

Technical Brief

A Method for the Estimation of Alcohol in Fortified Wines Using Hydrometer Baumé and Refractometer Brix

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Abstract: A novel method for the estimation of alcoholic strength of fortified wines has been developed, linking %v/v alcohol to two simple and rapid enological measurements: refractometer apparent Brix and hydrometer apparent °Baumé. The soluble solid content of fortified wines, measured as true Brix (refractometer) and true °Baumé (hydrometer), can be estimated by the application of experimentally determined correction factors, which compensate for alcoholic obscuration. A calibration plot of true °Baumé versus true Brix, for 35 port wines, having diverse apparent °Baumé and % v/v alcohol, was linear with $r^2 = 0.997$. Applying the obscuration formula and rewriting the equation in terms of apparent Baumé and apparent Brix, leads to an expression for alcoholic strength: % Alcohol (v/v) = 1.646 A.Brix – 2.703 A.°Baumé -1.794. This equation permits the rapid estimation of alcohol content of young fortified wines by two simple measurements: refractometer apparent Brix and hydrometer apparent °Baumé. The method is rapid, economical and extremely portable, and is proposed as a quality-control technique for the three standard fortified wine parameters: % v/v alcohol, hydrometer apparent °Baumé, and refractometer apparent Brix.

Key words: fortified wine, apparent Brix, apparent °Baumé, true Brix, true °Baumé

Wine alcohol is one of the most frequent and important analyses performed in the wine laboratory, carried out during processing and quality control (Rangel and Toth 1999). Numerous analytical methods have been used to determine wine alcohol, including distillation followed by densitometry (Vallesi and Howell 2002), hydrometry (O.I.V. 1978), refractometry (Jaumes et al. 1965), or pycnometry (A.O.A.C. 1970, Jaumes et al. 1972), chemical oxidation followed by titrimetric or photospectrometric determination (Flanzy et al. 1955, Caputi et al. 1968, Caputi and Wright 1969), ebulliometry (Vallesi and Howell 2002), enzymatic determination (Ribereau-Gayon et al. 1982), gas chromatography (Hunter et al. 1960, Morrison 1961), HPLC (Huthner et al. 1997), near infrared (Kirrane and Hill 2001), and automated methods (Ribereau-Gayon et al. 1982, Saris et al. 1969), including flow injection analysis in conjunction with enzymatic/spectrophotometric detection (Rangel and Toth 1999). However, many of these methods are exceptionally time-consuming, expensive to carry out on multiple samples, and nonportable.

Soluble solids can be monitored during fermentation by either hydrometry or refractometry and can be expressed in terms of Brix, °Balling, °Baumé, °Oechsle, or specific

gravity. In Portugal, apparent °Baumé is the preferred measurement used to follow alcoholic fermentation in order to determine the opportune fortification time. Fortification typically involves the addition of approximately 4 volumes fermenting grape must to 1 volume *aguardente*, a wine spirit. Adequate mixing is essential to ensure sample homogeneity. The required spirit volume for fortification can be estimated using tables (Pato and Miranda 1938) or the Pearson–Square formula (Rankine 1991). The alcoholic strength of newly fortified port wine is determined by distillation/hydrometry or ebulliometry. Corrective strength adjustments are made when required.

The present work investigates the possibility of linking the three standard enological parameters, apparent Brix, apparent °Baumé, and alcoholic strength, with the objective of formulating an equation to be used for the rapid estimation of alcohol content of sweet fortified wines.

Materials and Methods

Wines were centrifuged before analysis at 4 min, 4000 rpm (Megafuge, Heraeus Instruments, Cacém, Lisbon). Sample temperature was allowed to reach ambient ($\pm 2^\circ\text{C}$) before analysis. (Analysis location must have a stable ambient temperature and should be free from air currents.)

