The relationship between acetic acid and volatile acidity

Volatile acidity (VA) is well known as a major indicator of wine spoilage. It consists principally of acetic acid with lower amounts of steam distillable acids such as sorbic, formic, butyric and propanoic acid (Zoecklein et al., 1995). Small amounts of acetic acid and other volatile acids are formed during normal alcoholic fermentation and can also be produced during malolactic fermentation (Amerine and Ough, 1980). In Australia, the maximum possible limit for VA is 1.5 g/L (expressed as acetic acid), as specified in *The Australia and New Zealand Food Standards Code*, Standard 4.1.1 [http://www.foodstandards.gov.au/foodstandardscode/]. In the European Community, the maximum limit for red wines is 1.2 g/L, for white wines it is 1.08 g/L and for sweet botrytis infected wines 1.5 g/L, as specified in the Export Market Grid, [http://www.awbc.com.au/exporting/exportgrid/index.asp].

Use of the steam distillation method of analysis to determine volatile acidity in wines in the Australian wine industry is widespread with many wineries using the modified Markham Still (Figure 1). Our research shows that there is a strong correlation between volatile acidity and acetic acid. Conversion to methods such as enzymatic assay for the direct measurement of acetic acid would not only save time, but allow greater sample throughput, thereby providing a more cost effective way of analysing volatile acidity but with a minimal loss in accuracy.

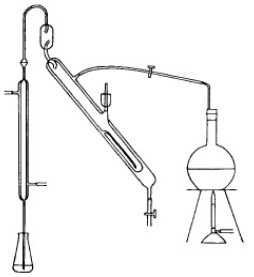

Figure 1. Modified Markham Still as per Analytical Service method LM10.

We analysed 353 wines using the modified Markham Still, enzymatic assay and high performance liquid chromatography (HPLC) (see Table 1). The modified Markham Still gave an average volatile acidity result for red wines of 0.64, (range 0.13–1.88g/L), for white wines the average result was 0.47 (range 0.12–1.77g/L) and for fortified and sweet white wines it was 0.60 (range 0.09–1.90g/L). Average volatile acidity results using the modified Markham Still method are higher than the results obtained using enzymatic assay and HPLC. This was expected as the latter two methods measured only

acetic acid. Volatile acidity measured by steam distillation and acetic acid measured enzymatically, showed a correlation coefficent ($r^2 > 0.94$) (Figure 2).

Table 1: Summary of the number of wines analysed and average results obtained using three different methods.

Wine type	Number of samples analysed	Average volatile acidity result g/L by reference method	Average acetic acid result by enzyme g/L	Average acetic acid result by HPLC	Range of acetic acid g/L across all methods
Red	194	0.64	0.55	0.58	0.13–1.88
White	139	0.47	0.4	0.44	0.12–1.77
Fortified and sweet wines	20	0.6	0.52	0.55	0.09–1.90
Total	353	0.57	0.49	0.52	0.09–1.90

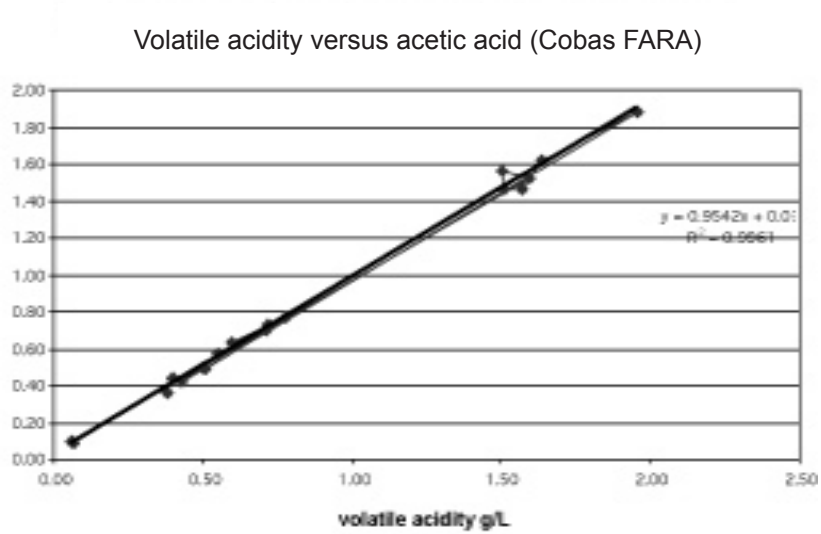

Figure 2: Plot between volatile acidity determined by steam distillation and acetic acid determined using the *Cobas* FARA.

More recently, we compared our current National Association of Testing Authorities (NATA) registered method for determining volatile acidity (modified Markham Still) with a *Cobas FARA* automated spectrophotometer instrument for the determination of acetic acid, which when used in conjunction with a *Boehringer Mannheim* enzymatic assay kit is capable of measuring acetic acid (Table 3).

Table 2: Summary of volatile acidity results by the reference method, versus acetic acid results by enzyme.

Sample number	VA result g/L	Cobas FARA result g/L	Difference g/L
F92411	0.07	0.09	0.02
F92412	0.06	0.1	0.03
L90905	1.59	1.53	-0.07
GA0408	1.5	1.57	0.06
GA1155	1.51	1.46	-0.05
HA2435	1.57	1.46	-0.11
JA1003	1.63	1.62	-0.01
IA2254	1.96	1.89	-0.07
JA1714	0.43	0.42	-0.01
JA1715	0.55	0.58	0.03
JA1718	0.72	0.73	0.01
JA1851	0.71	0.7	-0.01
JA1852	0.6	0.64	0.04
JA1853	0.78	0.77	-0.01
JA1859	0.51	0.49	-0.02
JA1860	0.4	0.44	0.04
JA1861	0.38	0.36	-0.02

The relationship presented in Figure 2 from the data in Table 2 shows an excellent correlation between the results obtained via the modified Markham Still volatile acidity method and the proposed enzymatic acetic acid method ($R^2 = 0.9961$).

Table 3: Summary of the results from standard additions of glacial acetic acid to both red and white wines as analysed by the Cobas FARA enzymatic method.

Addition	0.0 g/l	0.2 g/L	0.4 g/L	0.6 g/L	0.8 g/L	1.0 g/L
WHITE	0.45	0.63	0.86	1.1	1.25	1.45
Standard recovery		90%	103%	108%	100%	100%
Difference		-0.02	0.01	0.05	0	0
RED	0.22	0.47	0.65	0.86	1.08	1.27
Standard recovery		125%	108%	107%	108%	105%
Difference		0.05	0.23	0.44	0.66	0.85

Following examination of the validation data, not all of which are reported here, it is reasonable to conclude that the modified Markham Still and automated enzymatic assay methods give similar results. The automated enzymatic method appears to be accurate in determining the acetic acid content in all matrices commonly submitted to the Analytical Service. A more detailed report of this investigation will be published shortly.

NATA recently assessed and accreditied the automated enzymatic method for use within our laboratory. This method will be used to analyse all future samples submitted to the Analytical Service for volatile acidity unless we receive a specific request to use the modified Markham Still. Samples with results greater than or near the legal limit will be confirmed using the modified Markham Still method as this is the method referred to by the European Union.

References

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