PHENOLIC RIPENESS IN SOUTH AFRICA

by

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Assignment submitted in partial requirement for Cape Wine Masters Diploma

Stellenbosch

July 2006

Abbreviations

Absorbance	Abs
Anthocyanin extractability	Ea
Australian dollar	AU$
Cabernet Franc	CF
Cabernet Sauvignon	CS
Folin-Ciocalteau	FC
Gallic acid equivalents	GAE
High Pressure Liquid Chromatograph	HPLC
Institut Cooperératif du Vin	ICV
Malbec	MAL
Merlot	MO
Near-infrared	NIR
Pinotage	PI
Pip tannins in percentage	Mp
Revolutions per minute	rpm
Shiraz	SH
Total acidity	TA
Total phenol content (determined by Glories method)	PFT
Total phenolic index	TPI
University of Stellenbosch	US

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1. INTRODUCTION

The study of phenolic ripeness is an extremely complicated field including what to study and how to use results. The building blocks of phenolic compounds in wine are essentially separated into anthocyanins and tannins. It is understood that anthocyanins are responsible for the colour of red wine and it is also known that the intensity of colour in wine is in direct proportion to the quality of wine. Grape tannins can be separated into two categories, namely skin tannins and seed tannins. Tannins are essentially bitter, and need to polymerise together with anthocyanins to form stable, acceptable-tasting flavourants. Hence the study of phenolic ripeness could focus on anthocyanin analysis, tannin analysis, or the polymerization process. The chemistry of the study of grape phenolic ripeness is however extremely complex and requires very sophisticated instrumentation for analysis of individual chemicals such as the various anthocyanins. Furthermore, each of these focus areas can further be subdivided. The focus areas of phenol analysis are currently inadequately understood, and it is even more difficult to know how to apply any data obtained.

This manuscript is an overview of some of the techniques used to determine the ripeness of wine grapes and some of the techniques used to analyse the phenolic content of grapes. A selection of results of experiments, carried out locally, is presented to illustrate phenolic ripeness measurements. These results are interpreted and their influence on the wine making process and wine quality is discussed.

The Glories method, the method most widely used to determine phenolic ripeness, was used in this study. It was however slightly modified and adapted to local conditions. The author found that the determination of anthocyanins by this method was very successful, and that the Glories method is a very powerful tool to determine the quality of the grapes. In most cases the author was able to predict which blocks of grapes in a vineyard were the best, without physically ever visiting the vineyard.

The influences of certain viticultural practices on phenolic ripeness are also considered and highlighted in the study. To add to the study, several South African wine personalities were interviewed in order to obtain an insight into their understanding of phenolic ripeness. The study culminates in a summary of the current status of phenolic ripeness measurement in South Africa.

Besides the value of phenolic ripeness as an indicator of grape ripeness, phenolic ripeness is further important for the comparison of grape quality with that of other countries. This is because the traditional methods of assessing grape ripeness, namely sugar and acid content, cannot provide a comparison of grape quality between different countries; these two measurements do not incorporate any flavour or tannin evaluations.

2. THE PROCESS OF GRAPE RIPENING

2.1. Introduction

According to Hellman [1]: “Grape ripeness is an elusive concept for many people and sometimes an elusive achievement for vineyards. Much of the difficulty with discussions of grape ripeness is that there is often an implied standard, but in reality, ripeness is an entirely subjective judgment.” Hence, there are really two issues that need to be addressed:

- How do we define grape ripeness?
- How do we measure ripeness parameters to assist our harvest decisions?

According to Bisson [2], “Grape ripeness can be defined as the physiological age of the berry on the vine. The berry functions to attract animals for dispersal of grape seeds. Dispersal is always critical, but even more so if the vine is under limiting growth conditions. This is the main reason that a certain amount of vine stress is beneficial for development of grape flavourants. Berry ripening is therefore tightly classically related to seed development.”

“It is therefore important to define the optimal grape ripeness for wine production and to develop clear chemical or biochemical traits that can be used to define the peak of ripeness” [2]. The following will survey the current understanding of ripeness assessment. But, clearly, further work is needed to define the parameters best associated with optimal ripeness of grapes for wine production.

“The definition of optimum ripeness will vary as it depends upon the style of wine being made; the working definition of quality; variety; rootstock; site; interaction of variety, rootstock and site; seasonal specific factors; viticultural practices; and downstream processing events and goals” [2].

“If a clear descriptive analysis of the quality target exists, then the time of harvest can be optimised to meet those goals. Several grape and cluster characteristics have been used to assess ripeness. There are, of course, other non-compositional factors that influence the decision to harvest, including labour availability; seasonal changes such as rainfall; heat waves; tank space limitations; and other factors beyond the winemaker’s control” [2]. But these will not be considered here.

“Sugar is a component that is often used to assess ripeness and in general is the norm of assessing the quality as well. Sugar content increases during ripening and is therefore a function

of berry age. Sugar is also relatively easy to assess, adding to its value as an index of ripeness" [2].

"Sugar levels appear to be fairly uniform across the population of berries, meaning that the coefficient of variance is low (less than 10%) and thus the value at the press pan can be predicted with reasonable accuracy if appropriate vineyard sampling protocols are followed [2]. Variance is much greater if the fruit is not uniform across the clusters (as found with Zinfandel) or if the variation in cluster microenvironment is not correctly accounted for in the vineyard sampling protocol" [2].

"However, several studies have shown no relationship between sugar levels and accumulation of grape berry flavourants. Thus, while sugar can indicate ripeness level, it is not clear whether it is the best index of optimal ripeness" [2].

"Numerous grape ripeness indices have been investigated [2] and a few analytical laboratories are attempting to quantify grape ripeness through complex chemical analyses of flavour and aroma constituents, phenolics, colour compounds, sugars, acids and pH. But there will never be a single set of numbers that define ripeness for a particular grape variety under all circumstances and for all purposes. Ripeness is really defined by the individual, whether grape grower or winemaker, and it is primarily a function of the intended use for the grapes. Often an individual's definition of ripeness is also influenced by what is "typical" for that variety in their specific growing region. Some benchmark of ripeness is achieved in one or more seasons and all subsequent crops are compared to that benchmark" [1].

"Grape varieties have fruit characteristics that are often distinctive. Combinations of aromas and flavours, tannins, sugars and acids create the unique "varietal character" of a wine grape. But even for the common ripeness parameters of sugar, acid and pH, what constitutes a definition of ripeness in one variety may not be the same for another variety. The chemical composition of grape berries is determined by the genetic makeup of the variety and influenced by environmental conditions and growing practices. It is nature's seasonal influence on the expression of fruit characteristics that led to the practice of wineries printing the year of harvest on the wine bottle" [1].

"Grape berry development and ripening is a continuous process and there is no single stage of development or point in time that the fruit can be universally considered "ripe" [1]. It is to be remembered that the grapevine's objective in producing fruit is to provide an attractive vessel for the dispersal of its seeds, not to produce wine for our pleasure! So therefore, in order to achieve the desired fruit ripeness, a vineyard must be managed appropriately to enable the vines to

achieve the targeted ripeness. Fruit ripeness must then be closely monitored to determine the appropriate time to harvest.

“Winemakers commonly have a target (ripeness standard) for grape ripeness that they would like to have the fruit achieve for the wine they will produce. That target can vary, even within the same grape variety, depending on the type or style of wine that will be made. For example, Pinot Noir intended for sparkling wine production will have a very different ripeness target compared to that for a Pinot Noir still wine. Lower sugar, higher acidity and more neutral flavours are desired for sparkling wine compared to still wine, so “ripeness” for sparkling wine and harvest occurs earlier” [1].

“Grape growers must also be aware of the capabilities of their vineyards so they will have appropriate expectations for fruit ripening. Unrealistic expectations can cause a grower to postpone harvest without any real gains in ripening, but with a greater risk of crop loss from disease or dehydration. Conversely, a grower could unnecessarily sacrifice ripeness and better fruit quality by harvesting too early. Consider that crop load and seasonal weather can greatly influence a vineyard’s ability to ripen its fruit. Ripening can be delayed and the attainment of desired ripeness inhibited by an excessive crop load“ [1].

2.2. Sugar ripeness

Sugar concentration is measured on different scales and in English-speaking New World countries is expressed as Brix. Brix is the name of a density scale for measuring sugar content in aqueous solutions. Since grape juice is primarily sugar and water, the Brix scale is used for a quick and easy “sugar analysis” of juice. The Brix scale is very simple; each degree is equivalent to one per cent of sugar in juice.

Figure 1 shows a typical profile of traditional changes monitored in grape composition during ripening, including the total sugar concentration. Here the sugar may comprise various types of sugars, such as glucose and fructose. There is an initial rapid phase of sugar accumulation but at some point during berry development and ageing the vine ceases transport of sugar to the fruit.

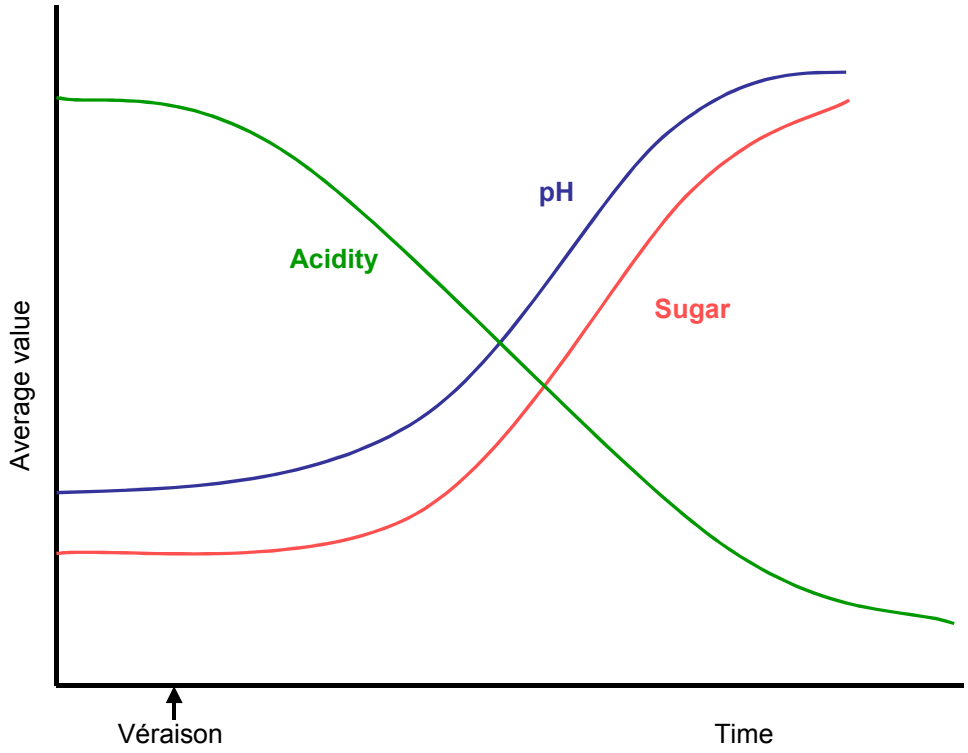


Figure 1: General trends of the traditional variants: sugar, acidity and pH, monitored during grape ripening, adapted from Rotter [3].

"Sometimes sugar accumulation will cease due to unfavourable environmental conditions, such as very high or low vineyard temperatures, but resumes once the conditions have changed. It is important to be able to distinguish a transient effect from a permanent cessation of transport of materials via the phloem. Once phloem transport has ended, any further increases in sugar level will be due to loss of water, not continued synthesis and translocation of sugar" [2].

"Assessing changes in berry weight, and noting the point at which the average berry weight starts to decrease significantly while the sugar content increases, can indicate the onset of dehydration. However, this can be quite difficult to monitor when fruit ripeness is not uniform across the clusters, or where great differences in berry weight already exist across the population. That is, the variation in "normal" berry weight will obscure early detection of dehydration onset" [2].

2.3. Physiological ripeness

"Physiological ripeness" [4] is a fashionable term loosely used by some New World winemakers to contrast with the ripeness measured by the standard analytical measures of sugar (Brix), acidity and pH. The terminology is imprecise because all grapes undergo physiological ripening irrespective of how it is assessed.

The concept of physiological ripening arises out of a distrust that these chemical measures can best predict optimum harvest date from a wine quality point of view. In its simplest form, the concept includes aspects of berry ripening which are not measured (but could often be) and which describe changes in a ripening grape berry that are important to eventual quality. These include skin colour, berry texture, seed colour and ripening, flavour, and phenolic changes. There is a notion that great wines are made when the harvest date coincides with the near optimum values of many of these parameters. Similarly, wines of lesser distinction arise when only a few parameters are at optimal value when the fruit is harvested. But factors such as weather conditions, site and viticultural technique can unbalance these relationships. A common example is the relatively faster rate of sugar increase in warm to hot climates compared to flavour increase and acid decrease. The resulting wines tend to be high in alcohol without necessarily being accompanied by ripe fruit aromas. On the other hand, varietal flavour appears to increase more quickly relative to sugar in cooler climates [5].

A likely important aspect of physiological ripeness that is overlooked in conventional ripening considerations is that of the condition of the grape skin. There is empirical evidence that wine quality can be affected, even though other aspects of fruit condition seem similar.

As analytical techniques improve, along with better understanding of the fruit ripening process and controlling factors, the concept of physiological ripening may later disappear from terminology. For the moment, however, it does serve to remind us that there is far more to determining when grapes are ready to be harvested than simply measuring sugar.

The onset of grape ripening (veraison) begins during the final stage of berry growth, when berries begin to soften and size increases due to cell enlargement. The sugar content of the berry increases rapidly, acidity decreases and the pH increases. See Figure 1. During veraison, berry skins lose chlorophyll and begin to synthesise and accumulate phenolic compounds that are responsible for the development of characteristic colours: yellow-gold (flavonols) and pink and red (anthocyanins).

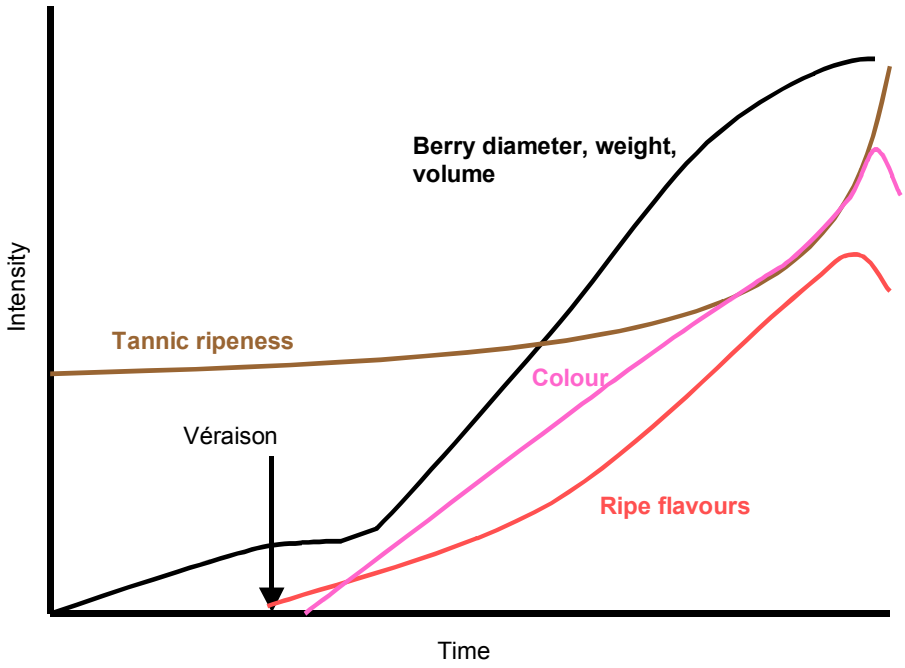


Figure 2: General trends in various fruit features during ripening, adapted from Rotter [3].

As previously mentioned, different fruit components change at different rates. Figure 2 shows ideal trends with regards to complementary component changes (e.g. full tannic ripeness coincides with full sugar ripeness). Such idealised behaviour is shown here as it is deemed most useful in understanding ripeness development as a whole. These trends represent the generalised behaviour of fruit ripening with relative accuracy.

It should be noted that Figure 2 shows the general trends of particular features averaged over the entire stem-skin-flesh-seed composite of a fruit. The preparation of this Figure [3] is based on results of scientific research (particularly on wine grape berry development). Such information is however not complete, and it should be kept in mind that some of the graphical information presented above is anecdotal. Additionally, the concentrations in the graph are not relative (just because "tannin" is shown to have a higher concentration than "colour" does not mean it is so). All features have been placed on the same graph, using a non-relative scale for ease of presentation. Note also that veraison is defined as the point during fruit ripening at which coloured fruit varieties begin to lose their green colour and attain the colour they will possess at final ripeness. "White" coloured fruit varieties will attain a translucent skin.

Figure 3 shows trends in specific tannin contents and skin colour during ripening. The "tannic ripeness" in this Figure is a measure of tannic polymerization, not of tannin quantity, and is an average over the entire stem-skin-flesh-seed composite.

Figure 3: Trends in tannin contents and skin colour during ripening, adapted from Rotter [3].

3. PHENOLIC COMPOUNDS AND THEIR CATEGORIES

Red wine, as it is commonly known, is produced exclusively from red-berried grapes. The grape juice of all grapes, including the red-berried ones, mostly has the same grey-green colour, and is certainly far from any resemblance to red. The colour in red wines frequently represents a discriminant factor as well as a prejudice in the evaluation of its quality. For many, the intensity of colour is directly related to the quality of wine, for others it simply represents an assessment in the style that the wine was made. The colouring substances of the grape, the ones that can make a wine red, are all concentrated in the skin, and the quantity of these substances, polyphenols, commonly called pigments, changes according to the variety, and the cultural and environmental conditions. For example, the colouring capacity of Sagrantino, the famous Umbrian red-berried grape, is higher than that of Nebbiolo, as well as Cabernet Sauvignon, and has a colouring capacity far higher than Pinot Noir. A higher colouring capacity also means a higher quantity of tannins, therefore astringency, which will also contribute to the body of wine. Extraction of the colouring substances from grape skins is done by macerating them in the must, and the longer the time of maceration the higher is the intensity of colour. Therefore, by using a grape having a high colouring capacity it is possible to make rosé wines, or paler red wines, by limiting the maceration period.

The quality of tannins in grapes is another important factor in the production of red wines. In white-berried grapes, the sugar content and acidity are the main criteria for ripeness but in red-berried grapes there is also a third and fundamental factor, namely phenolic ripeness.

Optimal phenolic ripeness must also consider the levels and the balance of acids and sugar in the grape. Generally tannins get a rounder and a more agreeable quality when the levels of sugar and acids in grapes have gone beyond their optimal ripeness levels. For this reason therefore it is not always possible to harvest phenolically ripe grapes because the risk of then making unbalanced wines with regards to the other organoleptic qualities would be very high. Should the time of harvesting be determined only by the phenolic ripeness of grapes, there would be the risk of harvesting overripe grapes, resulting in the making of wines with high percentages of alcohol, with aromas and tastes of fruit jams, and the acidity would be dangerously too low. However, the astringency of such wine would be very low and its character would be very velvety and smooth. The quantity of tannins and their level of astringency change according to the grape variety, yield per hectare, ripeness level, climate, area, and last, but not the least, wine making practices. For this reason the assessment of phenolic ripeness in grapes must also consider these factors, as well as the style of wine to be produced.

3.1. Phenolic acids and their derivatives

Grapes and wine contain benzoic and cinnamic acids. Their concentrations in red wine are in the order of 100-200 mg/L [6]. These phenolic acids are colourless in wine but may become yellow upon oxidation. From an organoleptic point of view phenolic acids do not have any odour or flavour.

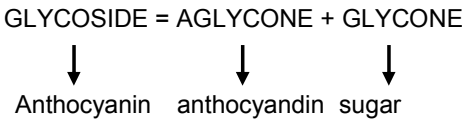
3.2. Flavonoids

Flavonoids are found mainly in grape skins, seeds and stems. Flavonoids are polyphenolic compounds possessing 15 carbon atoms; two benzene rings are joined by a linear three-carbon chain. They are a class of aqueous plant pigments [7], which are more-or-less intense yellow. Flavonoids are broken down into categories, though the issue of how to divide them is not universally agreed upon. One system breaks flavonoids into isoflavones, anthocyanidins, flavans, flavonols, flavones and flavanones [8]. Some of the best-known flavonoids are genistein in soy and quercetin in onions. In grapes three flavonoids (flavonols) are present: [6] kaempferol, quercitin, and myricetin. All three pigments are present in red wine grapes, whereas white wine grapes only have the first two [9]. Flavonoid compounds are found in the berry skin. Concentrations of the glycosides (the main group of flavonoids) in red wine are 100 mg/L.