Alcoholic strength was determined by standard procedures using either distillation/hydrometry or ebulliometry (Iland et al. 1993). For distillation/hydrometry, 250 mL samples of wine (at 20°C) were distilled to give 220 mL distillate. The volume was readjusted to 250 mL (at 20°C) with de-ionized water, and strength was measured using one of two alcohol hydrometers (Denis, Arnouville, France) (scales: 14 to 22; 20 to 30). The Churchward technique was used for ebulliometry, correcting for dissolved solids.

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Apparent °Baumé (A.°Bé) and apparent Brix (A.Brix) are respectively defined as the hydrometer and refractometer measurements of wine soluble solids in °Baumé and Brix. True °Baumé (true °Bé) and true Brix values are the same measurements, but corrected for alcohol obscuration (+0.152 Bé units and -0.358 Brix units for each degree of alcohol; Figure 1). Obscuration is defined as the amount by which the “true density or true refractometry” as measured by hydrometer °Baumé or by refractometer Brix is obscured by the presence of alcohol. Total soluble solids were measured by hydrometer (Denis) (ref. 27041; scale 0 to 10 °Baumé) and refractometer (Atago handheld refractometer N-1α): hydrometer calibration was verified using a specific gravity hydrometer, which had been calibrated at the Instituto Português de Qualidade. Measurements were corrected for standard temperature 20°C, using tables (Iland et al. 1993); the refractometer was zeroed using deionized water at 20°C in a room with temperature 20°C. Samples were analyzed at thermostated temperature (~20°C) and corrected for small variations to standard temperature (20°C) using tables.

Ethanol obscuration of soluble solids was determined for both hydrometer °Baumé and refractometer Brix. Six model hydroalcoholic solutions with 50 g/L D-glucose, 60 g/L D-fructose, and 5 g/L L-tartaric acid were prepared to have alcoholic strengths between 13 and 23% v/v and final pH 3.5 (pH was adjusted with 5 N NaOH). Each solution was measured for apparent Brix (refractometer), apparent °Baumé (hydrometer), and alcoholic strength.

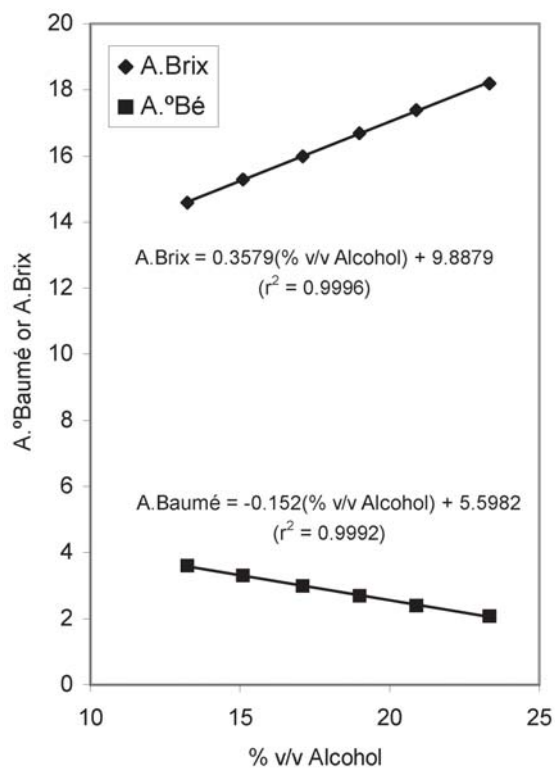


Figure 1 Evaluation of the effect of alcohol obscuration on soluble solids measured by hydrometer in °Baumé and by refractometer in Brix.

Alcoholic strength (distillation/hydrometer), apparent °Baumé (hydrometer), and apparent Brix (refractometer) were determined in duplicate for 35 port wines which had been chosen for their diverse sugar (A.°Bé: 1.5 to 7.2) and alcohol (15.3 to 23.8% v/v) content. Calibration used the averages of the reported duplicates (Table 1).

