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Rapid determination of phenolic components in red wines from UV-Visible spectra and the method of partial least squares

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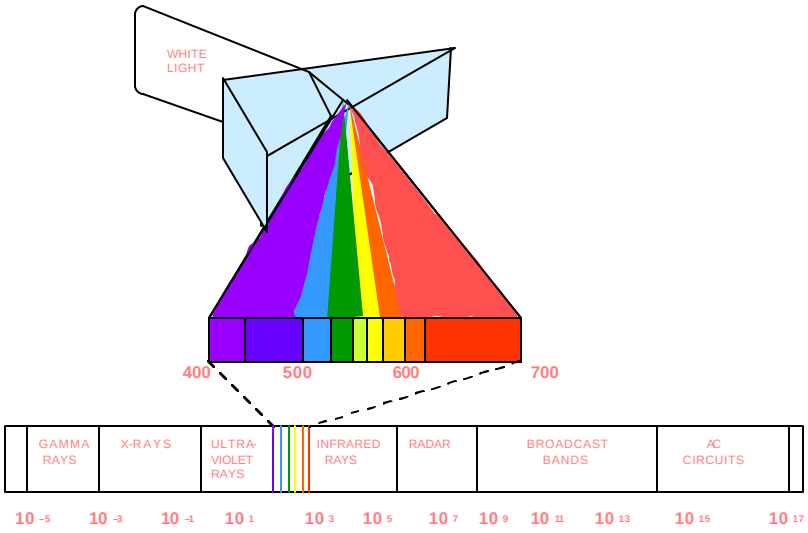
We all know about the practical value of the Harbertson-Adams tannin assay (UC Davis tannin assay) to generate data regarding the phenolic composition of grapes and wines. In this article, the authors explain how this phenolic data can be obtained using UV-visible spectroscopy, thus making the assay easier and faster.

• Today, there are a number of methods available to quantify the phenolic compounds in wines. However, all seem to have some kind of limitation that prevents them from becoming widespread in the winery lab. For example, the *Folin-Ciocalteau method* is unable to distinguish tannins from polymeric pigments. The *Glories method* that uses DMCA staining (dimethylcinnamaldehyde) is sample-dependent. And the *Somers*, the *Boulton*, and the *Harbertson-Adams* methods all involve multiple steps. Finally, methods that utilize *HPLC* (high pressure liquid chromatography) require costly equipment. But, as the authors emphasize, **the greatest limitation of all current methods is the extensive time required to generate useful information.**

• The authors are convinced that, for a method to become embraced by the industry, it must require minimal sample preparation, and must produce rapid results on multiple parameters at the same time. Currently, there is only one technique with the potential to achieve just that: spectroscopy. A spectrophotometric method for phenolics would work like this: it would use sophisticated statistics to correlate 1) data obtained using an analytical method with 2) data obtained using the same sample but measuring its spectra at specific wavelengths. Once a mathematical model is built and validated, the composition of unknown samples could easily be obtained directly from their spectra, bypassing the actual phenolic analysis.

• In fact, there have been several attempts to use spectrophotometric data to get wine composition information. As we know, depending on the wavelengths it measures, spectrophotometry can be divided into ultraviolet or UV (10-700 nm), visible (400-700 nm), and infrared or IR (700-100,000 nm). Most of the spectrophotometric methods to date have relied on the use of *infrared spectroscopy*, be it mid-infrared (MIR) or near-infra-red (NIR). But IR methods have the shortcoming of being too sensitive to the sample matrix - for example, the grape variety involved. On the other hand, *UV-visible spectroscopy*, supposedly less sensitive to sample matrix, has also been applied in the wine industry to predict basic wine parameters (pH, TA, VA, SO2, anthocyanins, tannins).



• **The authors believed that UV-visible spectroscopy had the potential to distinguish the different phenolic components in wines**. For this reason, in this study they explored the application of multivariate statistical methods to establish a relationship between UV-visible spectra of wines and the phenolic analytical data provided by the Harbertson-Adams assay.

• During harvest of 2006, the authors performed the Harbertson-Adams assay on 400 samples of juice, fermenting must, and finished wine that originated in several regions of Australia and that involved a large number of red varieties. (A limited number of white wines were included to provide wines low in phenols and tannin and without anthocyanin, SPP and LPP fractions.) Within 24 hrs, they also collected the UV-visible spectra of these samples, both diluted and undiluted. (For comparison, they also collected NIR spectra). Then, the authors used a statistical program that uses partial least squares (called Unscrambler) to correlate the spectral data set with the analytical data set. This process involved 2 steps. In the first step, they used 200 of the 400 samples (the *calibration* data set) to build a predictive mathematical model. In the second step, they used the remaining 200 samples (the *validation* data set) to compare "measured" and "predicted" data, thus proving that their model actually "worked".

• **Results. There was a strong positive correlation between the measured and the predicted values for: anthocyanins, polymeric pigments, small polymeric pigments, tannins, non-tannin phenols, and total phenols** (coefficient of determination, R^2, greater than 0.82). (By the way, considering the coefficient R^2 can range from 0 to 1, these are amazingly good correlations.) **Large polymeric pigments, however, were poorly estimated** by the spectral data (R^2=0.41). The authors attribute this to the low levels of these components in fermentation samples and young wines.

• To get an idea of whether UV-visible data was or was not independent of the matrix effects of grape variety, the authors did a preliminary study on how spectral data collected just from Cabernet Sauvignon or just from Syrah correlated with analytical data for <u>all</u> varieties (they did this for anthocyanins and tannins). They found that the predictive ability of the Cabernet model, or the Syrah model, was rather strong, and actually similar to the model built involving all varieties. In other words, the UV-visible model did appear to be independent of cultivar-specific effects.

As we have seen, the authors showed that UV-visible spectral data can be applied for the rapid determination of the different phenolic components in wines. At the end of the paper, the authors asked themselves 2 questions: do the calibration requirements for the model vary year-to year? Is the model universally applicable - that is, will it work with other wines? As they explain, it is too early to comment on year-to-year variations, or site-specific influences. But, to them, it is reasonable to anticipate that a fully validated UV-visible model may soon be widely available to the wine industry. For now, the Excel sheet (downloadable) that converts the spectra to the Adams Assay numbers can be found on Dr. Boulton's webpage: http://boulton.ucdavis.edu/uv-vis/index.htm

	Range of values found[1]	Lowest values in:	Highest values in:
Anthocyanins	0-1,100 mg/L	Chardonnay	Syrah (Bordertown)
Polymeric pigments	0-6.6 absorbance units	White samples	Cabernet (Barossa Valley)
Large polymeric pigments	0-3.1 absorbance un its		Cabernet (Barossa Valley)
Small polymeric pigments	0-4.2 absorbance units		Syrah (Barossa Valley)
Tannin	0-800 mg/L [2]	White samples	Merlot (Barossa Valley, Cabernet (Coonawarra)
Total phenols	20-2,272	Chardonnay	Syrah (Bordertown)

[1] In 400 samples of juice, fermenting must, and finished wine from South Australia

[2] According to the authors, this value is low, since there exist wines with much higher tannin levels than 800 mg/L

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