3.3. Anthocyanins

Anthocyanins are found in the skins of red grapes and are responsible for the colour and colour stability of red wines. The anthocyanins are pink, red, purple and blue pigments, widely distributed in plants. They are water-soluble flavonoid derivatives, which can be glycosylated and acylated. The aglycone is referred to as an anthocyanidin. There are five commonly occurring anthocyanidin structures in wine grapes (Vitus vinifera). However, anthocyanidins are rarely found in plants, rather they are almost always found as the more stable glycosylated derivatives, referred to as anthocyanins [10, 11]. Next to chlorophyll, anthocyanins are the most important group of plant pigments visible to the human eye [12]. The chemical structure is based on two benzene rings bonded together by an unsaturated cationic oxygenated heterocycle.

These anthocyanidins combine with glucosides to form anthocyanins. It is possible that more than one glucoside can attach to an anthocyanin. Several chemical or physio-chemical properties of the anthocyanins influence their structure and consequently their colouration.



In Vitis vinifera wines, the presence of ethanol works against co-pigmentation and the acylated anthocyanins disappear rapidly a few months after the wine is made, leaving only the five monoglucosides, predominantly malvidin. Concentrations of anthocyanins vary a great deal according to the grape varieties and the age of the wines. Starting at levels of 100 mg/L (Pinot Noir) to 1 500 mg/L (Syrah, Cabernet Sauvignon, etc.) after fermentation, they decrease rapidly in the first few years, during barrel and bottle ageing, until they reach a minimum value of the order of 0-50 mg/L. This concentration was determined by a free anthocyanin assay, using chemical and chromatographic methods [6]. However, the majority of these pigments combine and condense with tannins in wine to form another, more stable, class of colour molecules called procyanidins, that cannot be detected by standard analytical methods. Another relatively small fraction of the anthocyanins is known to 'disappear'; it is either broken down by external factors (temperature, light, oxygen, etc.) or precipitated in colloidal colouring matter. The elimination of these pigments is particularly detrimental to the quality of red wine as it leads to loss of colour.

3.4. Tannins

Bate-Smith [13] defines tannins as "water-soluble phenolic compounds having molecular weights between 500 and 3 000…(giving) the usual phenolic reactions (and having) special properties such as the ability to precipitate alkaloids, gelatine and other proteins". Haslam [14] has more recently substituted the term "polyphenol" for "tannin", in an attempt to emphasise the multiplicity of phenolic groups' characteristic of these compounds. He notes that molecular weights as high as 20 000 have been reported and that tannins complex not only with proteins and alkaloids but also with certain polysaccharides. The use of the term tannin is preferential as it emphasises the character that sets tannins apart from all other phenolics, namely the ability to precipitate proteins [15].

Tannins are special phenolic compounds characterised by their ability to combine with proteins and other polymers such as polysaccharides. The quality of tannins in grapes is another important factor for the production of red wines. In white-berried grapes ripeness is basically determined by the level of sweetness and acidity, while in red-berried grapes there is also a third and fundamental factor, namely phenolic ripeness. Tannins are chemical compounds belonging to the family of polyphenols, and are responsible in red wines both for astringency and the body, as well as for the

colour obtained by anthocyanins. The organoleptic quality of astringency is often an important factor for the agreeability of a wine: when it is too accentuated its agreeability is low.

During the ripening of grapes the quantity of the polyphenols increases and, in particular, the organoleptic quality of tannins is also increased. For this reason, in quality wines, harvesting begins only when the grape is considered as phenolically ripe. As the ripening proceeds, tannins get a rounder and more velvety organoleptic quality, that is less astringent and more agreeable and, moreover, they are also easier to extract from the skin [16].

To maintain stable complexes with proteins, phenolic molecules must be relatively large so that they can form sufficient bonds with the protein molecules. However, if the tannin molecule is too large, it will be unable to bind with the active sites on the protein and bonding will be less likely. Finally, protein-tannin complexes are more stable and the tannin qualities are highest when the molecular weight of the tannins is between 500 and 3 000.

From a chemical standpoint, tannins are formed by the polymerization of elementary phenolic molecules, according to the nature of these molecules. There are basically two chemical classes of tannins, hydrolysable (derivatives of gallic acid) and condensed (based on catechin). These two groups differ in nearly every characteristic, other than their ability to bind with proteins. Hydrolysable tannins bind with proteins by hydrophobic interactions. Condensed tannins bind with proteins through hydrogen bonding. Grape skins and seeds contain only condensed tannins. Hydrolysable tannins are derived from oak wood, or are wine additives.

- ***Hydrolysable tannins*** The hydrolysable tannins are composed of one glucosidic molecule to which different phenolic moieties are bonded, the most important being gallic acid. These are not the natural grape tannins but the principal commercial tannins (tannic acid) authorised by legislation to be added to wines. The oak tannins also belong to this family and may be added to wines stored in wooden casks.

- ***Condensed tannins*** Condensed tannins are also known as proanthocyanidins and are polymeric flavonoids. The tannins found in grapes are mainly in the seeds and in small concentrations in the skin, and wines. They are mainly condensed polymers from flavan-3-ols (catechins) and from flavan-3,4-diols (leucoanthocyanidins).

3.5. Taste and mouth feel of phenolic compounds

According to Ron S. Jackson [17]. “Flavonoid tannins have a significant influence on the taste and mouth-feel of red wines. They constitute the major group of phenolic compounds. Mouth-feel is a tactile sensation, which would rather pick up the astringency, which is an interaction of phenolic components or tannins with proteins from the saliva. In contrast, non-flavonoids constitute the major phenolic group in white wines.”

Although abundant in red wines, tannins directly contribute little to the taste of wine but contribute to astringency. Nevertheless, polymerization of anthocyanins with tannins is important to the retention of tannins in wine [18]. Thus, the absence of anthocyanins in white wine helps to explain the lower astringency of white wines, given long skin contact or fermented with the skins.

Flavonoids are slightly bitter but, because of their low concentration relative to other flavonoids in red wines, they are most likely to have a sensory impact only in white wines. For example, the bitter flavanone glycoside naringin could contribute to the bitterness of varietal wines such as 'Riesling' and 'Silvaner' [19].

Catechins, and their polymers, the procyanidins and condensed tannins, are the major sapid substances in red wine. As they occur at well above threshold levels, they constitute the predominant source of bitter and astringent sensations. The smaller catechins and procyanidins are relatively more bitter than astringent. Small condensed tannins are both bitter and astringent. The larger condensed tannins have little influence on taste. They appear to be too large to react well with taste receptors or to precipitate proteins.

The small flavonoid content of white wines usually comprises flavan-3-ols (catechins) and flavan-3,4-diols (leucoanthocyanins). They give the wine body, and can add to the perceived quality of the wine. The quality classification of German wines, customarily based on fruit ripeness, has been correlated with increasing flavonoid content [20]. Nevertheless, the role of flavonoids in browning and bitterness (~40 mg/L) places an upper limit on their desirability.

Hydrolysable tannins, extracted from wood cooperage, can play a significant role in the bitterness and astringency of wine. As a group, they tend to be more astringent than condensed tannins. Their significance is generally greater in white wines, which have milder flavours and generally lack significant amounts of flavonoid tannins. Cinnamaldehyde and benzaldehyde derivatives, extracted from oak cooperage, add to the cumulative bitterness of the nonflavonoid content of white wines. The derivatives of hydroxycinnamic acid found in grape juice are usually joined via

ester linkages to tartaric acid. They often occur at concentrations that could contribute to bitterness in white wines [21].

Most phenolic acids such as caftaric acid occur at concentrations below the detection thresholds in wine [22]. Nevertheless, combinations of phenolic acids have lower thresholds than the individual components. This property may increase with the alcoholic strength of wine. Thus, phenolic acids may contribute jointly to the bitterness and flavour of wine phenolics.

At the typical content of about 25 mg/L, tyrosol could contribute to white wine bitterness. It may be more important in this regard in sparkling wines, where its level increases during the second fermentation.

Some phenol-related compounds may contribute to the peppery sensation associated with certain grape cultivars. 2-Phenylethanol and methyl anthranilate appear to have this effect. Other phenol derivatives generate a pungent mouth-feel or add to the varietal aroma of some cultivars. Besides the direct influence on bitterness and astringency, phenols have complex influences on the perception of sweetness and acidity. They also may have direct effects on the sensation of body and balance.

Marais [23] recorded an excellent correlation between anthocyanin levels and the flavour quality of wine, as shown in Figure 4.

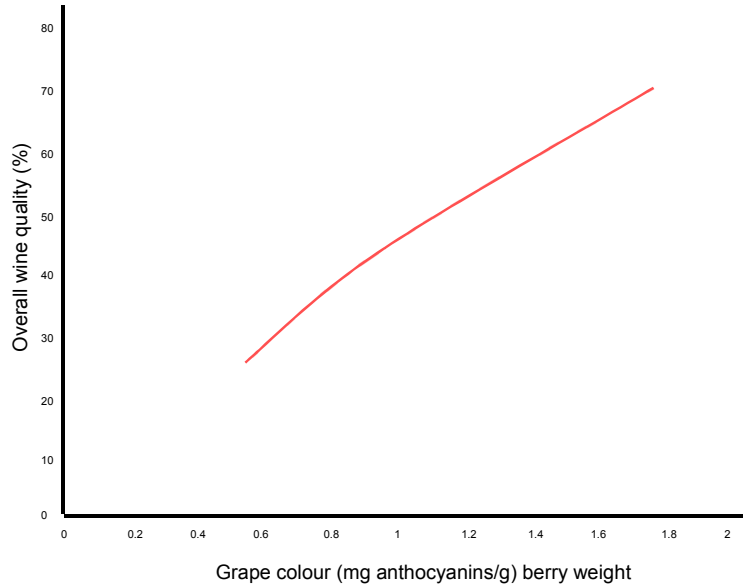


Figure 4: Correlation of concentration of anthocyanins vs. wine quality in Pinotage [23].

4. METHODS USED TO DETERMINE GRAPE RIPENESS

4.1. Determination of sugar concentration

Sugar is the component most frequently used to assess grape ripeness. It is used as a function of berry age because the sugar increases as the berry ripens. During ripening there is an initial rapid phase of sugar accumulation, but at some point during berry development and ageing the vine ceases transport of sugar to the fruit. Further increases in sugar concentration are due to dehydration.

Sugars are a category of carbohydrates distinguishable by the presence of several hydroxyl groups and an aldehyde or ketone group. The name 'carbohydrate' is also justified by the way these sugars are produced by photosynthesis in vine leaves, which shows the importance of water in ripening grapes. The principal grape sugars are glucose and fructose, and they occur in roughly equal proportions at ripeness. Sugars other than glucose and fructose do occur, but in relatively insignificant amounts. During ripening, the glucose-to-fructose ratio changes due to the action of an epimerase enzyme, which significantly increases the proportion of fructose. This ratio is monitored as a marker for grape ripening. The glucose-to-fructose ratio is in the order of 1.5 at colour change and drops below 1 at full ripeness.

In this study the percentage sugar (degrees Brix) of grape juice was measured by using a digital palm Brix refractometer. A high-resolution optical sensor measured the total reflection of a light emitted by a special LED light source after hitting the sample. This total reflection was then converted into degrees Brix. The Brix refractometer was zeroed using deionized water. A drop of the juice was placed on the inert sapphire prism and the sugar percentage in Brix was determined. Each degree Brix was equivalent to 1% of sugar in the juice [17, 24].

In practice, the sugar content is measured by a hand-held refractometer in the field. In the laboratory or winery the density of the juice is measured by a hydrometer, and read off as degrees Brix.

4.2. Other methods used to determine ripeness (excluding analysis of phenolic compounds)

4.2.1. pH of grape juice

Assessments of acidity are also used to define the optimal time of harvest. Acidity can be evaluated as either pH or titratable acidity or both [25]. pH is measured with an electronic pH

meter, normally calibrated with a standard buffer solution of pH 7.0 and pH 4.0. Titratable acid is measured by titrating the juice sample with a dilute standardised sodium hydroxide solution, using phenolphthalein as an indicator to determine the end-point of the titration. Changes in pH are complex and not necessarily a function of “berry age.”

4.2.2. Sugar/acidity ratio in grape juice

An historical index of ripeness suggests that an optimal sugar/acidity balance is achieved if the product of the Brix scale value multiplied by the square of the pH is in the range of 220 to 260. For example, a 22 Brix juice at pH 3.2 would yield a value of 225.3. Late harvest fruit at a higher pH (24 Brix at pH 3.6, for example) would yield a value (311) outside of this range.

Another scale relates titratable acidity and sugar level. In this case, the Brix value divided by the total acidity (TA) (g/100 mL tartaric acid equivalents) should yield a number around 30-32 for table wine production [26]. For a juice at 22 Brix with a TA value of 0.8, the number obtained would be 27.5. For a 24 Brix juice or must, the TA value could not drop much below 0.8 to meet this standard. Other authors suggest that this value can be higher (37-38) for late harvest fruit [27, 28].

However, the sugar/acidity ratio is quite variable across different varieties and growing conditions, and these kinds of universal rules of thumb may be of little general predictive value for wine quality, especially if indiscriminately applied [25]. Further, it is not clear whether the optimal sugar (ethanol)/acidity balance always coincides with optimal ripeness of grape flavourants.

From a survey of the literature, only the level of norisoprenoid flavourants appears to be correlated with sugar [29]. The norisopreniods are 13-carbon terpenoid molecules, thought to be derived from the degradation of carotenoids [29]. In general, the 13-carbon norisoprenoid characters (grassy, tobacco, smoky, kerosene, tea and honey) are far more stable than the fruity components (red fruit notes).

Changes in acidity level, as they reflect berry metabolic activities, may be useful to assess. It is well known that malate is consumed as an energy source in the berry during veraison, so malate levels decrease relative to tartrate. See Figure 5 [1, 3, 5, 6]. Tartrate levels generally remain constant during veraison, but may increase slightly during grape dehydration. Malate levels decrease as the acid is consumed by the fruit, and seem to plateau at a low level, at roughly 2 to 3 g/L [27,28].

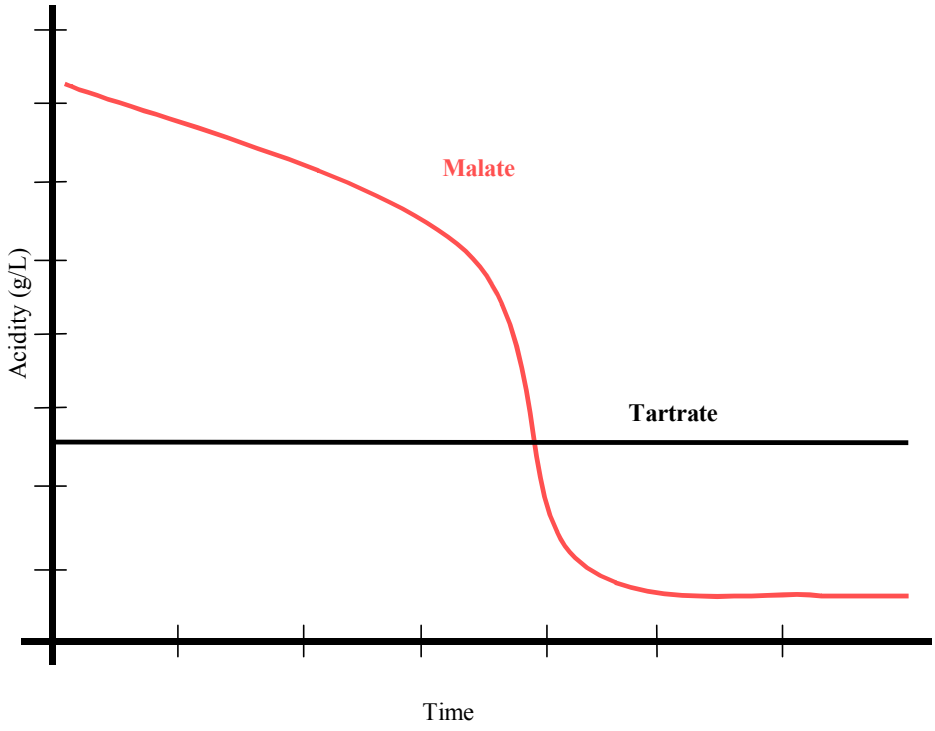


Figure 5: Changes in acidity during ripening, adapted from Bisson [2].

The grape may catabolize sugar if malate levels decline too much, but this varies significantly by varietal. Malate levels may be quite high in some red varietals post alcoholic fermentation. The synthesis of many grape flavour and aroma compounds requires energy, but the factors leading to cessation of synthesis of berry flavourants have not been well defined.

Sugar/acid balance models have commonly been used to determine fruit ripeness. An example of such a model is that described by Cox [30] to assess grape ripeness. This model is used to determine grape ripeness and is based on the sugar/acid balance. It states that if the product of the Brix and pH^2 is in the range of 220 for whites or 260 for reds then the fruit is ripe. Such models can be very useful when used in parallel with other fruit ripeness assessment techniques. (It should be noted, however, that the Cox index value range may not be suitable for red grapes grown in a warm climate, which often yield Brix*pH^2 values over 350 [31]). A similar model for determining grape ripeness uses the Brix value divided by the TA value (measured as tartaric and in units g/100 mL) of the grapes. Cox advocates a value of 30-35 for ripeness using this index, whereas Gallander recommends values between 30 and 32 [26]. Analysis of berry metabolites, proteins, or malate and tartrate content, are examples of other techniques that have been used.

However, the average home winemaker does not have access to the equipment required to carry out such analyses.

4.2.3. Malic acid vs. tartaric acid

Attempts to use the ratio of malate to tartrate as an index of ripeness also suffer from a lack of correlation of this ratio with grape flavourants development. Further, the ratio itself is quite variable across different varieties, growing conditions and seasons, and is of little true predictive value [25, 27, 28].

4.2.4. Berry weight

Any measure of grape ripening should correlate to wine aroma/flavour potential. Zoecklein [32], in a number of issues of the Vintner's Corner, has suggested the importance of using berry weight to help determine the progress of fruit ripening, as an aid in establishing consistent and optimum wine styles.

Many of the secondary metabolites (aroma/flavour and phenolic compounds) are located in the grape skins. Therefore, a change in berry size (easily measured by weight) can and should influence winemaking decisions. Berry weight should also influence fruit ripeness decisions.

The earlier the estimation of average berry weights, the more time the winemaker has to evaluate the crop load, make adjustments, and plan for the season. There is a relationship between berry weight at veraison and berry weight at ripeness. For Syrah, McCarthy (1997) determined that relationship to be the following:

$y = 1.35x + 0.53$

where: y = the berry weight at 23 Brix and x = the berry weight at about 5 Brix.

This relationship will differ by cultivar and site, but can easily be determined by collecting veraison and harvest samples over several seasons.

Changes in berry weight confound the measurement of degrees Brix, and is yet another reason why Brix must not be the sole parameter to monitor of fruit ripening. Research indicates that the maximum rate of production of aroma/flavour compounds in the fruit occurs at about the time when the berry stops importing water from the phloem, or shortly thereafter. Therefore, in most instances, maximum aroma/flavour occurs sometime after the berry reaches maximum weight. This is the reason why Syrah producers, for example, monitor the extent of berry shrivelling.

Results of studies carried out in Australia (Mike McCarthy, 2000) have revealed the optimum weight for this variety at harvest, for maximum concentration of secondary metabolites, to be about

1.2,g per berry. The decline in berry weight is more closely related to the time after flowering than to degrees Brix. The evaluation of berry weight is an important tool in stylistic winemaking.

4.2.5. Arginine levels

Another factor that has been reported in the literature as a useful indicator of berry status is arginine levels [35]. In theory, a decline in arginine content signals a deterioration of the fruit. However, arginine levels are so variable and subject to varietal and seasonal modification that this parameter is not always reliable [35].

4.2.6. Grape ripening (physical parameters)

Grape ripening can also be evaluated by assessing physical properties of the berry such as firmness and deformability [21]. Berry softening is due to changes in the composition of the cell walls of the fruit, particularly due to pectin and xyloglucan depolymerisation [22, 23] that accompanies arrest of xylem flow to the fruit [24].

Some winemakers taste seeds in order to assess grape ripeness. However, seed bitterness may be overpowering, especially to super tasters. Many individuals may not be able to accurately discriminate levels of seed bitterness. Physical characteristics of the seeds, namely colour, texture and brittleness, may be more important indicators of seed and therefore berry ripeness.