Sample wines were analyzed for alcoholic strength (distillation/hydrometer or ebulliometry), apparent °Baumé (hydrometer), and apparent Brix (refractometer). Analyzed wines (duplicate analyses) included 107 newly fortified port wines from the 2004 vintage, 22 aged port wines,

Table 1 Calibration data for 35 port wine duplicates (A & B): A.°Baumé, A.Brix, and alcohol content.

| Wine | A.°Baumé | | A.Brix ^a | | Distilled alcohol (% v/v) | |
|------|----------|------|---------------------|-------|---------------------------|-------|
| | A | B | A | B | A | B |
| BF1 | 3.15 | 3.20 | 16.10 | 16.16 | 16.40 | 16.30 |
| BF2 | 7.20 | 7.20 | 24.26 | 24.26 | 18.85 | 18.85 |
| BF3 | 6.10 | 6.10 | 21.00 | 21.00 | 16.20 | 16.20 |
| BF4 | 1.50 | 1.50 | 14.53 | 14.53 | 17.70 | 17.80 |
| BF5 | 5.35 | 5.35 | 21.67 | 21.77 | 19.60 | 19.55 |
| Cav1 | 4.85 | 4.85 | 19.97 | 20.07 | 17.70 | 17.75 |
| Cav2 | 6.65 | 6.65 | 25.73 | 25.73 | 22.75 | 22.75 |
| Cav3 | 2.60 | 2.60 | 20.03 | 20.03 | 23.85 | 23.70 |
| Cav4 | 5.40 | 5.40 | 24.30 | 24.30 | 23.25 | 23.25 |
| Cav5 | 3.60 | 3.60 | 18.33 | 18.33 | 19.05 | 19.10 |
| Jas1 | 6.60 | 6.60 | 23.86 | 23.86 | 19.65 | 19.60 |
| Jas2 | 3.90 | 3.90 | 19.27 | 19.17 | 19.20 | 19.20 |
| Jas3 | 3.20 | 3.20 | 18.65 | 18.65 | 20.10 | 20.00 |
| Jas4 | 4.75 | 4.75 | 19.94 | 19.84 | 17.90 | 17.80 |
| Jas5 | 5.15 | 5.15 | 20.97 | 20.97 | 19.15 | 19.20 |
| Mal1 | 3.85 | 3.85 | 19.17 | 19.07 | 19.55 | 19.40 |
| Mal2 | 6.65 | 6.65 | 24.14 | 24.14 | 19.95 | 20.05 |
| Mal3 | 5.25 | 5.25 | 22.14 | 22.04 | 20.00 | 19.95 |
| Mal4 | 5.10 | 5.10 | 20.13 | 20.20 | 17.50 | 17.45 |
| Mal5 | 2.75 | 2.80 | 16.04 | 16.09 | 17.20 | 17.10 |
| Mal6 | 7.15 | 7.15 | 24.56 | 24.46 | 19.15 | 19.00 |
| Ser1 | 1.85 | 1.85 | 16.23 | 16.23 | 19.95 | 19.85 |
| Sol1 | 3.65 | 3.65 | 18.65 | 18.65 | 18.70 | 18.65 |
| Sol2 | 3.30 | 3.30 | 18.17 | 18.17 | 18.85 | 18.80 |
| Sol3 | 3.80 | 3.80 | 18.67 | 18.67 | 19.05 | 19.00 |
| Sol4 | 4.15 | 4.15 | 19.60 | 19.60 | 19.40 | 19.50 |
| Sol5 | 4.05 | 4.05 | 19.40 | 19.50 | 19.35 | 19.40 |
| Sol6 | 4.10 | 4.10 | 19.40 | 19.40 | 19.20 | 19.20 |
| Sol7 | 2.45 | 2.45 | 15.94 | 15.84 | 18.00 | 18.00 |
| SR1 | 5.05 | 5.05 | 21.43 | 21.43 | 19.55 | 19.65 |
| Ves1 | 5.80 | 5.80 | 22.47 | 22.47 | 19.30 | 19.35 |
| Ves2 | 5.75 | 5.80 | 23.23 | 23.30 | 21.20 | 21.25 |
| Ves3 | 6.15 | 6.15 | 22.83 | 22.93 | 19.50 | 19.50 |
| Ves4 | 3.20 | 3.20 | 15.49 | 15.49 | 15.30 | 15.30 |
| Ves5 | 3.15 | 3.15 | 19.67 | 19.70 | 22.30 | 22.20 |

