The Australian Wine Research Institute

Fact Sheet
ANALYSIS

Measuring wine tannins using different analytical methods

Introduction

The WineCloud™ provides the ability to measure tannins, phenolics and colour attributes in grapes, as well as wines. The analysis is based on UV-Vis spectral readings and uses calibrations maintained by the AWRI. Wine measurements made through the WineCloud™ provide analytical data that can be directly related to measurements made using the Adams-Harbertson method. This fact sheet aims to help you understand the comparability of tannin, phenolics and colour measurements made using these different methods.

What is being measured?

Phenolics are a chemically diverse, important class of wine molecules that have a significant impact on the colour and taste of red wine.

For wine and ferment samples, five phenolic measures are available via the WineCloud™:

Wine total phenolics: This is a measure of all coloured and non-coloured phenolic molecules in wine that originate from grape skin, flesh and seed. Wine total phenolics are reported in absorbance units (a.u.).

Wine total tannin: Tannins are a sub-class of phenolics that can precipitate proteins. They contribute to wine texture, particularly astringency. When grapes are crushed, the tannins present in grape skin and seeds begin to be extracted into the grape must. Those from skins tend to be more easily extracted than those from seeds. Once extracted, the grape tannins begin to chemically rearrange, turning into wine tannins, which can be significantly different in structure from the original grape tannins. Wine tannin concentration is reported in g/L in epicatechin equivalents.

Wine total pigment: This is a measure of total red colour in the wine or ferment sample. It is reported in absorbance units (a.u.). Total

pigment is predominantly made up of free anthocyanins and pigmented tannins, both of which can also be calculated separately using the WineCloud™. A small amount of other pigmented compounds present in red wines contribute to the wine total pigment.

Free anthocyanins are the highly coloured compounds responsible for the colour of red grapes. They are found in grape must, ferments and young wines, but are not very stable under wine conditions so their contribution to wine colour decreases quite rapidly as wine ages. Anthocyanins are bleachable by SO_2.

Pigmented tannins are stable coloured compounds formed through the reaction of anthocyanins with tannins during fermentation and wine storage. Pigmented tannins have been shown to contribute up to 90% of the colour of red wine after two years' storage. They are not bleachable by SO_2.

How do the methods differ?

AWRI Method (WineCloud™)

The methyl cellulose precipitable (MCP) tannin assay is a simple and robust means of measuring the total grape or wine tannin in red grape homogenate extracts, red wine and other aqueous solutions (Sarneckis et al. 2005). The assay is based upon methyl cellulose-tannin interactions resulting in the formation of insoluble polymer tannin complexes which then precipitate. Tannin values are calculated from the difference between the absorbance values at 280 nm (A280) of solutions both with and without precipitation. This method is incorporated into the WineCloud™, along with the measurement of pigments (total anthocyanins), free (SO_2 bleachable) anthocyanins, pigmented tannins (non-bleachable pigments) and phenolics. Tannin content is calculated using a predictive algorithm based on the MCP method, developed by the AWRI (Dambergs et al. 2012), using UV-Vis measurements.

Adams-Harbertson (A-H) assay

The Adams-Harbertson tannin assay is a direct adaptation of a method previously used for grain and ecological tannin measurement (Hagerman and Butler 1978) and is designed to be an inexpensive and reliable measurement of tannin and colour in wine The Adams-Harbertson assay utilises protein precipitation with bovine serum albumin (BSA) and is used to quantify multiple classes of phenolic compounds: anthocyanins, tannins, pigmented polymers and non-tannin iron-reactive phenols. By combining protein precipitation and traditional bisulfite bleaching to distinguish monomeric anthocyanins from polymeric pigments, two classes of polymeric pigments in grapes and wines can be measured: small polymeric pigments (SPP) that do not precipitate with protein and large polymeric pigments (LPP) that do. The combination of SPP and LPP is equivalent to the SO_2 resistant pigments in wine (these are referred to as pigmented polymers by the A-H assay and as pigmented tannin by the AWRI method) – see Figure 1.

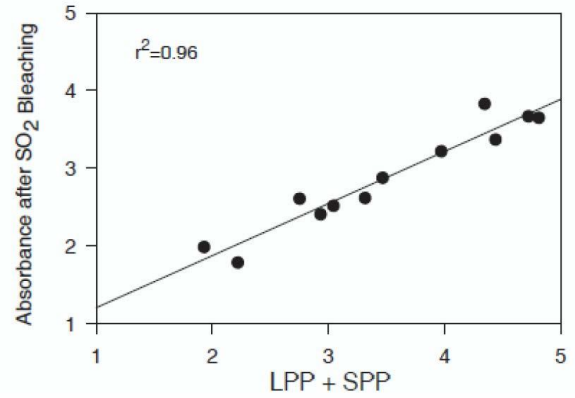

Figure 1: Correlation between sum of large polymeric pigments (LPP) and small polymeric pigments (SPP) and absorbance after SO_2 bleaching

How do the results compare?

Many research organisations have compared the two methods (Chittenden and Smith 2011, Harbertson et al. 2003, Mercurio and Smith 2008). Results generated show that:

- Tannin values generated using the MCP assay (utilised by the WineCloud™) are highly correlated with those generated using the A-H assay (Figure 2).
- The absolute values generated by the WineCloud™ method are consistently higher than those generated with the A-H assay.

It has been reported (Mercurio and Smith 2008) that the MCP assay removes more tannin material from the wine than the A-H assay and this may be explained by di- and tri-procyanidins and SPPs not precipitating with BSA. However, tannin concentration differences between the MCP and A-H tannin assays are not primarily caused by differences in the isolation of tannin material, but rather a function of the different detection methods used.

The different approaches to the quantification of the pigmented tannin portion of total tannin may impact on the correlation seen between the two methods and to the difference in final tannin concentrations determined using the two assays.

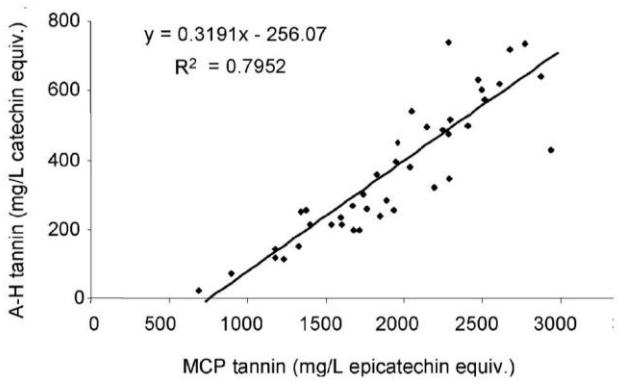

Figure 2: Correlation between tannin content determined by MCP assay and Adams-Harbertson assay

Reference and further reading

Chittenden, R. I. and Smith, P. A. 2011. Comparison between three different analysis methods for tannin in New Zealand Red Wines. *Proceedings of the American Society for Enology and Viticulture*.

Dambergs, R.G., Mercurio, M.D., Kassara, S., Cozzolino, D., Smith, P.A. 2012. Rapid measurement of methyl cellulose precipitable tannins using ultraviolet spectroscopy with chemometrics – application to red wine and inter-laboratory calibration transfer. *Appl. Spectrosc.* 66 (6): 656-664.

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Sarneckis, C.; Dambergs, R.G.; Jones, P.; Mercurio, M.; Herderich, M.J. and Smith, P. 2006. Quantification of condensed tannins by precipitation with methyl cellulose: development and validation of an optimised tool for grape and wine analysis. *Aust. J. Grape Wine Res.* 12(1): 39–49.

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