It is common to look at seeds, waiting for them to turn from bright green to tan-brown and begin to dry or become woodier-looking and feeling, as an assessment of ripeness. This also has some enological value, since more mature seeds in a maceration tank will yield less bitter and harsh tannins if they happen to be broken on pump over, or during pressing.

Cluster stems can also be evaluated to assess berry ripeness. Stems undergo a change from green and unripe, to brown or ripe stems, to overripe or brittle stems. These changes are varietal-specific. In some varieties, the stems never ripen beyond the green stage.

4.2.7. Grape tasting using the Institut Coopératif du Vin (ICV) method

Berry tasting constitutes a ripeness evaluation tool which, with a minimum of training, permits one not only to distinguish the degree of ripeness (and especially phenolic ripeness) but which equally helps indicate potential wine quality [36]. Indeed, there are important correlations between the sensorial profile of berries and wines; the gustative characteristics of tannins noted during the sensory analysis of berries are found later on in the wines they produce. Tasting is efficient when it is rigorous and guided by good sense.

In order for it to be both practical, rich in useful information, and passed on to a sufficient number of vintners, berry tasting requires a rigorous methodology, respecting rules of sensorial analysis. Institut Coopératif du Vin has fine-tuned a method of sensorial berry analysis comprising quantitative parameters. These parameters are called descriptors. They help establish the sensorial profile of berries, in the same way the sensorial profile of wine can be established. These 20 descriptors are listed below in Table 1. (Here the observations concern three types of grapes, chosen at random.)

Table 1: The 20 descriptors used in the ICV berry tasting method

	Whole berry	**Pulp**	**Skin**	**Seed**
Tactile examination	**1.** Mechanical resistance **2.** De-stemming aptitude			
Visual examination			**3.** Berry colour	**16.** Seed colour
Gustative examination		**4.** Skin adhesion Adherence to the pulp and the outer layer **5.** Sweetness **6.** Acidity **7.** Nature of aromas **8.** Intensity of aromas	**9.** "Chewiness": dilaceration aptitude during chewing **10.** Tannic intensity **11.** Skin acidity **12.** Astringency **13.** Tannic dryness **14.** Nature of aromas **15.** Intensity of aromas	**17.** Hardness of the seed **18.** Aromas **19.** Tannic intensity **20.** Astringency

The tasting procedure is a successive analysis of the pulp, skin and seeds. Apart from hearing, all senses are used: sight, touch, smell and taste. Each sense supplies important and complementary information. The different elements of the berry are successively analysed.

The following procedures are carried out in this order:

- Visual examination of the berries
- Pulp tasting (by chewing the berries, then by putting aside the skin and the seeds)
- Tasting the skin
- Visual examination and eventual tasting of the seeds.

After these procedures a grid of synthetic interpretation helps characterise the grapes degree of ripeness and its qualitative potential.

As berry tasting concerns 3-berry batches, it is necessary to carry out several tastings before passing an overall judgement to characterise a parcel or a batch of grapes. The tasted berries have to be chosen at random, from different clusters, from different areas of a parcel, for example during the harvesting of 200 berries for ripeness monitoring.

Berry tasting complements the chemical analysis monitoring ripeness. Up until now, so-called “technological” and “polyphenolic " ripeness have been defined according to chemical criteria. The pulp of berries contains sugars, organic acids, mineral substances and nitrogen. On a chemical plane, technological ripeness or pulp ripeness is achieved when the sugars reach maximum accumulation, with optimum ratios of sugar to acidity ratio.

The grapes’ most interesting polyphenols are essentially contained in the skin. The polyphenolic ripeness or skin ripeness is achieved on a chemical level when the concentration in potential anthocyanins that a grape can deliver starts to diminish after reaching a plateau.

With the ICV methodology, it is possible to note different sensorial evolutions for the three main compartments of the grape berry.

The pulp becomes sweet, low in acid, it softens, loses its adherence to seeds and the skin. It develops fruity aromas and darkens in colour when pulp ripeness is achieved.

The skin is more or less thick, depending on the grape varieties or vintages. During ripening, the colour becomes black for the red varieties, while it becomes golden yellow for the white varieties. The skin loses its suppleness, and the tannic intensity increases while the tannins become less acid and less astringent. The aromatic level increases and develops fruity notes, followed by jammy characteristics when skin ripeness is achieved. Recent studies show that the sensation of dryness and astringency of tannins is more linked to the presence of polysaccharides in solution than the tannins' actual nature.

The seeds change from green to a brown or a uniform yellow colour, and once all traces of green have disappeared it is then possible to taste them. The tannins become less dry, and less astringent. The seeds become hard and brittle, and lose their grassy aromas for toasted notes, which become roasted once the polyphenolic ripeness has been reached.

Skin ripeness is often reached after pulp ripeness. Technological ripeness or pulp ripeness is often reached when the grape is far from phenolic ripe or skin ripe – there can be a time-lapse of up to a week. Sometimes skin ripeness is not achieved, especially on certain loaded parcels, or during certain vintages.

4.2.8. Grape tasting using the Gironde method

The Gironde method [37] calls for a separation of skins from pulp and seeds. While potentially tedious, this is essential for good sensory work, and results in a wine-like supernatant that may be examined visually, tasted, submitted to analytical quantifications, and preserved for future comparison with results of subsequent samples. This protocol is entirely subjective and, therefore, dependent upon the style of wine desired. It is meant to be modified by each producer to meet his or her individual needs. It is suggested that careful records be maintained over time so a historical database can be built, using wine grape sensory data correlated to wine grape chemical ripeness data and, finally, to finished wine data – to develop a ripeness profile best suited for each wine style.

Comparative (rather than quantitative) anthocyanin determination is a critical element of any acceptable protocol. The Gironde method has the longest track record in field use and has earned acceptance in Europe for monitoring the peak and decline of pigment within a block during ripening. Since seed tannin is not extracted here, co-pigmentation may be minimal and this method should hence not be viewed as a total colour or extractable colour method for predicting wine composition.

The sensory and analytical protocols for the Grape Skins Sensory Evaluation Procedure are as follows:

- Reagents used:
  Citric acid solution (9.25 g/L)
  Ethanol (96% purity).

- Instruments and apparatus used:
  Waring variable-speed laboratory blender
  Mass balance, to determine mass to 0.1 g precision
  Beakers and volumetric cylinders.

- Method:
  The method involves the collection of 150 berries at random in a block to be sampled. The skins are removed by squeezing the pulp and seeds out between the thumb and forefinger. An alternate method states that the berries can be dissected using a razor blade, making a

slice around the equator of the berry and scooping the pulp out. Either method may be utilised to separate the skins for sensory evaluation. The skins are retained and weighed (approx. 60-120 g). The separated juice can be used for Brix, pH and TA determinations. The seeds can be utilised to test for their hardness, as another indicator of berry ripeness, as described by Gordon Burns [38].

- Procedure:

1. The skins are placed in a blender and 75 mL of the citric acid solution added. This mixture is blended using short pulsing strokes until well mixed. The final pH should be approximately 3.5.
2. The balance is tared prior to pouring the crushed skins/citric acid solution into the beaker. The blender is rinsed with a small aliquot of water that is added to the crushed skins mixture.
3. The equivalent of 8% alcohol is added to the crushed skins, calculated on the original mass (wt) of the 150 berries as follows:
   wt of 96% ethanol added = (dilution factor) x (0.08) x (wt of 150 berries)/alcoholic strength
   where the dilution factor is 1.09 for 96% ethanol or 1.17 for 90% ethanol.
4. Water is added to the tared beaker until the original mass of the 150-berry sample in step 2 above is reached.
5. This turbid solution is poured into a bottle that can be sealed and this sealed bottle stored overnight at room temperature. Alternately, the solution can be shaken every hour for 6 hours.
6. The solution is filtered through a rough pad to remove the solids.
7. The filtered solution is then tasted, and the intensity of the aromatics and the quality and concentration of the tannins present is recorded.
8. The points (in italics) below are to be used as a guide in the evaluation of the grape skins solution:
   Colour: Intensity from 1 to 5 (arbitrary, as extraction method will be the most important determinant of actual colour concentration).
   Flavour: Distinguished into unripe, slightly ripe, near ripeness and mature.
   Unripe grapes usually have cherry stem/vegetal/green type flavours and obvious high acid concentration.
   Slightly riper grapes give red fruit flavours such as strawberry/cherry or even green apple flavours, with marked tartness on the palate.
   Nearer ripeness, grapes begin showing black fruit flavours but lack real intensity and concentration, with slight green apple tartness still evident.
   Mature grapes show rich, deep black fruit/spice characters.
   Concentration of flavours: Given on a scale from 1 to 5.

Tannin quality: Ranking of the tannins: are they green, bitter, hard, softening, etc?

Finally, and most importantly, *is the ripeness appropriate for the style of wine to be produced?*

4.2.9. Near-infrared analysis

A correlation between near-infrared (NIR) spectroscopy and analysis of total anthocyanins (colour) has been developed by Dambergs et al. [39]. An excellent linear relationship with a high degree of confidence between NIR data and reference colour concentration was found. It has been known for some time that, within certain specific limitations, grape and wine colour generally correlate with wine quality [40, 41]. Thus this technique can be used to determine quality, however, the experimental procedure takes approximately four hours.

4.3. Methods of determining the phenolic content

4.3.1. Folin-Ciocalteau method

The Folin-Ciocalteau (FC) Micro Method for Total Phenols in Wine was initially developed by Skinard et al. [42] and modified by Andrew Waterhouse [43, 44]. It has been successfully used for more than 30 years in the wine industry. The first paper on this method was published in 1927, and in 1965 Singleton and Rossi improved the reproducibility of the assay. Swain and Goldstein in 1962 considered this the method of choice for estimating total phenol content in complex plant products. This is a sensitive and quantitative method, independent of the degree of polymerization.

This measurement involves the measurement of the concentration of total phenols (tannins and many phenols that are not tannin). The method involves a spectrophotometric analysis based on a colorimetric oxidation/reduction reaction, relative to a standard of gallic acid, i.e. all phenolic groups such as quercetin and anthocyanins will be measured. This is a colorimetric oxidation/reduction assay that measures all phenolic molecules with no differentiation between gallic acid, monomers, dimers and larger phenolic compounds. A gallic acid standard curve is used and results are typically expressed as gallic acid equivalents (GAE).

It can be summarised as follows:
Phenolics + alkaline + FC reagent + heat = blue coloured product (Abs 765 nm).

4.3.2. Patrick Iland method

The Patrick Iland method is based on the ethanol extraction of the pigments from a known mass of macerated whole grapes [45]. A portion of the ethanol extract is then diluted with 1 N HCl and the absorbance of this solution measured on a spectrophotometer at 520 nm. The calculation of red

pigments is based on the use of the extinction coefficient of malvidin-3-glucoside, and the result is expressed as equivalents of this anthocyanin.

Measurement of the absorbance of the diluted extract at 280 nm provides an estimate of the concentration of total phenolics in this solution. This is expressed as absorbance units.

Studies have shown that the measure of grape colour can serve as a predictor of wine colour. In practice, the measure of grape colour can generally predict if a wine will be lightly, moderately or intensely red coloured. In some cases it can also provide an indication of the flavour intensity of the wine and wine quality.

4.3.3. Roger Boulton method

The Roger Boulton method was originally designed by Somers [46], and modified by Roger Boulton [47], to include co-pigmentation corrections and to shorten the analysis time to two hours.

Total anthocyanins are calculated (Boulton) but this is a little confusing. Boulton defines "anthocyanin" as referring only to monomeric pigment compounds. Therefore, he does not consider polymeric pigment as part of "total anthocyanins". Contained in this definition is the presumption that bleachable pigment is only monomeric, and also that there are no significant un-bleachable monomers that can actually be called anthocyanins. While this value is good for attributing the contribution of these species to visible colour, the measure at pH 3.6 is on the shoulder of the ionisation curve of the Malvidin-3 Glucoside, which will vary within the anthocyanin group and with alcoholic strength. This makes the application of a molar extinction coefficient (in order to estimate the molar ratio against flavonoid monomer) likely to be inaccurate by as much as a factor of two.

4.3.4. Glories method

The Glories method involves an extractability assay as an indicator of phenolic ripeness. A sudden decrease in this assay will indicate a breakdown of the cellular structure of the skin and mark the beginning of over-ripeness [48]. Together with the traditional methods of determining grape ripeness, the analysis of phenolic ripeness is an invaluable tool to assess the ripeness of grapes. The Glories method is particularly useful to people who do not have the ability to taste phenolic ripeness as has been established by the author.

The Glories method can be used to determine the quantity and extractability of anthocyanins, the tannins in the seeds and the sum of the two, i.e. the total phenol content. This method entails rapidly (relative to wine fermentation) extracting the anthocyanins from the grape skins, gently at first and then under more extreme conditions, breaking the diffusion barriers of the cell walls.

Crushing the seeds results in partial extraction of their tannins, which is necessary to assess the characteristics of the grapes. In the Glories method two aqueous solutions, at pH 3.2 and pH 1, are used. The acid medium ruptures the proteophospholipid membrane, breaking the protein bonds and, consequently, releasing the contents of the vacuoles. All of the anthocyanins are then extractable and solubilised in the pH 1 solution. At pH 3.2, extraction is approximately comparable to the extraction occurring during the fermentation of wine. If the membrane is not porous, anthocyanins circulate very little, but if it is broken down by grape enzymes, the pigments are released from the vacuoles and extraction tends towards the same levels as during the fermentation of wine. The difference between the results obtained at both pH levels reflects the fragility of the membrane, as it relates to the pigment extraction potential and indicates the level of ripeness of the grapes.

The UV absorbance measured at 280 nm is used to determine the total phenol content. The smaller the difference between the extractable values of the pH 1 and pH 3.2 of the anthocyanins, the higher the value of the anthocyanin extractability (Ea), and therefore the more easily extractible are the anthocyanins. The anthocyanin extractability increases as the grapes ripen. The higher the contribution of the tannins from the seeds to the phenol content (Mp), the higher the tannin content of seeds and the greater the risk that the tannin concentration may have a negative effect on the flavour of wine. The Mp value decreases during ripening [6].

In order to determine the ripeness of grapes the amount of extractability can be measured by means of pressing the berries and comparing this to crushing the berries. It is important to calculate the contribution of extractables of the skin and pulp and compare this to the extractables from the seeds.

5. USE OF THE GLORIES METHOD TO DETERMINE PHENOLIC RIPENESS

5.1. Worldwide

This method was developed in Bordeaux by Glories in 1990, and is now accepted as the most commonly used method to evaluate the phenolic content of grapes. Several laboratories have however made some changes to the method or, in some instances, used other methods. In general it is found that individuals are secretive about the application of the results or the interpretation, possibly because of the topic of phenolic ripeness being so fashionable. Most people, at various laboratories, that the author has spoken to have all used this method as a starting point to their investigation into phenolic ripeness and hence the method is still accepted as the main method used in the determination of phenols. Brief mention is made below of the results of phenolic ripeness determinations carried out in other countries. No detailed explanation or interpretations is offered.

5.1.1. Chile

In two commercial vineyards of the Merlot variety, located in Molina (Curicó Valley) and Pencahue (Maule Valley) [49], periodic measurements were carried out using the Glories method. Several samplings were carried out in the same vineyard between the 22nd of February and the 10th of March 2002, to evaluate the application of the Glories analysis.

The results obtained showed that the anthocyanins increased and peaked at the date of harvest in the Molina vineyard, however, results found in the Pencahue vineyard were erratic and thus the harvest date was rather determined by sensorial evaluation. It was quoted that: “The method of Glories was capable to predict the phenolic content of wines in Molina, however in Pencahue, it failed to predict the harvest's date, due to unclear results” [49].

5.1.2. Spain, Rioja

The anthocyanin concentrations of Vitis vinifera Cabernet Sauvignon, Merlot, Syrah and Monastrell grape skins were determined together with anthocyanin extractability at the exact time of harvest by the Glories method. The method was slightly modified from the original method in that the extractable anthocyanin quantity was measured at a pH of 3.6 instead of 3.2. The data obtained, see Table 2, and is compared with the anthocyanin concentration in the resulting wines. Monastrell grapes from the Jumilla area had the highest anthocyanin concentration, but the extractability percentage was not that high. The extractability of the anthocyanins of the Cabernet Sauvignon, Merlot and Syrah indicated that they could be extracted easily, which was confirmed by

the chromatographic analysis of the resulting wines. Cabernet Sauvignon and Syrah wines presented the highest wine colour intensity, although their anthocyanin concentration in the grapes was lower than that of Monastrell grapes [50]. Results indicated that the above extractability assay could be useful for predicting some important chromatic wine parameters and for planning the fermentation process according to the characteristics of the grapes at the exact time of harvest and the desired wine.

Table 2: Results of Glories method analyses, illustrating examples of analyses carried out in Spain [50]

Sample	A pH1 (mg/L)	A pH3.6 (mg/L)	Ea (%)	PFT (pH 3.6)	SRI (%)
Monastrell-B	556.2	266.9	52	24.1	55.8
Monastrell-J	652.3	304.6	53	28.1	56.5
Cab. Sauv.	524.4	358 8	32	35.3	57.4
Syrah	669.2	455.0	32	34.4	47.0
Merlot	481.0	329.0	31	40.7	67.6

A pH1: anthocyanins extracted at pH 1; A pH3.6: anthocyanins extracted at pH 3.6; Ea: extractability index; PFT (pH 3.6): total phenol content of the solution at pH 3.6; SRI: seed ripeness index.

In addition, the Rioja vintages were reported on by the Control Board [51], the 2003 vintage was rated as "good" based on the total phenol index (TPI). The tables below show data for the 2003 vintage, as well as the vintages from 1995 leading up to the 2003 vintage.

Table 3: Analytical data for Rioja, 2003 vintage rating, using TPI

Wine	Alcohol (%)	TA (g/L))	pH	Volatile acidity (g/L)	Total SO_2 (mg/L)	Colour index (A420+A520+A620)	TPI
Red	13.25	4.99	3.68	0.50	54.08	7.34	50.6
Rosé	12.97	5.69	3.36	0.30	78.25	0.68	11.9
White	12.61	5.78	3.29	0.26	83.18	0.14	9.42

Table 4: Analytical data for Rioja, 1995-2003 vintage rating, using TPI

Parameters	**1995**	**1996**	**1997**	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**
Alcohol content (% vol.)	12.78	12.69	12.81	12.53	12.89	12.55	13.26	13.28	13.25
Total acidity - Tartaric (g/L)	4.96	5.20	5.06	5.09	5.23	5.09	5.13	5.42	4.99
PH	3.72	3.64	3.74	3.66	3.71	3.66	3.68	3.70	3.68
Volatile acidity - Acetic (g/L)	0.44	0.41	0.50	0.42	0.46	0.47	0.47	0.51	0.50
Total SO_2 (mg/L)	44.0	40.72	68.94	50.06	56.16	43.48	45.48	44.83	54.08
Colour Ind. (A420 + A520 + A620)	6.84	6.94	5.56	5.64	5.70	6.92	*9.80	*9.38	*7.34
Total polyphenol index (TPI)							50.63	52.78	50.61

*Includes A620

5.1.3. Italy, Alba

The centre for oenology is the main analysing body for the region of Alba. The method of evaluation employed is a modified Glories Method (modified by Mattiwi, F) [52]. Approximately thirty percent of the estates use phenolic ripeness as a tool to monitor ripeness. This method is extensively used for grape varieties such as Barolo; most estates do not use it on the other varieties grown in the area. The modification of the method is a slight shift in the absorbance at which the anthocyanins are measured. Barbera, Dolcetto and Cabernet Sauvignon are measured at 540 nm and Nebbiolo at 536 nm.

5.1.4. Italy, Sicily

A variety of cultivars (Merlot, Cabernet Sauvignon, Syrah and Nero d'Avola) were evaluated during the 2000 harvest in Sicily. This particular harvest showed some extreme temperatures, some days being as high as 45 ^{o}C, and, in addition, little rainfall was experienced. The Cabernet Sauvignon vineyards were not irrigated. The anthocyanins for the three vineyards that were measured were, 2 280, and two at 1 700 mg/kg. The lower two values were attributed that the plant shutting down due to excessive temperatures whereas the third vineyard was at some altitude. Seed tannins (Mp) were high and the extractabilities around 45%, indicating that the grapes were not really phenolically ripe. In contrast, the Merlot grapes showed a higher potential anthocyanins of around 2 400 mg/kg. Similarly, Syrah also showed higher levels of anthocyanins of around 2 400 mg/kg. Nero d'Avola showed the lowest amount of anthocyanins of 1 700 mg/kg. In all cases the extractability was very low – the highest was 50%. This indicated that the grapes were not ripening phenolically due to the extreme heat [53].