^aThe tabulated refractometer Brix values are averages calculated for two or more replicate readings.

three fortified Moscatel wines, and five Madeira wines. The following aged port styles were investigated: two ruby (blends of young, vibrant fruity red wines from different vintages, barrel aged for an average of 3 years); four aged tawny (blends of tawny colored wine with average of 10, 20, or 30 years in cask); two Colheita (tawny-style ports, from a single harvest year, barrel aged for a minimum of 7 years); four late-bottled vintage (blends of premium wines from a single vintage year, aged in oak casks and bottled after 4 to 6 years); two vintage (single-harvest, rich, concentrated, full-bodied, top-quality wines, bottled after 2 years wood aging); five Geropiga (intensely sweet wines, of low color intensity, used for blending); and three white (from white grapes).

Linear regression analysis of data was performed according to standard methods (O'Mahony 1986).

Results and Discussion

Alcohol obscuration. Increasing the percentage ethanol concentration of an aqueous sugar solution has the opposite effect on the measured soluble solids as determined by °Baumé (hydrometer) and Brix (refractometer). Hydrometer °Baumé decreased linearly with increasing percentage alcohol content, being obscured by -0.152 units for each additional degree of alcohol, whereas refractometer Brix increased linearly by $+0.358$ units (Figure 1). Effectively, a greater volume of less dense solution (higher % v/v alcohol) is displaced by the hydrometer, leading to a

decrease in °Baumé. Conversely, increased ethanol concentration increases solution atomic refractivity, increasing Brix readings. The two extrapolated zero points (% v/v alcohol = 0) were 9.89 and 5.60, respectively, giving a true Brix/true Baumé ratio of 1.77, which approximates the literature value of 1.80 (Boulton et al. 1998). The influence of alcohol on measured soluble solid content, leads to the following formula linking true and apparent values:

$$\text{true } ^\circ\text{Baumé} = \text{A.}^\circ\text{Baumé} + (0.152 \times \% \text{ v/v alcohol}) \quad (\text{eq 1})$$

$$\text{true Brix} = \text{A.Brix} - (0.358 \times \% \text{ v/v alcohol}) \quad (\text{eq 2})$$

True °Baumé and true Brix. For grape must, where there is no interference from alcohol, 1 true °Bé approximates 1.8 true Brix. This relationship does not hold true for apparent Bé and apparent Brix values of wine. These observations lead to the question of whether application of obscuration correction factors (eq 1 and eq 2) to soluble solid measurements of wine results in a linear correlation between hydrometer true °Baumé and refractometer true Brix.

To investigate this point, alcohol, apparent °Baumé, and apparent Brix were determined for 35 young port wines with diverse sugar and alcohol content (Table 1). Applying obscuration correction factors for alcoholic strength (eq 1 and eq 2), permitted calculation of true °Bé from A.°Bé and true Brix from A.Brix. The four plots (Figure 2) show that the correlation improves with obscuration correction. The coefficient of linear regression, for the

