color change during titration; the second light-blue color change signaling the endpoint was not a problem.

Conclusions

Based on single-test measurements (N=1), these results show that the three methods studied for measuring ABV in are within by 0.37% ABV. Given that there was no test sample with a known and exact ABV that could be used as reference, and given the possible ranges of theoretical ABV values of samples, which depend on the Brix-to-PA conversion calculation used, no conclusion can be drawn as to which method measured ABV most accurately. It is observed, however, once the accuracy of the ebulliometer and Vinmetrica method are factored in (it is not known for the distillation method), that the ebulliometry method measured ABV values close to the theoretical ABVs for the model solution and dry wines, while the Vinmetrica method measured ABV values close to the theoretical ABVs for the model solution, dry wines and sweet wine.

More exhaustive testing with multiple tests performed for each sample and method would allow performing an analysis of experimental errors and accuracy of each method.

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