5.1.5. France, Bordeaux

In Bordeaux, with the release of the 2005 statistics, it is a numbers game. The producers have run out of superlatives and are turning to statistics to get their point across – namely the use of the total phenol index (TPI) [54].

The world's wine hacks are inundated with figures and indices – measures of sugar and alcohol, tannin and acid. Ancient cellarmen's memories are invoked to give credence to the claim that 2005 is the best vintage in living memory.

Paul Pontallier at Margaux first described the gossamer airiness of his wines, and then turned to the TPI tannin index. The quantity of tannins is measured on the total polyphenol index (TPI). In 2000 it was 70 and in 2003 it was 73. This year it is 78. Just to put this in perspective, in 1982 it was between 62 and 63.

Pontallier claims that the Merlot alcohol levels were the highest that had been seen in 100 years – 'it went up to levels unheard of.' However, he made clear that the higher-alcohol Merlot was only used for the second wine, Pavillon Rouge.

Margaux itself is a powerful, though balanced wine. It was “no special effort”, he said, “to make the biggest, most concentrated wine. It is even more concentrated than the 2003.” Steven Spurrier said, “It is wonderful, seductive. It is final proof of an appellation of distinction.”

Pontallier was also at pains to point out there are limits to alcohol levels. For the Margaux terroir, there would never be a truly great wine at 13.5% or above. “For me, high alcohol is a real enemy of fine wine.' With the spectre of global warming in mind he added, “Ideally nature will stop here.”

At Chateau Teyssier in St Emilion, Jonathan Maltus was picking Merlot at 15.5% alcohol – two degrees higher than normal, and Philippe Blanc at Chateau Beychevelle said, “…the Merlot has never reached levels as high as this. Many batches were coming in at 14.2 or 14.3.” The normal level is 13.5 degrees.

If sugar and alcohol are high, tannin measurements are equally unusual. Mouton-Rothschild's director Herve Berland said various parcels had “enormous” TPI of “more than 100”.

Berland stressed that TPI measures quantity not quality. This year of course, as in everything, quality is excellent. “The tannins are ripe, well put-together, and clear.”

There are properties at which the levels of acidity, tannin and alcohol are high but not astronomical. At Pichon Lalande, technical manager Thomas Do-Chi-Nam recognised “quite high acidity” but made it clear that 2005 is actually bringing the levels back to normal. “In previous years – especially 2003 – acidity has been too low.”

What every producer is hoping for, as always, is balance, and it seems that this year the elements have come together to create this equilibrium. The wines are not big in the sense of over-extracted – successive critics across the region attest to this – but they are “voluptuous, and silky” as Jean-Guillaume Prats described his Cos d'Estournel

This is true of wines in all regions of the left bank, from St Estèphe to the Graves and Sauternes. But many critics are sounding notes of caution when it comes to the right bank.

One tasting in particular, the new grouping of the Cercle du Rive Droit – some 120 wines primarily from St Emilion, Pomerol and satellites – has come as a relative disappointment. Tasters consider some the wines not up to the general standard – “some are over extracted, overly oaked, even showing some green notes,” one prominent critic said.

5.1.6. Tunisia and Turkey

Nicolas Vivas, of Demptos France has extensively used the Glories method for vinification in France, Tunisia and Turkey [55]

5.2. In South Africa

5.2.1. Wine estates and wine farms

Fairview [56] was one of the earliest estates to analyse the phenolic ripeness using the Glories method. The operator had been trained in Bordeaux for a one-month period, however, the erroneous use of some of the calculations proved how secretative the French were in sharing the methodology. A typical example of phenolic ripeness results, as determined by the Glories method, is given below in Table 5.

Table 5: Phenolic ripeness results from Fairview, as determined by the Glories method [2003]

Sample	Date	Brix	pH	TA	Mass 200 berries (g)	PFT	Total anthocyanins. (Δd1 – Δd2) x 875	Ea (%)
Houmoed [CS] Stellenbosch	11 Mar	23.9	3.85	3.85	215.5	55.3	39.4	52.3
Block 14 [MO]	10 Feb	24.3			263.2	44.2	61.3	67.0
Block 14 [MO]	12 Feb				242.7	38.6	35.9	55.0
Houmoed [MO] Stellenbosch	6 Mar	23.3	4.00	4.70	288.0	19.0	11.4	47.8

Vrede en Lust [57] was, to the author's knowledge, the first estate in South Africa to evaluate phenolic ripeness via the Glories method. The reason for this was that they employed a French winemaker who had been trained in the methodology. Stephane de Saint Salvy, the winemaker, expressed that he had used the method very successfully and that he was extremely happy with the additional information that it provided him with in assessing the ripeness of his grapes. Although very helpful in sharing the assessment of the grapes, any results were secretively guarded. It is difficult to assess whether the quality of the wine produced was influenced by any results from the Glories method.

Vergelegen, Andre van Rensburg, the winemaker, is very controversial to say the least, but during the 2003 and 2004 season he was very happy about employing the Glories method as an additional tool. He quoted that the extractions values that he obtained were extremely good and that this was one of the contributing factors towards the quality wines he made.

When Andre van Rensburg was interviewed during 2006, however, he expressed that phenolic ripeness was of little value and that the aim was to pick grapes at a lower Brix in order to achieve a lower alcohol, which was required for the export market. Unfortunately no more comment was received.

Lourensford has set up a laboratory to evaluate the Glories method. See report on interview with the viticulturist in Section 7.

Various other estates have used the Vinlab laboratory [60], details were not obtained.

Various other estates have used the Author's laboratory [61] for the commercial evaluation of phenolic ripeness from 2004 onwards. Results may be mentioned later, where necessary, to

highlight significant findings. In addition, KWV Limited made use of the author's laboratory to evaluate the intake of the 2006 vintage.

6. GRAPE PRICING IN AUSTRALIA BASED ON COLOUR

Brown Brothers [62], for the last nine years, have been measuring berry colour and using it for grape pricing. The reason for this is that there are many growers in the King Valley (which has an excess vigour) and some of the fruit was not meeting expectations. Most growers had 10-year contracts, which did allow the price to be varied on fruit quality, but did not specify how quality was to be determined.

The following are some of the benefits of using a colour measure according to Brown Brothers [62]:

- "Colour has a direct correlation with quality. All other things being equal, and in the quality range we were dealing with, the best wines had the highest colours, and the worst wines had the lowest colours.
- The measure is readily understood and accepted. As opposed to some other chemical parameters we could have measured, colour was well understood by the growers as a quality factor.
- It allows immediate feedback to growers. The growers are told of their colour score within a few days of delivering their fruit, so they can then assess their vineyard management and plan what they can do the next year. The Brown Brothers thought that colour measurement was preferable to a vineyard grading scheme based on wine classification, as we didn't have enough history on the vineyards. If the growers made changes and improved their grapes, we wanted them to be immediately rewarded.
- The system is objective and quantifiable.
- It is a grape measure, not a wine measure. Any measure of wine quality has the added complication of winemaking variables. To keep it simple, and maintain grower confidence in the measure, we wanted to be looking at grapes, not wine.

Some of the drawbacks however are:

- Extra work is involved.
- The price is not known until harvest. This presents challenges in cash flow planning, for the grower and the winery, but that's farming!
- Colour is not everything. It is a good guide to quality, but it is not quality.

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So how do we use this in our grape pricing? There are four elements in our pricing scheme. The following is the pricing model we use for Cabernet, Shiraz, and Merlot. Firstly we take the base price, which for these varieties is AU$ 1,100**. To get the base price, the fruit must be delivered at 23.5 Brix. There is a 2% bonus for every 0.2° above 23.5°, up to a maximum of 24.3°. And there is a 2% deduction for every 0.2° below 23.5°. So the base price can vary from about AU$ 600 to AU$ 1,210 just on a Brix reading.

The next element of our pricing is a botrytis deduction. We make deductions for fruit infected with botrytis based on a laccase measurement, laccase being the enzyme produced by botrytis, and it is the laccase that does the damage, destroying colour and tannins. The test is fairly simple and reliable. It is a propriety test from Novo Nordisk [63], with the result being a colour change that is measured either against a colour chart or on the spectrophotometer.

On the basis of the result of that test, deductions may be made.

0.1 or less laccase units	No deduction
0.2 to 1.0 laccase units	10% deduction
1.1 to 3.0 laccase units	20% deduction
3.1 to 8.0 laccase units	40% deduction
Greater than 8.0 laccase units	60% deduction

These are pretty savage penalties, but botrytis can do severe damage to wine quality. We find this is more accurate than visual assessment in determining the amount of damage that botrytis is doing to the wine. The highest levels of laccase tend to be in berries with "slipskin" botrytis, rather than "furry" botrytis. Slipskin botrytis, what you might call the pink berry stage in white grapes, cannot be detected visually in reds, so we gave up on visual assessments.

The final element of our grape pricing is the colour bonus. We take the berry colour figure we measured in the lab. For the three main varieties, Cabernet, Shiraz and Merlot, the colour is usually in the range of 11 to 20 colour units. We pay a bonus of $100 for every colour unit above 10, giving a total colour bonus of between $100 and $1,000. With a base of AU$ 1,100, this bonus can make up a significant part of the total payment.

How has the colour improvement been achieved? A number of things have changed over the period and contributed to the increase:

• Canopy modification. Nine years ago, most of our growers' vines were trained on a two wire vertical system and left to sprawl during the season. That has changed completely, with some form of divided canopy being the norm, no one system has been adopted. Each grower seems to have his own version of a Scott Henry or Smart Dyson system, as suits his site and personal preference. The end result has been to make canopies less dense, the leaves more effective and to expose the fruit more than in a sprawl canopy but not so much that it burns or cooks.

• Better vine balance. Here I'm talking about crop load, and leaf area to fruit weight ratios.

• Better irrigation scheduling.

• Grower turnover. To some extent market forces have driven this, without us needing to be too interventionist about it. The King Valley has been our primary source area for premium grapes. Other wineries buying in the area are either much smaller, or are large wineries buying in many districts. All our competing wineries have, until recently, paid a standard price with provision for a small subjectively assessed quality bonus. Our prices start well below our competitors' standard prices, and finish well above it. It didn't take long for the good growers to work out they would do better with us. And likewise, growers who still wanted to produce huge crops of poorly coloured fruit from sprawl canopies worked out that other wineries weren't quite as discerning, and they went elsewhere. And that suited us just fine.

The growers want to grow better grapes, and are happy to put in the extra effort and manage their crops better, provided they are rewarded for it. The dollars we allocate to the colour bonus have increased over the years to ensure the return-per-hectare incentive is there for the better fruit. We started fairly tentatively with a high base price and a colour bonus of AU$ 40 per unit. As our confidence, and our growers' confidence in the scheme increased, the colour bonus moved to AU$ 70, then AU$ 100, with concurrent reductions in the base price. We are very happy with the way the scheme works now. The only foreseeable change is the possible adoption of Near Infrared Reflectance technology to simplify and improve reliability of the colour measurement."

**AU$ = Rand 5.30

7. RESULTS AND DISCUSSION OF AUTHOR'S EVALUATION OF PHENOLIC RIPENESS IN SOUTH AFRICA

7.1. Introduction

Grape samples were taken by the author over a four-year period in and around the Stellenbosch area. These and several other samples were analysed commercially in the author's laboratory [61]. The aim of the experimentation was to search for a cost effective method that the grape farmer could use as an evaluation tool, and hence the use of expensive equipment such as a high-pressure liquid chromatograph (HPLC) was not utilised in this study. In 2003, 144 samples were evaluated using the Glories method as well as the GAE method, as a comparison. In 2004, 325 samples were evaluated using the Glories method and use of the GAE method continued. Simultaneously, the methodology of the Glories method was evaluated. Results were used to evaluate the optimum experimental conditions and to establish whether the total analysis time of five hours could be reduced. In 2005, 432 samples were evaluated using the Glories method and the GAE method was abandoned. During this year various factors that might influence the phenolic ripeness were evaluated. In 2006, 924 samples were evaluated using the Glories method and a few comparisons made with the Patrick Iland method.

In the case of the samples taken by the author, these were always sampled during the early morning hours, between 05h30 and 08h30. Samples were never taken on a day when it was raining or on a day when rain had persisted during the night. Each block sampled was restricted to the same number of rows evaluated, which numbered between two and six rows. The analysis was limited to these rows so as to evaluate the same section at each sampling. Berries were taken at random and half the sample was always taken from one side of a row, to have at least average sun and shade exposure. Berries were taken at random from bunches at the top, middle and bottom. Bruised or infested berries were never included in the samples. Samples were always evaluated on the day of picking, except in the instance of the commercial service when it was not viable due to the late arrival of the samples. In this case the samples were immediately refrigerated at 4 ^{o}C until the following day. The refrigerated samples were allowed to acclimatise to room temperature for 30 minutes prior to analysis.

7.2. Various methods used to analyse phenolic ripeness

7.2.1. Folin-Ciocalteau

Reagents used:

Gallic acid stock solution. In a 100-mL volumetric flask, dissolve 0.5 g of dry gallic acid in 10 mL of ethanol and dilute to volume with water. To store, keep closed in a refrigerator, for up to two weeks.

Sodium carbonate solution. Dissolve 200 g of anhydrous sodium carbonate in 800 mL of water and bring to the boil. After cooling, add a few crystals of sodium carbonate. After 24 h, filter and make up to 1 litre with distilled water and FC reagent (Sigma Aldrich). FC is an oxidising agent of heteropolyphosphotungstate-molybdate.

Instruments and apparatus used:

Perkin Elmer Lambda 2 UV/VIS spectrophotometer.

Procedure:

A standard curve must be drawn up each time the analysis is run.

1 To prepare a calibration curve, add 0, 1, 2, 3, 5, and 10 mL of the above phenol stock solution into separate 100-mL volumetric flasks and then dilute to volume with water. These solutions will have phenol concentrations of 0, 50, 100, 150, 250 and 500 mg/L gallic acid – the effective range of the assay.
2 From each calibration solution, sample, or blank, pipette 20 µl into separate cuvettes and to each add 1.58 mL water and then add 100 µL of the Folin-Ciocalteau reagent (Sigma) and mix well. Wait for between 30 sec and 8 min and then add 300 µl of the sodium carbonate solution and shake to mix. Leave the solutions at 20°C for 2 h and determine the absorbance of each solution at 765 nm against the blank (the "0 mL" solution). Plot absorbance vs. concentration. Alternatively, solutions can be left at 40°C for 30 min before reading the absorbance.
3 For red wines, dilute the wines by 10 first, then add 20 µl (or skip the dilution and add 2 µl if you have an accurate micro pipette).
4 Create a calibration curve with the standards and determine the phenol levels in the samples. Do not neglect to multiply the observed concentrations by any dilution factor of the original sample. Results are reported as gallic acid equivalents, because the phenols in wine contain mostly other phenols and only small amounts of gallic acid.

Interferences have been noted due to reducing sugars, sulphites and ascorbate.

Reducing sugars such as glucose and fructose cause minor interferences and must be corrected.

Sulphites also cause interference but the magnitude is variable. It is usually not an important factor except for white wines with medium to high sulphite levels (>50 mg/L) and low phenol levels (<250 mg/L).

Ascorbate is another chemical compound that can cause interference with the spectral analysis. It has a relative mass response of 0.68, so a wine with 30 mg/L ascorbate must be corrected by subtracting 20.4 mg/L from the total phenol value. This assay is responsive to any reducing substance, so if applied to other types of samples, large errors could be encountered.

Since the assay measures all phenolics, the choice of gallic acid as standard is based on the availability of a stable and pure substance – and gallic acid is both. It is also less expensive than other options. In addition, the response to gallic acid has been shown to be equivalent to most other phenolics in wine on a mass basis. The stability of gallic acid standard solutions has been tested and found to lose less than 5% of their value over two weeks when refrigerated and kept tightly closed.

Calculation for the determination of the gallic acid equivalent (GAE):

A standard curve of absorbance versus the concentration of gallic acid (in mg/100mL) is drawn up and the equivalent amount of gallic acid calculated from this by comparing the absorbance of the grape sample after adjusting for the absorbance of the blank solution. The gallic acid equivalent (GAE) value is expressed as a concentration of gram/L and is obtained by multiplying the concentration from the standard curve by 10 000.

To illustrate an example of the calculations for the gallic acid equivalent, grapes from Kanonkop Estate [64] Block 103 were used. Results are shown in Table 6 and 7, and graphically depicted in Figure 6. The grapes were sampled on 1 March 2004.

Table 6: Data obtained from Kanonkop Estate to draw up a calibration curve for GAE analysis

Gallic acid concentration (mg/100mL)	**Absorbance at 765 nm**
0.1992	0.2586
0.3984	0.4934
0.5976	0.7164
0.7968	0.9051
0.9960	1.1180

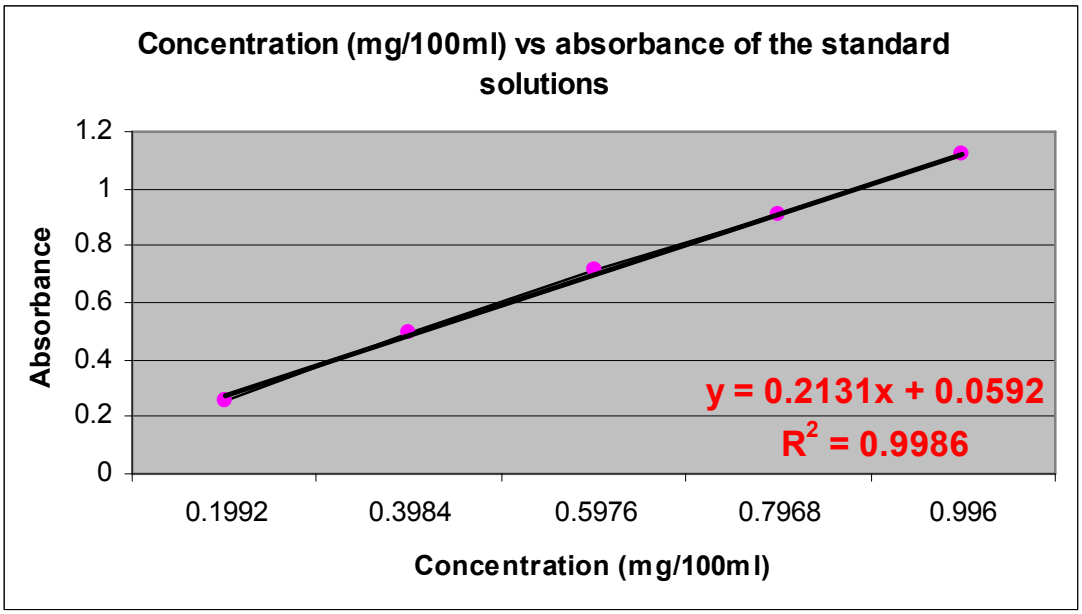

Figure 6: Graph indicating the calibration curve of absorbance versus gallic acid concentration.

Table 7: Results of the absorbencies of grape samples and a blank, illustrating the GAE analysis

Samples	Absorbance at 765 nm
Blank	0.0041
Block 103	0.1395

Calculation of GAE for Block 103:

$Abs_{Corrected}$ $= Abs_{Sample} - Abs_{Blank}$
$= 0.1395 - 0.0041$
$= 0.1354$

From calibration curve $Abs_{Corrected}$ $= 0.2131*GAE\ (mg/100mL) + 0.0592$
Gallic acid (mg/100mL) $= 0.3576$
GAE (g/L) $= 0.3576*10\ 000$
$= 3576$

7.2.2. Patrick Iland method

Reagents used:

1 N HCl solution.

Instruments and apparatus used:

Perkin Elmer Lambda 2 UV/VIS spectrophotometer

Homogeniser capable of 24 000 revolutions per minute (rpm).