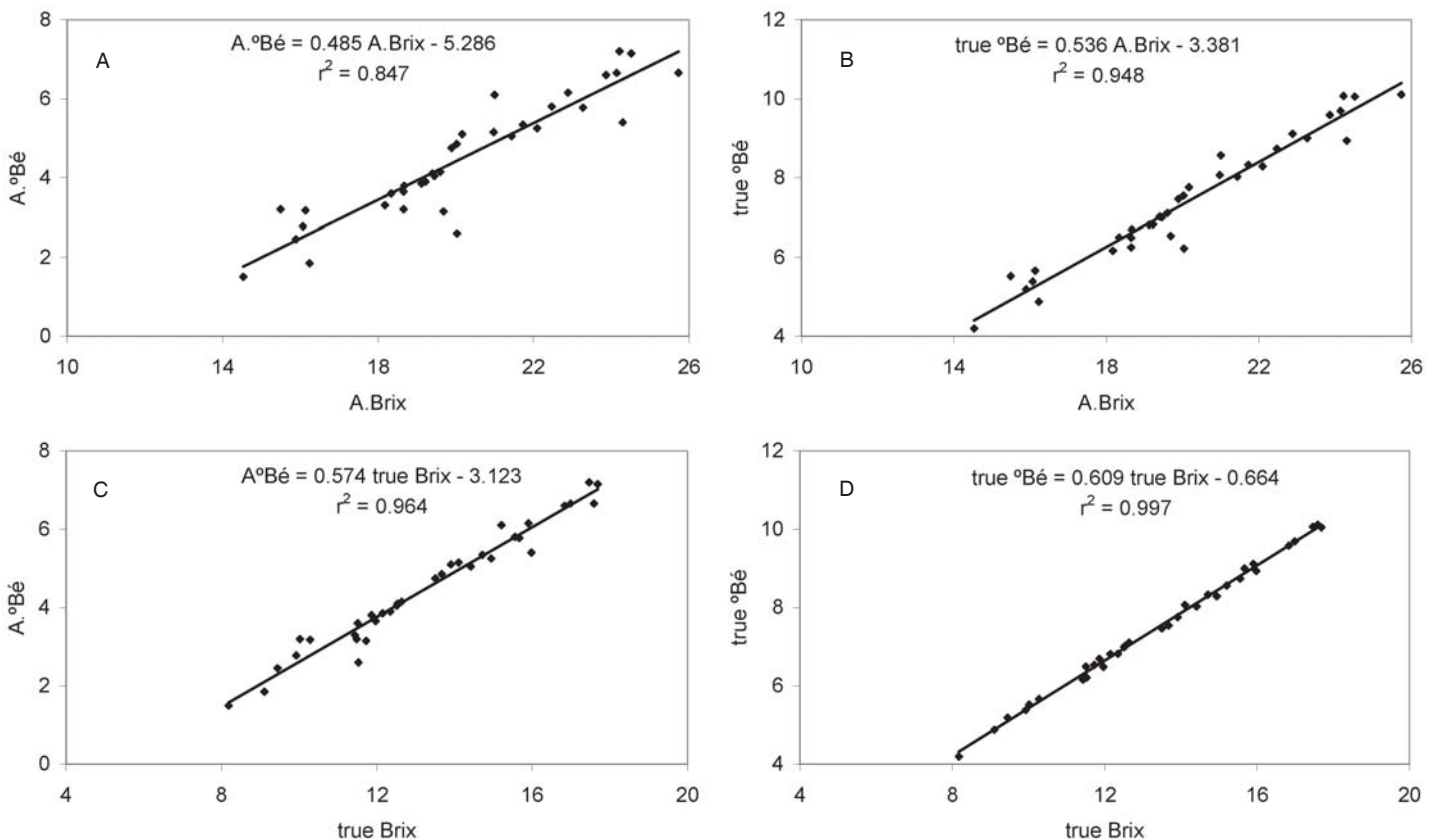


Figure 2 Plots evaluating the Baumé and Brix relationship for the calibration standards: (A) A.°Bé versus A.Brix; (B) true °Bé versus A.Brix; (C) A.°Bé versus true Brix; and (D) true °Bé versus true Brix.

plot of true °Bé against true Brix for the 35 port wines gave an excellent correlation (eq 3; $r^2 = 0.997$).

$$\text{true } ^\circ\text{Baumé} = 0.609 \text{ true Brix} - 0.664 \quad (\text{eq 3})$$

Relationship among alcohol, °Baumé, and Brix. By combining the two equations for obscuration correction (eq 1 and eq 2) with the true °Baumé/true Brix calibration equation (eq 3) and rearranging, an expression for alcoholic strength in terms of apparent °Baumé and apparent Brix is formulated:

$$\% \text{ v/v alcohol} = 1.646 \text{ A.Brix} - 2.703 \text{ A.}^\circ\text{Baumé} - 1.794 \quad (\text{eq 4})$$