Procedure:

1 Weigh a sample of 50 berries.
2 Transfer the berries to a homogenising vessel, normally a 125-mL plastic container.
3 Homogenise the berries at high speed, e.g. 24 000 rpm for about 30 seconds. The homogeniser should macerate the flesh, skins and seeds into a homogeneous mixture, so that a representative sub sample can be taken in step 6. There should not be any large pieces of skins or seeds in the mixture.
4 Scrape any homogenate from the shaft of the homogeniser into the homogenising vessel and repeat the homogenising step for about 15 seconds.
5 Scrape any homogenate remaining on the shaft of the homogeniser back into the homogenising vessel.
6 Thoroughly mix the homogenate by stirring it with a small spoon-type spatula and immediately take a scoop of approximately 1 gram of homogenate using the spatula.
7 Transfer the scoop of homogenate into a pre-tared centrifuge tube. Record the weight. This is termed 'the weight of homogenate taken for extraction'.
8 Pipette 10 mL of 50% v/v aqueous ethanol adjusted to pH 2.0 into the centrifuge tube containing the homogenate. Cap the tube and mix the contents periodically by inverting the tube about every 10 minutes over a period of 1 hour.
9 After 1 hour, centrifuge the tube and contents at 3 500 rpm for 5 minutes. The supernatant is termed 'the extract'.
10 Pipette 1.0 mL of 'the extract' into 10 mL 1N HCl and mix this solution thoroughly.
11 Pour the remaining volume of 'the extract' into a tall, thin measuring cylinder and record the volume. Add the value of this recorded volume and the value of the volume of 'the extract' that had previously been taken in step 10 to obtain a value, which is termed 'the total extract volume'. (Note: This step is required because although 10 mL of 50% v/v aqueous, pH adjusted, ethanol was added in step 8, the final extract volume is greater than 10 mL because it includes the added 10 mL plus a small volume of liquid that comes from the sample of homogenate, e.g. 'the total extract volume' from 1 gram of homogenate might be 10.4 mL).
12 Allow the diluted HCl extract solution to stand for about three hours.
13 After 3 hours, using a spectrophotometer, read the absorbance of the diluted HCl extract in a 1-cm cell at 700 nm, 520 nm and 280 nm.

Calculations:

$$\frac{\text{Colour per berry}}{\left(\begin{array}{l}\text{milligrams of anthocyanins}\\ \text{per berry}\end{array}\right)} = \frac{A_{520}^{HCl}}{500} \; x \; \text{*dilution factor} \; x \; \frac{\text{final extract volume}(mL)}{100} \; x \; \frac{\text{weight of 50 berries}(g)}{\begin{array}{l}\text{weight of hom ogenate}\\ \text{taken for extraction}(g)\end{array}} \; x \; \frac{1000}{50}$$

$$\frac{\text{Colour per gram berry weight}}{\left(\begin{array}{l}\text{milligrams of anthocyani ns}\\ \text{per gram berry weight}\end{array}\right)} = \frac{A_{520}^{HCl}}{500} \; x \; \text{*dilution factor} \; x \; \frac{\text{final extract volume}(mL)}{100} \; x \; \frac{\text{weight of 50 berries}(g)}{\begin{array}{l}\text{weight of hom ogenate}\\ \text{taken for extraction}(g)\end{array}} \; x \; \frac{1000}{\begin{array}{l}\text{weight of 50}\\ \text{berries}(g)\end{array}}$$

$$\frac{\text{Total phenolics per berry}}{(\text{absorbance units per berry})} = A_{280}^{HCl} \; x \; \text{*dilution factor} \; x \; \frac{\text{final extract volume}(mL)}{100} \; x \; \frac{\text{weight of 50 berries}(g)}{\begin{array}{l}\text{weight of hom ogenate taken}\\ \text{for extraction}(g)\end{array}} \; x \; \frac{1}{50}$$

$$\frac{\begin{array}{l}\text{Total phenolics per gram}\\ \text{berry weight}\end{array}}{\left(\begin{array}{l}\text{absorbance units per}\\ \text{gram berry weight}\end{array}\right)} = A_{280}^{HCl} \; x \; \text{*dilution factor} \; x \; \frac{\text{final extract volume}(mL)}{100} \; x \; \frac{\text{weight of 50 berries}(g)}{\begin{array}{l}\text{weight of hom ogenate taken}\\ \text{for extraction}(g)\end{array}} \; x \; \frac{1}{\text{weight of 50 berries}(g)}$$

7.2.3. Glories method

Reagents used:

pH 3.2 Solution: 5 g tartaric acid + 22.2 mL of 1 N NaOH solution in 1 L distilled water. The pH was adjusted to 3.2 by using either 1 N HCl solution or 1 N NaOH solution

pH 1 Solution: 0.1 N HCl solution

0.01 N NaOH solution

0.1% ethanolic hydrochloric acid solution (0.1 mL of hydrochloric acid was pipetted into a 100-mL volumetric flask and filled to the mark with ethanol)

2% hydrochloric acid solution

15% sodium bisulphite solution.

Instruments and apparatus used:

Perkin Elmer Lambda 2 UV/VIS Spectrophotometer

Metrohm 744 pH meter

Mettler PM 2000 balance

Atago Palette digital palm Brix refractometer

Waring variable-speed laboratory blender.

Method:

The method involves the collection of 400 berries at random in a block to be sampled and then dividing the total number of berries into two samples of equal mass.

1 The one sample is pressed in a plastic bag to obtain the juice, which is filtered to enable the following determinations:

- Sugar content measured by the amount of sugar (Brix)

- pH
- Acid content by titration with sodium hydroxide.

2 The second sample is crushed in a Waring blender or a typical bladed kitchen mixer to yield a mash.

3 This mash is then divided to give two equal 25-g portions, with the excess being discarded.

4 Each 25 g portion is diluted 1:1 with 25 mL of a pH 3.2 and pH 1.0 solution respectively. The pH solutions are made up as follows:
pH 1 Solution: = 0.1N HCl solution, and
pH 3.2 Solution: = 5 g tartaric acid + 22.2 mL of a 1.0 N NaOH solution in 1L distilled water. The pH of this solution is adjusted pH to 3.2.

5 The mixtures are allowed to homogenise for a four-hour period prior to filtering through a coarse filter such as glass wool or a sintered glass frit. The filtrates are marked as filtrate pH 3.2 and filtrate pH 1.0.

6 A small volume of filtrate pH 3.2 is diluted 100 times (0.5 mL in 50 mL) and the absorbance of this diluted solution is measured at 280 nm. This absorbance value is multiplied by the relative dilution values of the mash, i.e. 200 times.

7 The anthocyanin concentration is measured on the filtrate pH 3.2 and filtrate pH 1.0. Into two small beakers, 0.5 mL of filtrate pH 3.2 and filtrate pH 1.0 are added, respectively. To each beaker 0.5 mL of 0.1% ethanolic HCl solution is added and 10 mL of a 2% HCl solution.

8 Then 2.5 mL of each of the pH solutions is pipetted into two 1-cm plastic spectrophotometric cuvettes. The two sets of cuvettes are treated in the following manner: 1mL distilled water is added to the one cuvette and 1 mL of a 15% sodium bisulphite solution to the other.

9 The solutions are allowed to stand for 20 min. The absorbance of each solution is then measured at 520 nm.

Calculation of the concentration of anthocyanin [A]:

$$[A](mg/l) = (Abs(sodium bisulphite) - Abs(distilled water)) \; x \; 875 \; x \; 2$$

The value “875” is a mathematical constant which was established from data obtained from various red grape cultivars [6].

Interpretation:

$$Extractable\,anthocyanins \;=\; \frac{[A]_{pH3.2}}{[A]_{pH1}} \;x\; 100$$

$$Total\ phenol \;=\; Tannin(skin) \;+\; Anthocyanin(skin) \;+\; Tannin(pips)$$

$$Where: \quad s = skin; \quad p = pips; \quad T = Tannin; \quad A = Anthocyanin;$$

$$P = Phenolic\ \ compounds.$$

$$Abs280 \;=\; Abs[A]_s \;+\; Abs[T]_s \;+\; Abs[T]_p$$

$$[P]_s \;=\; Abs[A]_s \;+\; Abs[T]_s \;=\; [A]_{pH3.2} \;x\; 40$$

$$[T]_p \;=\; Abs280 \;-\; dskin$$

$$\%[T]_p \;=\; \frac{Abs280 \;-\; dskin}{Abs280} \;x\; 100$$

Mp is the tannin concentration due to the seeds. As the Abs 280/anthocyanin ratio of extracts at pH 3.2 is between 35 and 45 for ripe grapes from all varieties investigated, an average of 40 is used. Once the concentration of total phenolic compounds (Abs 280) and anthocyanin (A) in the extract at pH 3.2 is known, it is possible to calculate the proportion of the phenolic compounds derived from the skins (Abs 280 = Abs pH 3.2 x 40). The remainder, therefore, originated from the seeds [6].

$$\%PFT \;=\; [A]_{280(dil)} \;\times\; 100 \;\times\; 2$$

The Glories method was modified by using smaller amounts in the last stages of the preparation of the samples to make it easier and to save much time. The reagents, apparatus, and instruments that were used were exactly the same, as was the first part of the preparation. The only part of the method that changed occurred after the samples were allowed to stand for four hours. By directly pipetting the samples into separate plastic cuvettes much time was saved, making the procedure much faster.

The method was changed as follows:
Into two small beakers 0.5 ml of pH 3.2 filtrate and of pH 1 filtrate were added, separately. To that 0.5 ml of a 0.1% ethanolic hydrochloric acid solution and 10 ml of a 2% HCl solution were added. A 2.5 ml volume of the pH 3.2 mixture was pipetted into two 1-cm plastic cuvettes. To the one cuvette 1 ml distilled water was added, and to the other 1 ml of a 15% sodium bisulphite solution was added. The same was done for the pH 1 mixture. The solutions were allowed to stand for 20 minutes. The absorbance of each solution was measured at 520 nm.

The following results were reported:

- Maximal anthocyanins that the grape could deliver (under the method of evaluation employed) - A pH1
- The amount of anthocyanins which could be extracted under wine making conditions – A pH3.2.
- The percentage extraction of anthocyanins obtained under wine making conditions - Ea.
- The amount of tannins ascribed to have originated from the seeds - Mp
- The total amount of phenolic compounds present - PFT.

In addition, at all times the sugar and acid contents were reported, as well as the pH. As a comment is offered with each evaluation it was imperative that these parameters were analysed (without which no comment could have been offered).

To illustrate an example of the calculations for the Glories method grapes from Kanonkop Estate Block 103 were used. See Table 8. The grapes were sampled on 1 March 2004.

Table 8: Results illustrating the absorbencies used for the calculations of Kanonkop Estate Block 103 to determine the phenolic ripeness by the Glories method

Sample	280 (100dil)	3.2 + W	3.2 + Na	1 + W	1 + Na
Block 103	0.1478	0.2335	0.0346	0.4834	0.0257

W = distilled water, Na = sodium bisulphite

Example of calculation of parameters as determined by the Glories method for Block 103:

[A] (mg/L) = (Abs sodium bisulphite – Abs distilled water) * 875 * 2
[A] pH 1 = (0.4834 – 0.0257) * 875 * 2
= 801 mg/L

[A] pH 3.2 = (0.2335 – 0.0346) * 875 * 2
= 348 mg/L

% Extractable anthocyanins (Ea) = ([A] pH 3.2 / [A] pH 1) * 100
= 348 / 801 *100
= 43.4 %

% Seed tannins (Mp) = {[A] $_{280(dil)}$ – (([A] $_{3.2 + W}$ – [A] $_{3.2 + Na}$) * 4/100) / [A] $_{280(dil)}$ }* 100
= {0.1478 – ((0.2335 – 0.0346) * 4/100) / 0.1478 }* 100
= 9.4 %

Total amount of phenols = [A] $_{280(dil)}$ * 100 * 2
= 0.1487 * 100 * 2
= 29.6 %

7.3. Typical examples of results of phenolic ripeness analysed

Although numerous analyses of grape and wine samples were carried out, the volume of data is too large to include in this assignment, data are directly available from the author at Roediger Agencies [61]. A few examples are, however, here included to highlight certain findings that illustrate how the results of the Glories method analysis can be interpreted and applied.

7.3.1. Ripening process and the quality of grapes

A typical example of the reporting and interpretation of the results with data obtained at Jordan [65] during 2003 is tabulated in Table 9. Since there is no classical definition of phenolic ripeness, Glories has interpreted that the potential anthocyanin concentration (A1) should be at a maximum and the extraction of anthocyanins (Ea) should also be at a maximum, while the contribution of seed tannins (Mp) should be a minimum.

Table 9: Glories data obtained, Jordan block M3 [CS] 2003

Date	Winery	*Sample*	*Cultivar*	A3.2	A1	Ea (%)	Mp (%)	PFT	Brix	pH	TA	S/A
06-Feb	Jordan	*Block M3*	*CS*	1140	2388	47.70%	26.4%	68.0				
07-Feb	Jordan	*Block M3*	*CS*	983	2388	41.10%	27.4%	68.0	20.6%			
13-Feb	Jordan	*Block M3*	*CS*	1130	2368	47.70%	23.9%	64.0	21.5%	3.36	6.72	32.0
18-Feb	Jordan	*Block M3*	*CS*	1133	2375	47.70%	20.5%	58.6	23.5%	3.46	6.13	38.3
20-Feb	Jordan	*Block M3*	*CS*	1086	2108	51.50%	18.9%	55.6	23.0%	3.21	5.75	40.0
24-Feb	Jordan	*Block M3*	*CS*	1210	2585	46.80%	20.4%	59.4	23.5%	3.40	5.51	42.7
27-Feb	Jordan	*Block M3*	*CS*	1673	2412	69.40%	18.5%	61.7	24.5%	3.36	6.12	40.0
03-Mar	Jordan	*Block M3*	*CS*	1224	2666	45.90%	24.5%	66.0	24.5%	3.39	5.91	41.4
06-Mar	Jordan	*Block M3*	*CS*	1473	2518	58.50%	24.8%	69.1	24.8%	3.45	5.32	46.6

Figure 7 shows a steadily increase in the potential anthocyanins (A1) of block M3. The analysis was terminated at the time of picking and in this case it appears that the potential anthocyanin concentration had peaked – hence the grapes where picked at an ideal ripeness. The traditional parameters of monitoring ripeness also indicate that the grapes were ripe and the extraction percentage had almost achieved the desired amount of 60%.

The curve of potential anthocyanins (A1) versus time often appears erratic and may show enormous declines of up to 500 mg/L between samplings. This decline is not due to the sampling technique or due to the analytical method, as in several occasions where this phenomena has been noted, blocks have been re-sampled within 24 hours later to obtain similar results or at least within 5 per cent of the original analysis data. In addition, in some cases several samples have been taken from the same rows and analysed separately to achieve results within five per cent of each other. It must be borne in mind that the sampling and the subsequent analysis can not always produce identical results, however, over the four years of sampling the author is confident of a maximum of a five per cent variation in results, which demonstrates the margin of error that this type of sampling yields within the parameters of mixing 200 berry samples. This percentage has also been set as cut-off criteria of accuracy by the Australian Wine Research Institute [66].

The enormous fluctuations of anthocyanin concentrations found during the progression of ripening are attributed to stress, either heat or water as is shown in Section 7.3.2. What happens to the anthocyanins is beyond the scope of this study and would be an interesting posy graduate study.

At the same time as the concentration of total anthocyanins (A1) vary, the amount of extractable anthocyanins (A3.2) varies to a lesser degree and almost stays constant within the margin of experimental error. This results in the extraction percentage (Ea) showing enormous fluctuations, as Ea is based on the percentage difference between (A3.2) and (A1). These fluctuations need to be taken into account when assessing overall ripeness, as extraction percentages reported tend to be high after the berry has experienced a stress.

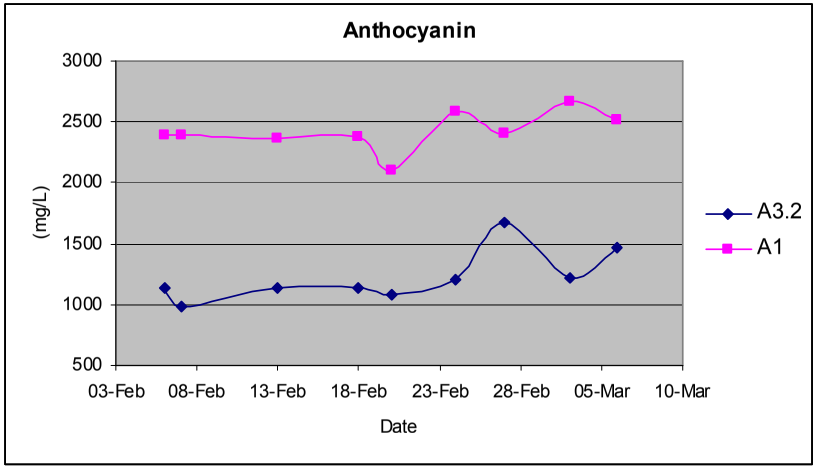

Figure 7: A3.2 and A1 Jordan block M3 [CS] 2003.

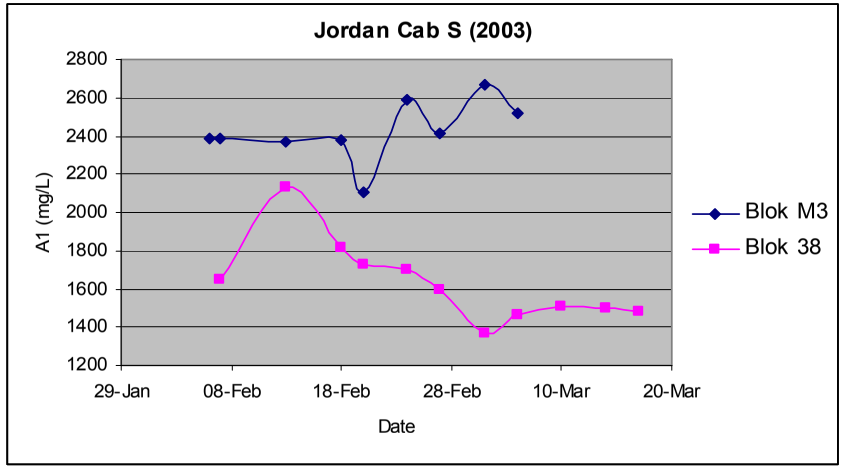

Figure 8: A1 Jordan blocks M3 and 38 [CS] 2003.

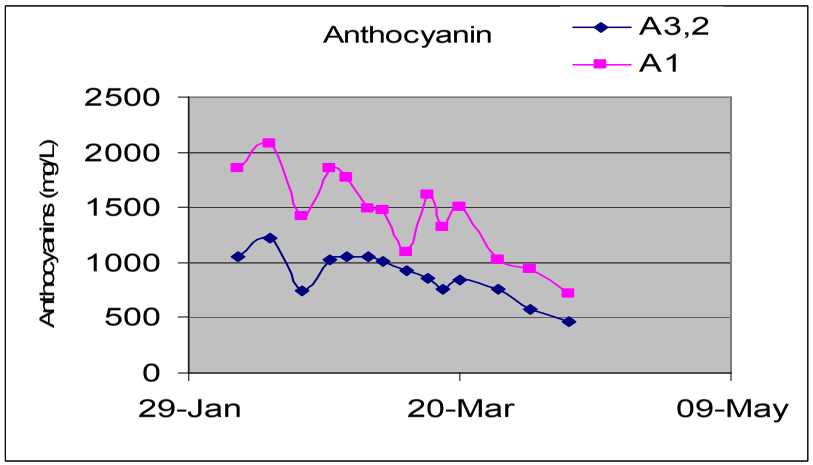

Figure 9: A3.2 and A1 Kanonkop Estate block 103 [CS] 2003.

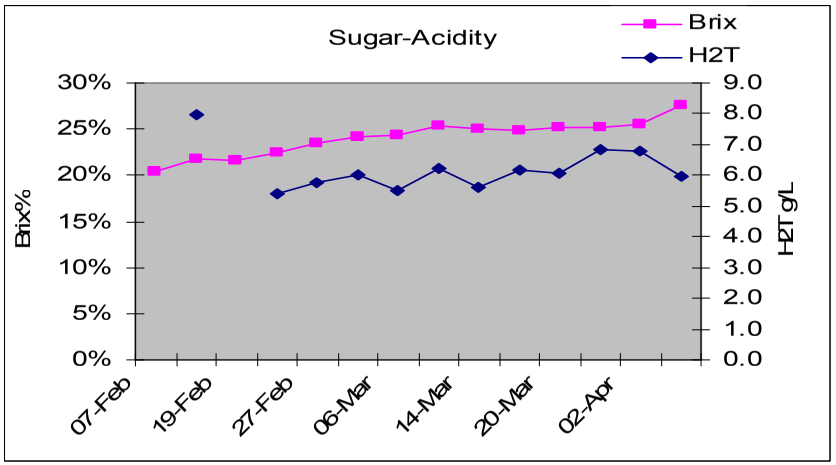

Figure 10: Sugar ripeness Kanonkop Estate block 103 [CS] 2003.