Estimates for alcoholic strength for 107 young fortified port wines from the 2004 vintage were obtained by applying A.°Bé and A.Brix values to eq 4. Resulting strengths gave good association with the corresponding alcohol values determined by distillation/hydrometer (Table 2). The average difference in alcohol content between the methods was only -0.06 ± 0.25 . A plot of true °Baumé and true Brix (Figure 3B) gave excellent association ($r^2 = 0.993$), whereas the plot for A.°Bé versus A.Brix (Figure 3A) gave considerably greater scatter ($r^2 = 0.947$).

The new method permits good estimates for alcohol content of young Port wines of varying sweetness (Table 2). It is not applicable for the analysis of dry wines, whether fortified or not, which contain insufficient soluble solids for Baumé determination by hydrometer, and is yet to be evaluated for sweet table wines, such as sauternes.

Good estimates for alcoholic strengths were also obtained for both older port wines of various styles (Table 3) and Portuguese fortified wines (Madeira and Moscatel) from different controlled denomination of origin (D.O.C.) (Table 4). Good alcoholic strength estimates were obtained, regardless of whether the fortified wines were prepared from red or white grapes and irrespective of region/terroir, wine style, and wine sweetness.

The calibrated formula is a useful technique to give an estimate for alcohol content of fortified wines; however, it should not be considered as a replacement for more rigorous established methods.

Quality control. The formula has a second application as a quality-control tool linking the important parameters of “strength” (% v/v alcohol), “sweetness” (°Baumé), and refractometer Brix. It has been successfully used since the

2001 vintage as a process-monitoring tool, highlighting erroneous measurements associated with newly fortified port wines. Of wines evaluated during the 2001 vintage, those that gave an alcohol level as measured by Baumé–Brix which differed by greater than 0.5 % v/v above or below the values determined by distillate or ebulliometry were reexamined in duplicate. Corrections to erroneous measurements resulted in improved correlation for alcoholic strength (Table 5).

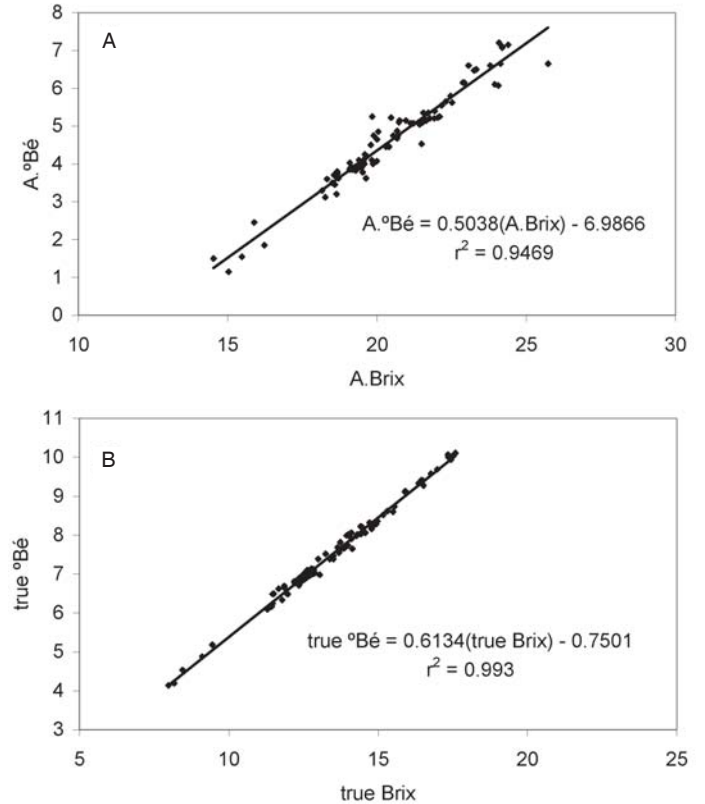


Figure 3 Plots showing the correlation between (A) apparent °Bé and apparent Brix and (B) true °Bé and true Brix for young port wines from the 2004 vintage.

Table 3 Statistical summary of the difference between the two methods of distillation and Baumé–Brix using aged Port wines (average and standard deviation).

| Wine style | n | Distilled alcohol - Formula alcohol | |
|-----------------------|----|-------------------------------------|------|
| | | Avg | SD |
| Aged tawny | 4 | 0.13 | 0.23 |
| Colheita | 2 | 0.19 | 0.27 |
| Ruby | 2 | -0.05 | 0.25 |
| Late-bottled vintage | 4 | 0.02 | 0.29 |
| Vintage | 2 | 0.23 | 0.29 |
| Geropiga (Bé > 5) | 5 | -0.08 | 0.19 |
| White (Bé 1.2 to 5.6) | 3 | 0.15 | 0.07 |
| All | 22 | 0.06 | 0.22 |

Table 2 Statistical summary of the difference between the two methods of distillation and Baumé–Brix using young Port wines from the 2004 vintage (average and standard deviation).

| Wine style | n | Distilled alcohol - Formula alcohol | |
|----------------------------|-----|-------------------------------------|------|
| | | Avg | SD |
| Port wine (Bé > 2; Bé < 5) | 66 | -0.08 | 0.25 |
| Sweet port (Bé > 5) | 37 | -0.02 | 0.26 |
| Dry port (Bé < 2) | 4 | -0.09 | 0.19 |
| All | 107 | -0.06 | 0.25 |

Table 4 Alcohol strength data for Madeira and Moscatel fortified wines, as determined by distillation (D) and Baumé–Brix (B).

| Wine style (region) | Distilled alcohol (D) % v/v | Formula alcohol (B) % v/v | Difference D–B |
|-----------------------------------|-----------------------------|---------------------------|----------------|
| Madeira Alvada 5 yr (Madeira) | 19.13 | 19.03 | 0.10 |
| Madeira Bual 5 yr (Madeira) | 18.70 | 18.64 | 0.06 |
| Madeira Bual 10 yr (Madeira) | 19.33 | 19.03 | 0.30 |
| Madeira Malmsey 10 yr (Madeira) | 18.73 | 18.70 | 0.03 |
| Madeira 1995 harvest (Madeira) | 19.23 | 19.23 | 0.00 |
| Average | | | 0.10 ± 0.12 |
| Moscatel (Setúbal) | 17.03 | 17.32 | -0.29 |
| Moscatel, Favaios (Douro Favaios) | 17.48 | 17.26 | 0.22 |
| Moscatel, Alijo (Douro Alijo) | 16.83 | 16.49 | 0.34 |
| Average | | | 0.09 ± 0.33 |

Table 5 The Baumé–Brix alcohol formula as a quality-control tool. Data represents the percentage of wines from the 2001 vintage with formula predicted alcohol (Baumé–Brix) within ±0.3, ±0.4, and ±0.5% v/v of alcohol determined by standard methods: (A) original 2001 data; (B) 2001 data, following quality-control corrections.

| Difference (% v/v alcohol) | (A) Initial measurement | | (B) With correction | |
|----------------------------|-------------------------|----------------------|---------------------|----------------------|
| | Distillation n = 98 | Ebulliometry n = 116 | Distillation n = 98 | Ebulliometry n = 116 |
| <0.5 | 81 | 80 | 100 | 100 |
| <0.4 | 76 | 74 | 99 | 99 |
| <0.3 | 60 | 60 | 92 | 88 |

Conclusions

A new method is presented for rapid estimation of alcoholic strength of sweet fortified wines, using two simple enological measurements, apparent °Baumé and apparent Brix. The derived formula, which links fortified wine alcoholic strength to apparent °Bé and apparent Brix, serves as a useful tool for rapid quality-control assessment of these three enological measurements. Refractometer Brix is a useful enological measurement for fortified wines.

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