Figure 8 shows a direct comparison between two blocks of Cabernet Sauvignon sampled at Jordan. Block M3, situated at the crest of Jordan, overlooking False Bay, shows considerably higher potential concentrations of anthocyanins than block 38, situated in the valley. The former is therefore considered to be the better of the two blocks. This observation was confirmed by Gary Jordan, owner of the estate. Furthermore, his decision as to when to harvest block M3 was confirmed by results of the Glories method to be an ideal timing.

Figure 9 shows a block of Cabernet Sauvignon that was monitored at Kanonkop Estate way beyond the date of harvest. Figure 10 shows that the degrees Brix increased to above 32 which is an extreme sugar concentration normally associated with the loss of water resulting in the grapes becoming raisin-like. Figure 9 shows that the Glories method does not merely measure colour concentration, which normally would be associated with a longer hang-time. Here, the extractability of the anthocyanin concentration at pH 1 started at a value of 2 100. From all the data collected, there were very few pH 1 anthocyanin concentration values above the 2 000 figure in 2003. This indicated that this vineyard is a quality vineyard because of the high concentration of anthocyanins. The general trend is a decreasing one, which indicated that maximum phenolic ripeness was achieved early on. In other words, phenolic ripeness was achieved early in the season. But the sugar content was then too low (Brix 21.7%) to make a good alcoholic wine. Figures 11 and 12 show the measurement of total phenols by two different techniques. Figure 11 shows results of the Glories method, which represents the total phenols, namely tannins and anthocyanins, and is represented by the value PFT. Figure 12 is the concentration of GAE determined according to the FC method. It can clearly be seen that the shape of the two curves are totally different. This indicates that there is no correlation between the total phenols as determined by the Glories method (PFT) and the gallic acid equivalent (GAE) content as determined by the Folin-Ciocalteau method.

Initial analysis of grapes from the Lanzerac [67] estate on Cabernet Franc showed very low anthocyanin values, as can be seen in Figure 13. The then winemaker Wynand Hamman was approached and it was pointed out to him that the quality of the Cabernet Franc analysed was perhaps not as desirable as it should be. The winemaker responded that he was quite aware of this and that he had a far better block of Cabernet Franc that the author could analyse, namely block CF. It emerged that the potential anthocyanin analysis showed that the second block was indeed superior. Subsequently, the 2003 vintage block D7A was utilised to make a rosé wine as it was not considered to be of sufficient quality to produce a normal cabernet Franc wine. Furthermore, the winemaker was informed on the 3rd of March 2003 that he should consider harvesting block CF3 as the potential total anthocyanins (A1) had turned downwards and the extraction percentage had climbed above 60%, Figure 14. The winemaker in turn confirmed that part of the block had already been harvested on the 28th of February 2003, thus confirming that the

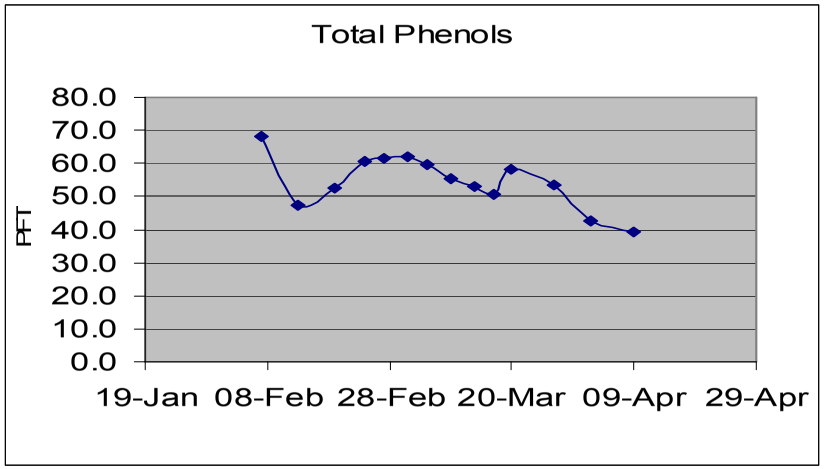

Figure 11: PFT (Glories method) Kanonkop Estate block 103 [CS] 2003.

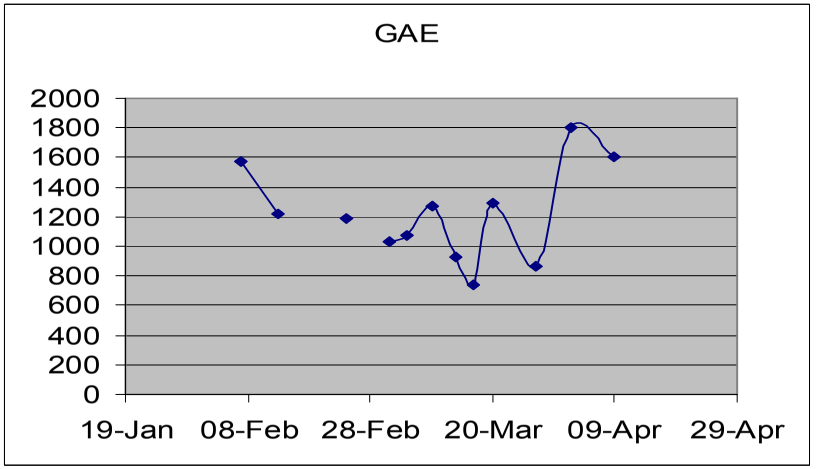

Figure 12: GAE (FC method) Kanonkop Estate block 103 [CS] 2003.

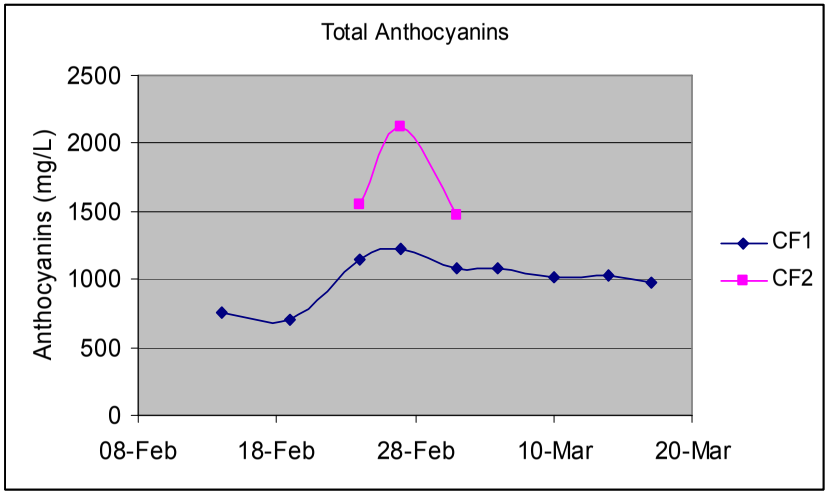

Figure 13: A1 Lanzerac block D7A and CF3 [CF] 2003.

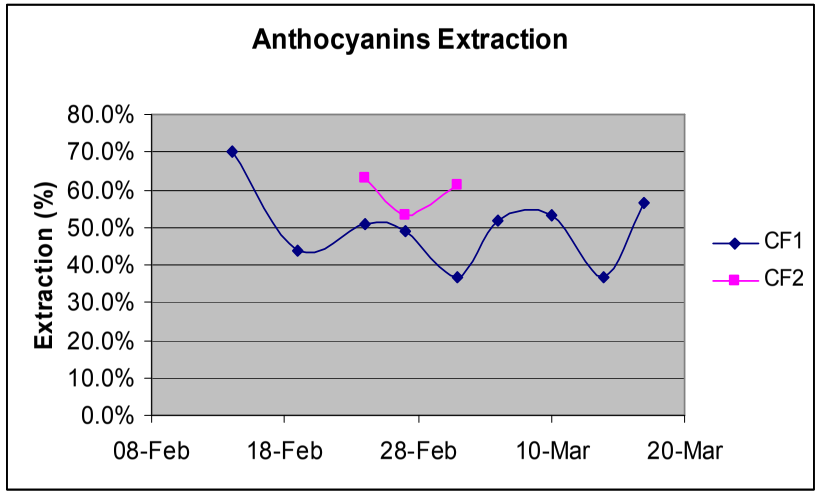

Figure 14: Ea Lanzerac block D7A and CF3 [CF] 2003.

interpretation of Glories method of phenolic ripeness was in agreement with conclusion which the winemaker himself had taken, namely to harvest.

Figure 15 shows Shiraz grapes that were monitored at Rust en Vrede estate [68] until harvest at 27.5 Brix. The graph indicates that these grapes had not reached the true potential of phenolic ripeness as A1 was still increasing. However, the decision to harvest was forced by the Brix value and the declining acid concentration.

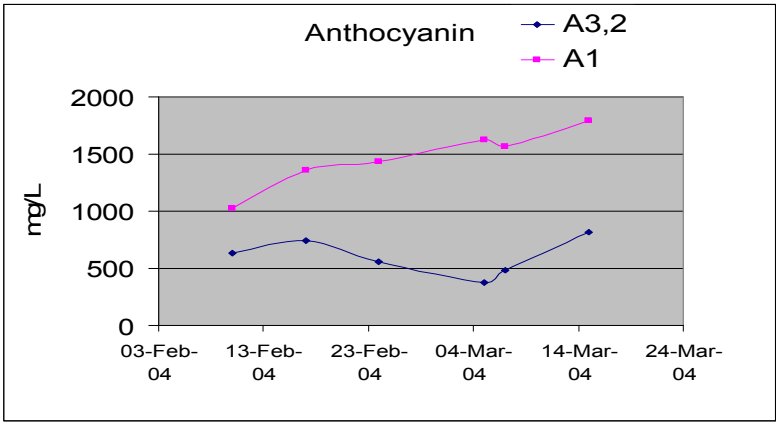

Figure 15: A3.2 and A1 Rust en Vrede block RV1 [SH] 2004.

Table 10 shows the influence of virused vines at Tokara [69] on the potential anthocyanin concentrations; virused vines take longer to achieve sugar ripeness and sometimes never ripen, depending on the intensity of virus. Table 10 is the analysis of healthy vines and virused vines within the same block, and it can clearly be seen that the virused vines yield a lower amount of potential anthocyanins and hence will yield a lower quality of vine. The maximum A1 achieved in the healthy vines was 2 362, whereas the virused vines produced an A1 of 2056 on the same date – a 15% lower value.

Table 10: Glories and GAE data obtained, Tokara block R3 [CS] 2004

Date	Winery	*Sample*	*Cultivar*	A3.2	A1	Ea%	Mp%	PFT %	Brix	pH	TA g/L	S/A	GAE
09-Mar-04	Tokara	*R3 no virus*	*CS*	482	2036	23.7%	4.9%	26.4	21.6%	3.07	9.51	2.3	2085
16-Mar-04	Tokara	*R3 no virus*	*CS*	640	2362	27.1%	4.1%	28.6	24.2%	3.17	8.34	2.9	3719
23-Mar-04	Tokara	*R3 no virus*	*CS*	554	1740	31.9%	4.8%	27.8	24.1%	3.24	8.16	3.0	2629
30-Mar-04	Tokara	*R3 no virus*	*CS*	592	2354	25.2%	3.7%	27.2	24.7%	3.25	7.44	3.1	2437
09-Mar-04	Tokara	*R3 virus*	*CS*	399	1233	32.3%	1.6%	20.8	20.3%	3.05	10.26	2.0	2031
16-Mar-04	Tokara	*R3 virus*	*CS*	543	2056	26.4%	3.9%	26.5	22.1%	3.10	9.35	2.4	3022
23-Mar-04	Tokara	*R3 virus*	*CS*	620	1771	35.0%	5.8%	30.3	22.2%	3.22	8.70	2.6	2360
30-Mar-04	Tokara	*R3 virus*	*CS*	701	1748	40.1%	7.1%	33.4	23.0%	3.25	7.74	3.2	2471

During the 2006 season the entire intake of grapes of KWV Limited [70] was analysed by means of Glories and Iland methods. The report was voluminous and only a single item has been included here to illustrate the findings. When the report was discussed with the chief winemaker, Bertus Fourie, the author was asked to highlight certain findings. It became apparent that most of the quality grape parcels taken in, which were highlighted by the Glories method as superior, were subsequently earmarked for the premium label of KWV. In Table 11, an example of Pinotage is highlighted. When the author was asked to comment on the difference between the earlier harvest and the harvest that occurred later, a concurrence in opinion was that the later harvest was better. From the authors point of view this was because of higher A1 levels, lower seed tannins and better extraction results, while from the winemakers point of view is was from an organoleptic point of view. Thus without having knowledge of the subsequent wine being made the author could predict quality using the Glories method.

Table 11: Glories data obtained for KWV Limited, Marklew Family Wines [71] [PI] 2006

Date	Winery	*Sample*	*Cultivar*	A3.2	A1	Ea%	Mp%	PFT %	Brix	pH	TA g/L
08-Feb-06	KWV	*Marklew Family Wines 7/2 Pino*	*PI*	945	1346	70.2%	28.1%	68.8	26.0%	3.43	7.0
08-Feb-06	KWV	*Marklew Family Wines 7/2 Pinotage*	*PI*	842	1390	60.6%	37.3%	83.8	26.7%	3.50	6.5
10-Feb-06	KWV	*Marklew Family Wines A71T5 9/2*	*PI*	607	954	63.7%	25.6%	60.4	25.0%	3.37	7.3
10-Feb-06	KWV	*Marklew Family Wines A71T53 8/2*	*PI*	914	1428	64.0%	24.3%	62.0	27.3%	3.48	6.6
17-Feb-06	KWV	*Marklew Family Wines Stb A7/T68 15/2*	*PI*	922	1575	58.6%	29.3%	70.6	25.4%	3.53	7.1

7.3.2. Influence of water on grape quality

Figure 16 is the first of many figures that show the influence of water on the quality of the grapes (data given here is from Jordan). South Africa has a warm climate and this will only tend to increase in future with the event of global warming, and hence the administration of water to the grapes will become increasingly important. Figure 16 shows a dramatic drop in potential anthocyanins at an early stage of ripening and hence this phenomenon could not be attributed to the polymerization of the anthocyanins. Once again, the owner, Gary Jordan, was consulted as to whether he had administered an excessive amount of water to the grapes, to which he responded that this was hardly possible as the pump had broken down. Thus the drop in anthocyanins was attributed to stress that the grapes had experienced due to lack of water. A second sample of grapes was taken the following day to eliminate possible faulty analytical techniques. The second sample revealed a very low level of anthocyanins, thus eliminating a possible faulty experimental error. This was the first indication of the influence of stress on the grapes and it appears that these extremes have not been reported elsewhere in the world, as most curves of anthocyanin concentration follow the idealic curves as presented by Glories.

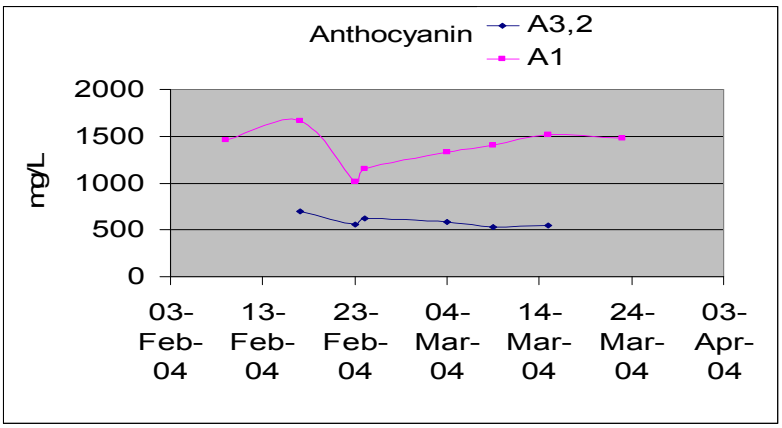

Figure 16: A3.2 and A1 Jordan block M3 [CS] 2004.

Tables 12, 13, and 14 all indicate the effects of water on the quality of the grapes. In each of these cases the column of the potential anthocyanins (A1) needs to be observed to highlight the phenomenon. At Jordan in block 38 it was noticed that every second row in the vineyard was equipped with a commercial, small garden sprinkler. Hence the question that arose was whether this watering system was efficient enough to water the alternate rows as well, or whether these alternate rows, not equipped with a sprinkler, would suffer from stress. Hence samples of the two types of rows were taken and analysed separately. In addition, a sample of the row that was irrigated was taken from both sides, namely the side facing the sun and the side that was more shaded. The results of the three samples are depicted in Table 12. Observing the results of A1, it is noticed that all three samples showed a similar amount of potential anthocyanins, which indicated that the amount of water administered was adequate. This also showed that the sampling techniques used were reasonably reproducible, as only a small amount of scatter was found within the A1 result.

Table 12: Glories data obtained, Jordan block 38 [CS] 2005

Date	Winery	*Sample*	*Cultivar*	A3.2	A1	Ea%	Mp%	PFT %	Brix	pH	TA g/L	S/A
07-Feb-05	Jordan	*J38*	*CS*	704	1424	49.4%	12.0%	40.1	20.8%	3.24	9.3	2.2
07-Feb-05	Jordan	*J38 sprinkler /shade*	*CS*	548	1476	37.1%	4.2%	27.0	20.3%	3.24	9.3	2.2
07-Feb-05	Jordan	*J38 sprinkler /sun*	*CS*	626	1438	43.5%	14.8%	42.9	20.7%	3.33	8.3	2.5

Table 13: Glories data obtained, Buitenzicht block 6 [SH] 2005

Date	Winery	*Sample*	*Cultivar*	A3.2	A1	Ea%	Mp%	PFT %	Brix	pH	TA g/L	S/A
10-Feb-05	Buitenzicht	*Block 6*	*SH*	922	2101	43.9%	17.1%	50.8	23.7%	3.48	7.4	3.2
14-Feb-05	Buitenzicht	*Block 6*	*SH*	649	1195	54.3%	8.1%	33.8	21.3%	3.38	6.7	3.2
17-Feb-05	Buitenzicht	*Block 6*	*SH*	694	1143	60.7%	6.0%	31.8	22.8%	3.51	7.4	3.1

Table 13 shows the results that a severe amount of watering had on a vineyard at Buitenzicht. Buitenzicht [72] is situated on the slopes of Sir Lowry's. In 2005 a fire was threatening the vineyard and, as a preventative maintenance, the vineyard was irrigated to prevent potential damage from the fire. The effect, however, was a drastic reduction in potential anthocyanins, from an extremely high value of 2101 to a low value of 1195. The vineyard has never recovered the high potential anthocyanin values up to the date of harvest.

Table 14: Glories data obtained, Blue Creek block BC1 [CS] 2005

Date	Winery	*Sample*	*Cultivar*	A3.2	A1	Ea%	Mp%	PFT %	Brix	pH	TA g/L	S/A
21-Feb-05	**Blue Creek**	***BC***	***CS***	880	2046	**43.0%**	**15.8%**	**48.3**	**22.9%**	**3.16**	**7.1**	**3.2**
01-Mar-05	**Blue Creek**	***BC***	***CS***	898	2052	**43.7%**	**16.5%**	**49.6**	**23.4%**	**3.21**	**7.8**	**3.0**
01-Mar-05	**Blue Creek**	***BC Dry***	***CS***	708	1836	**38.6%**	**15.7%**	**45.7**	**23.5%**	**3.45**	**5.9**	**4.0**

An experiment conducted at Blue Creek [73] during the 2005 season was to cut-off the water to a certain section of a vine row within the vineyard and to measure the effect of the water deficiency. Samples were taken from the same row, from a section with watering and a section without water, and the results compared. Table 14 shows that a 10% difference in the potential anthocyanins was experienced within a week, thus showing that the water stress resulted in a lower concentration of potential anthocyanins.

Figure 17 shows the effect of irrigation on the amount of potential anthocyanins in different vineyard blocks by means of the highlighted circle. The blocks depicted in this figure were all watered on the 28th of February 2005. Various phenomena were experienced; the amount of potential anthocyanins decreased in some instances whereas it increased in other instances. This indicates that watering and the amount of watering is extremely crucial in the balance of the anthocyanin concentration within the grape.

Figures 18 and 19 show that the vineyard reproducibility remains the same vintage after vintage if the viticural practices are not changed. In each case the curve of the potential anthocyanins was

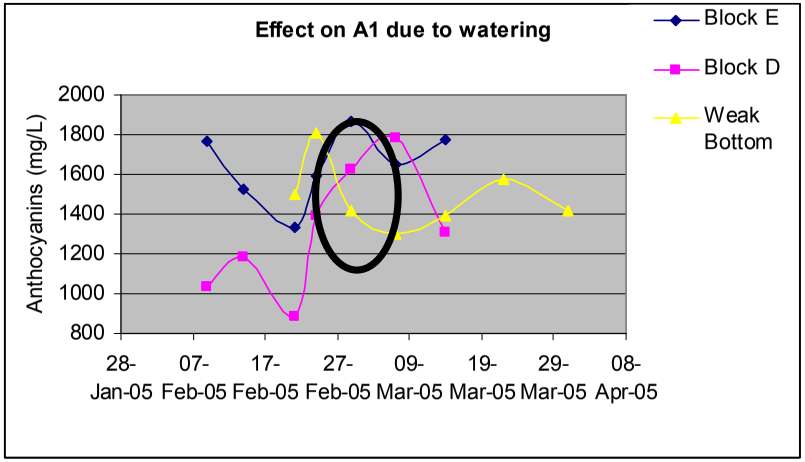

Figure 17: A1 De Toren Private Cellar [CS] 2005.

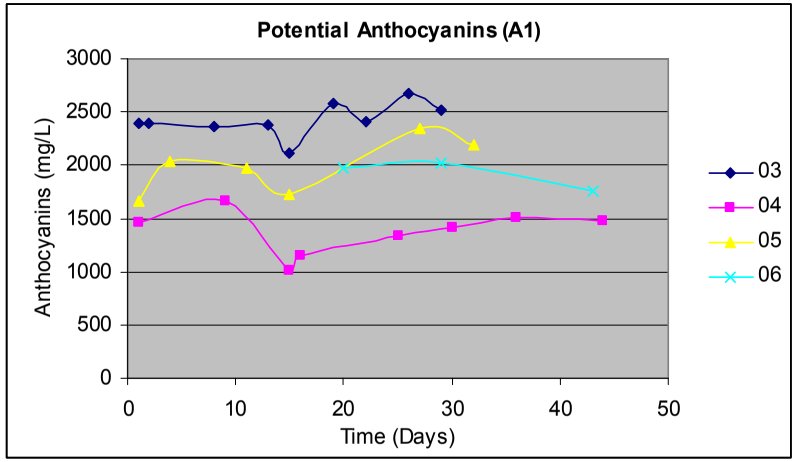

Figure 18: A1 Jordan block M3 [CS] 2003-2005.

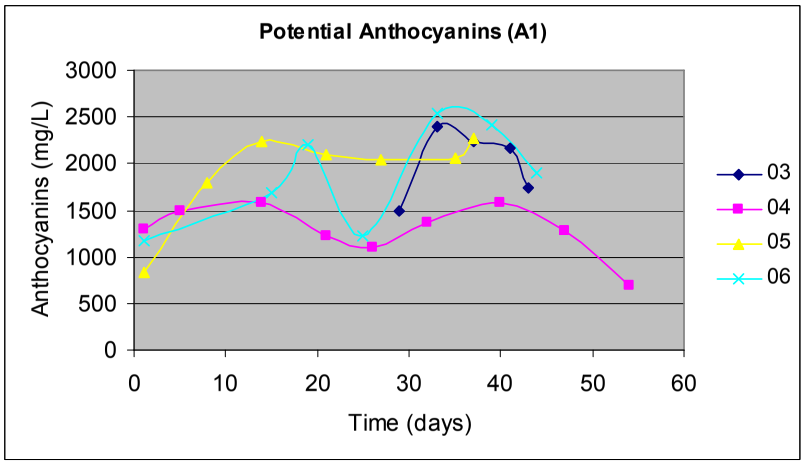

Figure 19: A1 Blue Creek block BC [CS] 2003-2005.

moved to accommodate the stage of ripening as the date of harvest is not always on the same date. In the case of Jordan, Figure 18, the maximum concentration of the vineyard is always achieved towards the harvest date, indicating that in attempting to achieve the maximum amount of anthocyanins in the grape, the potential is there to possibly produce high alcohol content wines. In 2004, however, the anthocyanins did not peak at the end of the season, possibly due to the water stress mentioned elsewhere in this thesis. In the case of Blue Creek it is evident that the vineyard appears to have a 'double-humped' curve, year after year. These two graphs also indicate the quality of the vintages' in the case of Jordan the 2003 vintage was the best followed by the 2005, while the 2004 vintage yielded the lowest in terms of anthocyanin concentration. In the case of Blue Creek the 2006 vintage was the best, followed by that of 2003, while the 2004 vintage yielded the lowest anthocyanin concentration.

Danie Steytler, owner of Kaapzicht [74] was going to purchase grapes from his neighbour, however concern was expressed that the neighbour's grapes would not reach a sugar content of 24% Brix and therefore were possibly of inferior quality. The author was therefore asked to assess the phenolic ripeness of three blocks on Kaapzicht (all labelled as Kaap), and to compare these to two of the neighbour's blocks (labelled as Groen). Results of the phenolic ripeness determination, see Table 15, showed that the extractability at pH 1 was in one instance better on the neighbouring blocks than on Kaapzicht itself. In addition, one of the Kaapzicht blocks showed a very low value for the extractability at pH 1. Results of these analyses showed that the neighbouring blocks were as good as, or even better than, those of Kaapzicht. The one block of Kaapzicht showing a low value of the extractability at pH 1 was a very young vineyard and hence had not reached its full potential to offer good quality wine. Discussions with the winemaker, six months after the harvest of all these blocks, indicated that the wine originating from neighbouring property was indeed of very high quality.

No comment can actually be made on the anthocyanin extractability and the contribution of the tannins from the seeds to the phenol content as only one single measurement was taken. However, since the values of the anthocyanin extractability and the tannins from the seeds to the phenol content were similar, the indication was that the quality of the blocks was similar.

Table 15: Glories data obtained, Kaapzicht [MO] 2004

Date	Winery	*Sample*	*Cultivar*	A3.2	A1	Ea%	Mp%	PFT %	Brix	pH	TA g/L
01-Mar-04	Kaapzicht	*Groen House*	*MO*	545	1531	35.6%	12.2%	37.6	22.2%	3.65	5.31
01-Mar-04	Kaapzicht	*Groen Hall*	*MO*	604	1783	33.9%	13.2%	40.1	21.7%	3.90	4.71
01-Mar-04	Kaapzicht	*Kaap LOR*	*MO*	620	1565	39.6%	7.8%	32.9	21.9%	3.70	4.65
01-Mar-04	Kaapzicht	*Kaap ROR*	*MO*	438	1190	36.8%	10.3%	32.8	20.6%	3.69	5.82
01-Mar-04	Kaapzicht	*Kaap LOT*	*MO*	562	1638	34.3%	13.3%	39.5	22.3%	3.65	5.09

7.3.3. The influence of topping and bunch thinning on grape quality

Table 16 includes highlights of the influence of viticultural practices such as canopy management. Kanonkop Estate had topped, 'cutback', the growing shoots in order to encourage lateral growth; one half of a particular block was done too heavily and the influence of this on the grape quality was determined using the Glories method. It can be seen from the potential anthocyanin column, A1, that the topped section of the block yielded higher initial anthocyanin concentration. It will be shown later that it is not of importance when the peak in potential anthocyanins is reached but rather how large the value of the anthocyanin concentration is. Thus the topped section had actually yielded a better quality of grape than the section of the block that was not topped.

The viticultural practice of bunch thinning is carried out in order to reduce the crop load of the vine in order to concentrate flavours within the grape, resulting in a better and more concentrated wine. At Zorgvliet [75] an experiment was conducted where a Shiraz block was bunch thinned to yield about 7.5 tons per hectare. Certain sections of each row where not bunch thinned – these were marked with plastic stripes. The areas with plastic stripes were calculated to yield approximately 11 tons per hectare. The difference between the two sections within the vineyard where monitored using the Glories method. The data is represented in Table 17 and graphically represented in Figures 20 and 21. From Table 17 it can be seen that both sections of the vineyard showed similar traditional values of monitoring ripeness, namely a sugar concentration of 22 Brix, pH of 3.5 and a total acid of 5.6 on the 24th of February 2005 in the case of the bunch thinned section, and 22.3 Brix, pH of 3.4 and a total acid of 5.7 in the case of the section which was not bunch thinned. Using these traditional ripeness indicators, no difference could be detected at all, however, if the potential anthocyanin values are viewed a different picture arises. On the 9th of February 2005 the A1 of the bunch thinned section was 1 829, whereas the maximum attained by the section which was not bunch thinned was 1 642 on the 2nd of March 2005. Two phenomena emerged: the bunch thinned section showed earlier phenolic ripeness and yielded a better quality grape than the section which was not bunch thinned.

Table 16: Glories and GAE data obtained, Kanonkop Estate block 103 [CS] 2004

Date	Winery	*Sample*	*Cultivar*	A3.2	A1	Ea%	Mp%	PFT %	Brix	pH	TA g/L	S/A	GAE
12-Feb-04	Kanonkop Estate	*Block 103*	*CS*	745	1071	69.5%	20.6%	53.8	19.2%	3.18	5.80	3.3	2819
16-Feb-04	Kanonkop Estate	*Block 103*	*CS*	446	1004	44.4%	20.6%	49.4	18.5%	3.12	6.22	3.0	3237
23-Feb-04	Kanonkop Estate	*Block 103*	*CS*	320	798	40.2%	8.4%	27.4	20.2%	3.54	7.17	2.8	3102
01-Mar-04	Kanonkop Estate	*Block 103*	*CS*	348	801	43.5%	9.4%	29.6	20.6%	3.62	6.51	3.2	3576
07-Mar-04	Kanonkop Estate	*Block 103*	*CS*	412	987	41.7%	8.7%	29.9	22.1%	3.49	5.64	3.9	3099
16-Mar-04	Kanonkop Estate	*Block 103*	*CS*	331	785	42.2%	5.3%	23.5	23.6%	3.54	6.51	3.6	2797
23-Mar-04	Kanonkop Estate	*Block 103*	*CS*	447	996	44.9%	8.1%	29.9	23.2%	3.60	6.33	3.7	4526
30-Mar-04	Kanonkop Estate	*Block 103*	*CS*	274	694	39.4%	6.5%	23.6	23.4%	3.59	6.09	4.1	3149
12-Feb-04	Kanonkop Estate	*Block 103 Topped*	*CS*	669	1316	50.9%	22.0%	55.1	18.9%	3.17	6.07	3.1	3418
16-Feb-04	Kanonkop Estate	*Block 103 Topped*	*CS*	495	1195	41.4%	16.2%	42.9	19.1%	3.16	5.58	3.4	2701
23-Feb-04	Kanonkop Estate	*Block 103 Topped*	*CS*	337	669	50.3%	3.8%	21.7	20.2%	3.49	7.43	2.7	3652
01-Mar-04	Kanonkop Estate	*Block 103 Topped*	*CS*	384	1000	38.4%	9.8%	31.0	20.5%	3.67	6.48	3.2	2689
07-Mar-04	Kanonkop Estate	*Block 103 Topped*	*CS*	439	709	62.0%	9.7%	32.0	21.7%	3.49	5.97	3.6	2587
16-Mar-04	Kanonkop Estate	*Block 103 Topped*	*CS*	318	794	40.1%	8.7%	27.8	23.1%	3.48	6.35	3.6	4120
23-Mar-04	Kanonkop Estate	*Block 103 Topped*	*CS*	309	621	49.8%	6.0%	23.8	22.2%	3.57	6.00	3.7	4367
30-Mar-04	Kanonkop Estate	*Block 103 Topped*	*CS*	274	716	38.3%	5.9%	22.8	22.7%	3.55	5.97	3.9	3169

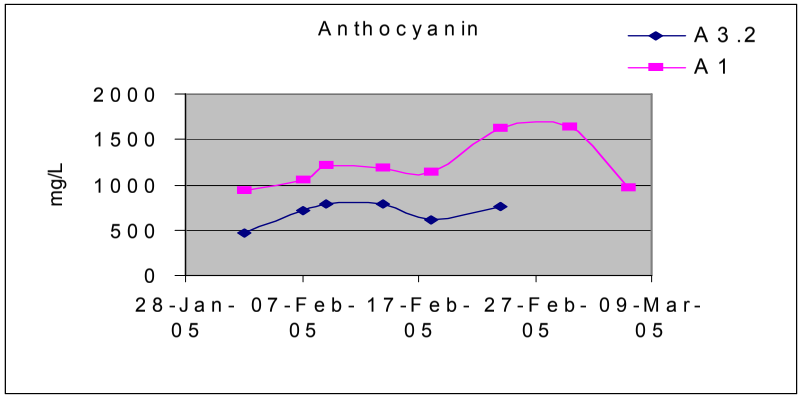

Figure 20: A3.2 and A1 Zorgvliet block C5 [SH] 2005.

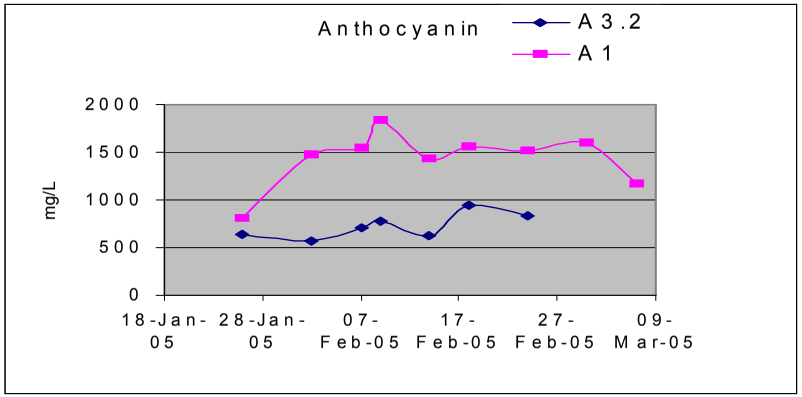

Figure 21: A3.2 and A1 Zorgvliet block C5 (bunch thinned) [SH] 2005.

Table 17: Glories data obtained, Zorgvliet block C5 [SH] 2005

Date	Winery	*Sample*	*Cultivar*	A3,2	A1	Ea%	Mp%	PFT %	Brix	pH	TA g/L	S/A
26-Jan-05	Zorgvliet	C5	*SH*	637	804	79.3%	13.2%	40.8	18.0%	3.24	8.8	2.0
02-Feb-05	Zorgvliet	*C5*	*SH*	569	1471	38.7%	3.3%	26.3	18.6%	3.18	7.3	2.6
07-Feb-05	Zorgvliet	*C5*	*SH*	712	1546	46.0%	8.7%	35.7	20.9%	3.28	8.9	2.4
09-Feb-05	Zorgvliet	*C5*	*SH*	784	1829	42.9%	9.1%	37.4	21.1%	3.46	6.9	3.1
14-Feb-05	Zorgvliet	*C5*	*SH*	619	1431	43.3%	5.9%	30.4	21.2%	3.32	6.9	3.1
18-Feb-05	Zorgvliet	*C5*	*SH*	940	1553	60.5%	14.4%	47.1	21.4%	3.54	5.9	3.7
24-Feb-05	Zorgvliet	C5	*SH*	832	1513	55.0%	11.8%	41.9	22.0%	3.51	5.6	4.0
02-Mar-05	Zorgvliet	*C5*	*SH*	1071	1603	66.8%	17.9%	53.9	23.5%	3.59	5.9	4.0
7-Mar-05	Zorgvliet	*C5*	*SH*	686	1164	58.9%	13.3%	41.7	24.3%	3.61	5.5	4.4
02-Feb-05	Zorgvliet	*C5 Stripes*	*SH*	461	931	49.5%	3.7%	24.5	17.8%	3.06	7.7	2.3
07-Feb-05	Zorgvliet	*C5 Stripes*	*SH*	708	1047	67.7%	9.3%	36.4	20.3%	3.15	7.6	2.7
09-Feb-05	Zorgvliet	*C5 Stripes*	*SH*	783	1216	64.4%	9.2%	37.5	20.0%	3.32	6.6	3.0
14-Feb-05	Zorgvliet	*C5 Stripes*	*SH*	790	1189	66.4%	9.0%	37.4	21.9%	3.46	6.6	3.3
18-Feb-05	Zorgvliet	*C5 Stripes*	*SH*	611	1144	53.4%	10.5%	36.3	19.7%	3.45	6.7	2.9
24-Feb-05	Zorgvliet	*C5 Stripes*	*SH*	762	1622	47.0%	10.2%	38.5	22.3%	3.39	5.7	3.9
02-Mar-05	Zorgvliet	*C5 Stripes*	*SH*	664	1642	40.4%	12.7%	40.4	21.9%	3.40	5.9	3.7
7-Mar-05	Zorgvliet	*C5 Stripes*	*SH*	479	957	50.0%	12.9%	37.5	21.8%	3.42	5.3	4.2

7.3.4. Influence of temperature on anthocyanin levels

The development and accumulation of anthocyanins is known to be influenced by temperature [76]. The formation of anthocyanins requires cooler temperatures and it has clearly been demonstrated that anthocyanin levels can be as much as five times higher in grapes which are cultivated at 20 ^{o}C compared to the same grapes cultivated at 30 ^{o}C [77]. Some publications [78] have cited that at above 35 ^{o}C the grape totally shuts down and no increase in anthocyanins are experienced. The effect of temperature is so great that, to date, the author has not detected Merlot, Shiraz, and Cabernet Sauvignon grapes from regions warmer than Stellenbosch, such as Wellington and Robertson to exhibit high anthocyanin levels in. Mediterranean varieties have not been evaluated in South Africa by the Glories method and thus the effect whether higher temperatures will tend to higher anthocyanin concentrations within these varieties cannot be comment on.

7.3.5. Optimising the Glories method

Table 18 shows the laboratory variables that were changed in order to achieve the optimum experimental conditions.

Table 18: Variables modified to optimise the Glories method, Roos [79] block E2 [SH] 2004

Date	Winery	Variations in experimental conditions	*Cultivar*	A3.2	A1	Ea%	Mp%	PFT %
05-Apr-04	**Roos**	**3 h[a]**	***SH***	353	619	**57.1%**	**3.9%**	**22.3**
05-Apr-04	**Roos**	**4 h[a]**	***SH***	443	855	**51.9%**	**4.7%**	**25.4**
05-Apr-04	**Roos**	**5 h[a]**	***SH***	513	903	**56.8%**	**5.5%**	**27.8**
05-Apr-04	**Roos**	**6 h[a]**	***SH***	515	880	**58.5%**	**5.3%**	**27.6**
05-Apr-04	**Roos**	**20 sec[b]**	***SH***	531	743	**71.4%**	**7.1%**	**30.2**
05-Apr-04	**Roos**	**40 sec[b]**	***SH***	521	815	**63.9%**	**10.7%**	**35.0**
05-Apr-04	**Roos**	**60 sec[b]**	***SH***	703	910	**77.2%**	**15.4%**	**45.0**

[a] Extraction time; [b] Blending time.

Table 18 and Figure 22 highlight the experimental results obtained after modifying Glories method of extraction. Figure 22 shows that as the time of extraction increased (hours), the % extractability at pH 1 and pH 3.2 also increased until after 5 hours, but showed a slight decrease after 6 hours at pH 1 and a slight plateau at pH 3.2. A general plateau region was achieved between 4 and 6 hours, where the extractable values were within 10% of each other. This 10% variation was considered acceptable as the entire procedure was based on a rough analytical procedure, since 400 berries were analysed and it was difficult to assess where the berries were picked from within a bunch. In other words, percentage variations due to picking grapes at the bottom, middle and top of a bunch would give a wide variation in results.

The Glories method employed states that the extraction period should be 4 hours. The 4-hour period was used so that results could be given to the wine farmers on the same day as the sampling. From the graph of extractability against time, it was evident that a 5-hour extraction period would be slightly better.

The percentage Ea, Figure 23, increased until after 4 hours, after which it decreased as the time of extraction increased. This showed that a 4-hour extraction period was sufficient. As the hours of extraction increased, the % Mp and % total phenol content increased until after 5 hours. Thereafter a slight plateau was reached. This again showed that the extraction period should be increased to 5 hours. Although comparisons were made at the same extraction times, this should give a reasonable comparison. For scientific purposes and accuracy, it is recommended that the extraction time should be extended to 5 hours.

For the extraction at pH 3.2, there was not a big difference in the values between 20 and 40 seconds, see Figure 24, (although there was a slight decrease), but an increase was observed after 60 seconds. As the mashing time increased, the extraction at pH 1 also increased. This was also the case with the % Mp and % total phenol content. The % Ea increased from 20 to 40 seconds, but decreased after 60 seconds, see Figure 25.

The least variation in the time used for mashing appeared to be between 20 and 40 seconds. Thereafter larger variations were noticed which tended to give higher values of parameters used. The recommendation is to mash between 20 and 40 seconds to avoid these variations.

Table 19: Glories data obtained using two different types of blenders, Eagles Nest 2006

Date	Winery	*Sample*	*Cultivar*	A3.2	A1	Ea%	Mp%	PFT %
22-Feb-06	Eagles Nest	*6#*	*MO*	726	2035	35.7%	13.6%	42.8
22-Feb-06	Eagles Nest	*6 Mashed**	*MO*	882	2074	42.5%	18.6%	52.6
22-Feb-06	Eagles Nest	*10 Top#*	*SH*	1171	1971	59.4%	3.7%	36.6
22-Feb-06	Eagles Nest	*10 Top Mashed**	*SH*	1393	2459	56.7%	13.0%	51.0

Waring blender for 30 seconds

*Homogeniser for 10 seconds

Two samples of grapes from the Eagles Nest Winery [80] were mashed by means of a Waring blender, which was used for the entire author's experimentation of the Glories method as well as with a homogeniser, which is used in the Patrick Iland's method. The homogeniser yields a mash, which is extremely fine and also tends to break up the seeds a lot finer. A distinct difference in results was found using the two different techniques of mashing, A1 in the case of the Merlot remained the same, the extraction was marginally better, and the seed tannins slightly higher with a resulting higher total phenol content as was expected due to the finer mashing of the seeds. In the case of the Shiraz sample, a similar trend was found except that the A1 was also a lot higher.

The use of various mashing techniques makes it difficult to compare results between laboratories. Koelenhof laboratory [81] only uses a homogeniser since the 2006 season, whereas most other laboratories and wineries use a Waring blender.

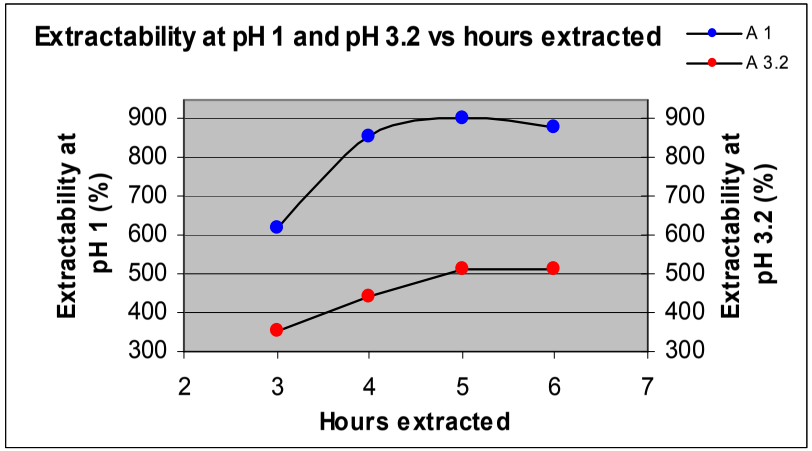

Figure 22: % extractability at pH 1 and pH 3.2 against hours extracted from the seeds to the phenol content against hours extracted.

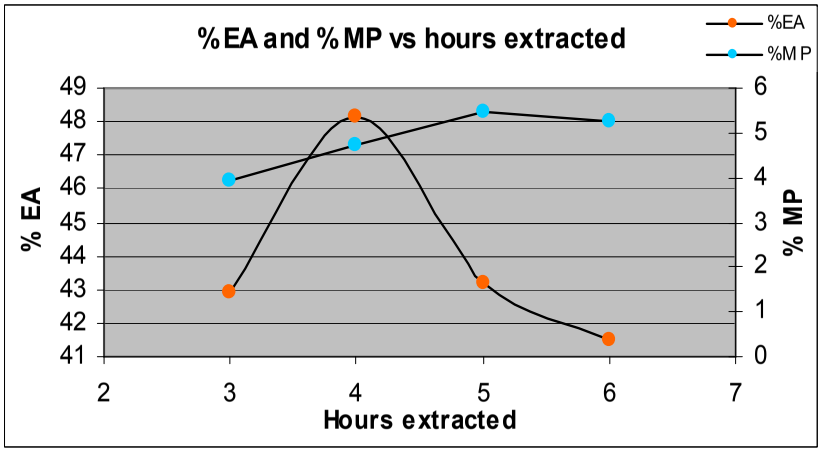

Figure 23: % anthocyanin extractability and % contribution of the tannins

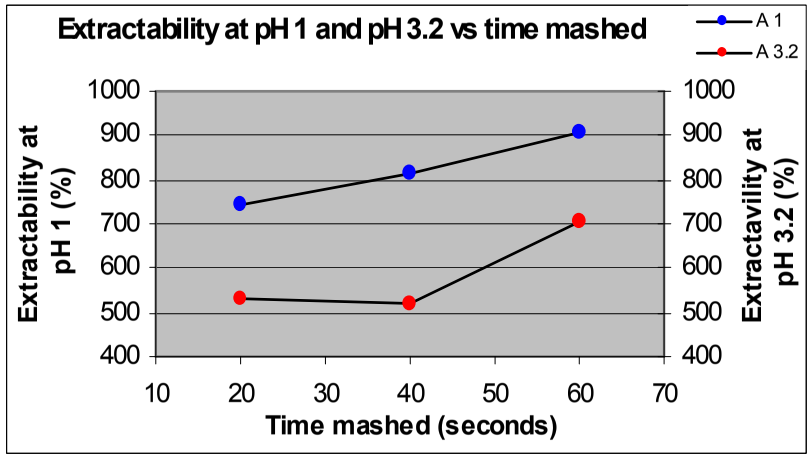

Figure 24: % extractability at pH 1 and pH 3.2 vs. time mashed (sec) mashed (sec).

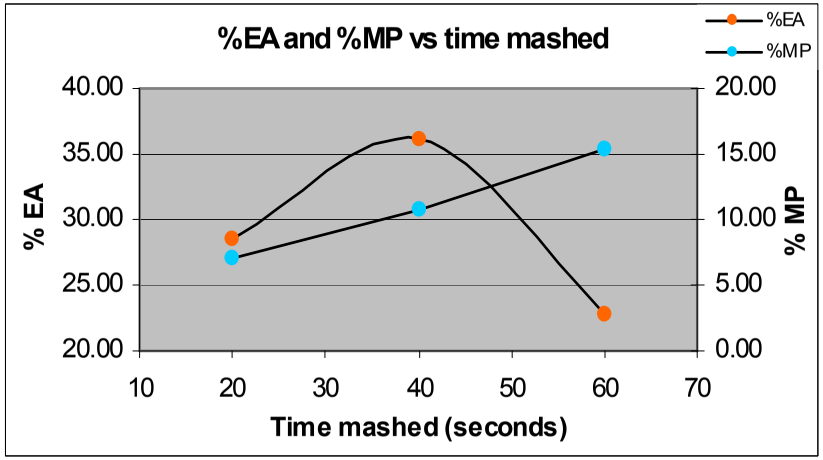

Figure 25: % extractability and contribution of seed tannins vs. time

7.3.6. Glories vs. Iland method

Identical grape samples of Eagles Nest were analysed by means of the Iland and Glories method and results tabulated in Table 20.

Table 20: Comparison of Iland and Glories method, Eagles Nest [MO] 2006

Iland method

Date	Winery	*Sample*	*Cultivar*	Colour per gram berry weight	Total phenolics per gram berry weight
22-Feb-06	Eagles Nest	*5A*	*MO*	1.006	0.978
22-Feb-06	Eagles Nest	*6*	*MO*	1.074	1.076
22-Feb-06	Eagles Nest	*9A*	*MO*	0.942	0.844
22-Feb-06	Eagles Nest	*9B*	*MO*	1.098	0.999

Glories method

Date	Winery	*Sample*	*Cultivar*	A3.2	A1	Ea%	Mp%	PFT %	Brix	pH	TA g/L
22-Feb-06	Eagles Nest	*5A*	*MO*	721	1365	52.8%	13.2%	42.0	21.8%	3.30	6.6
22-Feb-06	Eagles Nest	*6*	*MO*	726	2035	35.7%	13.6%	42.8	20.3%	3.14	8.6
22-Feb-06	Eagles Nest	*9A*	*MO*	686	1323	51.9%	9.6%	36.4	19.0%	3.23	9.6
22-Feb-06	Eagles Nest	*9B*	*MO*	774	1334	58.0%	7.2%	34.8	19.9%	3.20	8.3

The Iland method indicates that of the four blocks analysed, block 9A has the lowest colour, whereas the Glories method indicates that block 6 has by far the highest potential anthocyanins. The total amount of phenols and PFT do not compare either and the advantage of the Glories method is that the percentage extraction can be calculated. From the above results it is difficult to compare the two methods, despite that the two methods both take about five hours to yield results, the Iland method takes one hour to extract whereas the Glories method takes four hours.

7.3.7. Comparison of anthocyanins evaluated in grapes and in resultant wine made

In several instances at De Toren Private Cellar [82] the amount of potential anthocyanins measured at certain blocks was compared with the amount of anthocyanins found in the resultant wine. De Toren Private Cellar vinifies each block separately and hence this was possible. A typical result is depicted in Figure 26, which indicates a peak in anthocyanin concentration early on in the process of fermentation. This was also found by Somers and Evans [83]. The correlation of the amount of anthocyanins found in the resultant wine to the maximum found in the grape is depicted in Table 21. The correlation shows that in all cases the wine showed a 16% greater amount of anthocyanins than found in the grape, irrespective of when the grape was harvested. This indicates that it is more important to attain a high value of potential anthocyanins in the grape than at what stage these appear. In addition, it is not possible for the wine to have a higher concentration of anthocyanins than the grape, indicating that during the experimental stage of the Glories method not all anthocyanins are liberated. This is due to the type of mashing employed. Yet the reproducibility indicates that the method employed does lead to conclusive results.

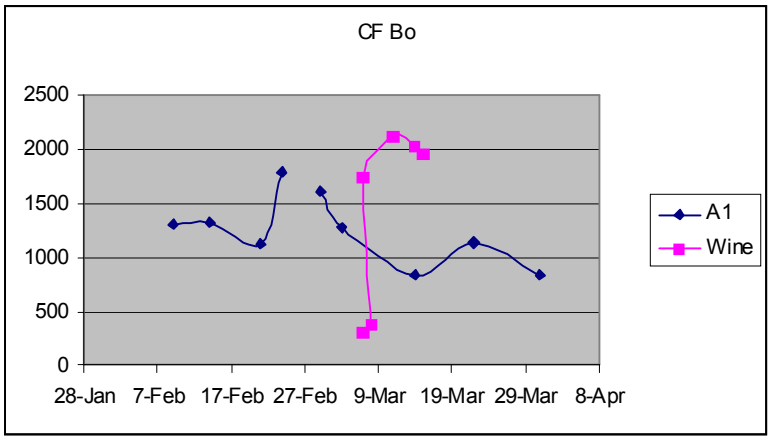

Figure 26: A1 grapes and wine De Toren Private Cellar block D [CS] 2005.

Table 21: A1 of various blocks and resulting wines, De Toren Private Cellar 2005

Cultivar	Block	Wine (A1)	% of Grapes (A1)
CF	Top	2259	119
CF	Bottom	1873	112
CS	D	2249	126
CS	E	2147	115
MO	Left	2139	113
MO	Right	2442	110
MAL		3588	118
Average			116

Kennedy [84] collected data during the 2002 vintage, to establish how much of the tannins and anthocyanins were extracted. He claimed that approximately 40% of the anthocyanins measured in the grape ended up in the wine, after fermentation. However, he also mentioned that after the sixth day of fermentation approximately 65% of anthocyanins detected in the grape were present in the wine [85].

8. COMMENTS ON PHENOLIC RIPENESS BY LOCAL VITICULTURALISTS, PEOPLE IN THE INDUSTRY AND WINEMAKERS

The aim of the interviews was to obtain an overview of what the understanding of phenolic ripeness in South Africa was and to assess the value that it was adding to the industry.

8.1. South Africa

Dr Johan Marais (Head researcher ARC Infruitec-Nietvoorbij, Stellenbosch, South Africa)

Johan Marais said that neither he nor Nietvoorbij were actually involved in the study of phenolic ripeness. He emphasised that the study was focused towards the colour of wine and the taste of wine, from an aroma point of view. In determining the colour of wines, the different types of anthocyanins were measured quantitatively by HPLC. Forty-one different polyphenols were isolated [86].

Patrick Iland worked together with Johan Marais for a month on this and an excellent correlation between colour and quality of taste was found. At least two publications [23, 86] were published but quite a bit of data remained unpublished, especially on Shiraz.

Johan Marais believes that there is very limited knowledge in South Africa about phenolic ripeness and that we have not even scratched the surface of the topic. His comment on the Glories method was that it had been developed for Bordeaux and should be adapted for the South African conditions. He also mentioned that a project would start at Nietvoorbij in 2007 to monitor the change in various anthocyanins over the ripening period of the grape. He also believes that the addition or spiking of various anthocyanins would add a lot of knowledge toward the aroma profile. The anthocyanins could also have a synergistic effect, which would further complicate the studies.

Dr Liezel Coetzee (Laboratory manager, Koelenhof wine cellar laboratory [81])

The Koelenhof laboratory was involved with the evaluation of anthocyanins for the Pinotage project [87]. Although this evaluation was not really focused on phenolic ripeness as such, it was more focused on detecting the amount of anthocyanins at harvest date to attempt to correlate the amount to the taste of the grape.

Koelenhof was also involved with carrying out phenolic ripeness by the Glories method for a few local wine estates, however, most of this ceased during the 2005 harvest. Liezel emphasised that

the laboratory did offer a comment on the results and she felt that this was very important since most recipients of the analysis could not interpret the data provided. Currently the laboratory is involved with analysis with the Institute for Wine Biotechnology, University of Stellenbosch [88]. In particular, analysis was carried out on a comparison of the Glories and Iland methods. These two methods were used together with the analysis of the ratio of malic to tartaric acid. Liezel was of the opinion that the assessment of malic acid was a far more important indicator for optimum ripeness than the phenolic analysis.

Liezel is further of the opinion that grape analysis in South Africa is far behind the rest of the world and she also believes that a couple of years of data is required before making an assessment of a particular vineyard. She also believes that too little is known about the whole subject of phenolic ripeness and that this makes it difficult to educate the viticulturist and winemakers. She also believes that a standardised method should be used in the industry so that various parties can compare their results, which is not the case at the moment.

Hannes Nel (Oenologist, Lourensford [59])

Hannes has been evaluating the Glories method for two vintages; however the data from the 2004 vintage was discarded because of lack of experience in being able to apply the data significantly to obtain meaningful results such as extraction values and concentration of phenolic compounds. During the 2005 vintage Hannes developed his own method of interpreting the results, which at this stage is a closely guarded secret. Ultimately Lourensford will employ this analysis for the top blocks, which will then be earmarked to make an icon wine. He believes that the aim is to manipulate a block viticulturally to obtain a maximum amount of anthocyanins as well as to obtain the maximum amount of extraction. The targets of anthocyanins levels for Merlot are 1 800 mg/L and for Pinotage 1 650 mg/L. This is using his technique of analysis and therefore might not be comparable to values cited by other researchers. Lourensford is using a Waring blender to crush the grapes. Hannes has separated the analysis of tannins into seed tannins as well as skin tannins. He also believes that the size of the berries is a very important factor in the analysis of phenolic ripeness. He has also followed the quantity of anthocyanins through to the wine analysis and has compared the values to those obtained from the relevant grapes. He also believes that the monitoring of anthocyanins during fermentation has given him some insight as to when to press the wine. This has led to their wines being pressed slightly earlier than previous vintages.

He believes that there is a very important place for this scientific method and, further, that it is an added tool to measure ripeness, and may assist in the decision making of when to harvest. It is however definitely not a replacement for the traditional methods of ripeness analysis. He believes it is not used much because although everybody has heard about the technique, very few

understand it. He ultimately is of the opinion that he has developed a pallet to taste phenolic ripeness in the vineyard and he uses the Glories method to assess his tasting ability.

He has also found very erratic results in that his analyses do not give text-book-types of curves. He attributes this to the influence of water, be it due to rain or irrigation. He believes there is a possibility that the quantity of anthocyanins could be incorporated in a method to determine grape prices. His most important aim is to achieve phenolic ripeness in the vineyard at an earlier stage in order to obtain wines with a lower alcohol. He is therefore attempting to manipulate the canopy and is monitoring the results by employing the phenolic ripeness method. He very strongly believes that the Glories method determines the quality of the grapes and the suitability of the terroir to certain grape varieties. He goes as far as to say that he would use the results in assisting him to determine whether certain blocks should be uprooted.

He also believes that the malic acid content is a very important factor in determining ripeness and may even be a better method than phenolic ripeness. He also mentioned that the sampling technique is extremely important and he has thus marked the rows in his vineyard that he uses for phenolic ripeness sampling.

Brad Gold CWM

Brad believes that phenolic ripeness is a very fashionable item and that this may lead to higher alcohols, which lead to wines that are out of balance. He believes that there is not enough education on the subject of phenolic ripeness and therefore there is a limited understanding of the subject. He believes that the emphasis should be on phenolic ripeness at lower sugar levels so that wines of lower alcohol content can be made.

When questioned how he would measure phenolic ripeness he indicated that he would assess the colour of the pips as well as the colour of the grape stems and that this would give him a good indication. He strongly believes that any assessment of phenolic ripeness should give a feedback to viticultural processes so that grapes could be picked at optimal ripeness at lower alcohol levels. He mentioned that although South Africa is a hot country and would thus obviously produce wines of a higher alcohol level he believes that South Africa is missing the point in producing wines of a 15% alcohol level. He emphasised that the desirable level of alcohol limit overseas is 14% and hence we should be producing wines of 13-13.5% alcohol rather than 14.5%.

He also believes that phenolic ripeness would only play a role in the higher priced wines as the higher the ripeness attained, the more amount of wood tannins are necessary to balance the wines. This would obviously elevate the price of the resultant wine.

He also strongly pointed out that there should always be a balance of fruit flavours versus the amount of tannins.

Dr. Karin Bindon (Temporary lecturer, Wine Biotechnology) and **Ciska du Plessis** (MSc student, US, 2006)

The MSc student started off with her MSc project evaluating the Glories versus the Iland method of phenolic ripeness analysis. However, the study topic was later changed because she was unable to obtain suitable reproducibility of the Glories method. It was said that some results varied by as much as 20%, and hence she believed that the Glories method was not really applicable as a scientific tool. Although the Iland method was a lot faster than the Glories method, the Glories method still gave some important data especially where the total amount of anthocyanins as well as the extraction was of importance. She also believed that it was most important to separate the tannin analysis into skin as well as seed tannins. She believed that the possible erroneous results of the Glories method that she obtained were due to the technique of her dilution method. She believes that sample preparation is of utmost importance and she is aiming to introduce an industry standard that all users and researchers of phenolic ripeness could use to compare their results.

Anita Oberholster (Head technical assistant – Wine Biotechnology)

Anita is in the process of completing her PhD in the polymerization of tannins. She is of the opinion that the analysis of any types of phenol compounds should tie up with sensory mouth feel of wine. She believes that the definition of phenolic ripeness is the maturity of the grape that will yield the best quality of wine that is required for the style of wine intended to be made. She also mentions that there are various styles of wine and that the viticultural practices employed will dictate what style of wine will ultimately be made. She mentions that it is very important to combine the phenolic ripeness analysis with the traditional methods of assessing wine ripeness. Without the traditional methods phenolic ripeness means nothing.

She also states that the tannin analysis should be split into seed and skin tannins. She also believes that a study of terroir versus seed tannins would be an important indicator of grape ripeness.

While she agrees that the amount of anthocyanins is related to the intensity of the colour and the resulting quality of the wine, she mentions that the ratio of anthocyanins to tannins is very important. This ratio has been studied in France and optimally should be a 4:1 ratio of anthocyanins to tannins, but this subject has hardly been studied elsewhere. She also believes

that phenolic ripeness can be used to manipulate the taste of wine and she emphasises that the French have been doing this indirectly for many years, but have not really disclosed their technique. One of these techniques is to introduce oxygen into the wine to assist the polymerisations, resulting in the softening of the tannins. She believes that the aim of the research should be to soften the tannin structure.

She believes that phenolic ripeness should be employed to assess white grape varieties such as Chenin Blanc, Sauvignon Blanc and Chardonnay. She believes the white grape variety to be most suitable for this study would be Chardonnay. Even though white wines do not spend a lot of time with skin contact the flavours derived in the wine still come from the skin and hence it is important to monitor the building blocks (phenolics) of the flavour compounds.

Anita believes that the flavour structure is important because the market dictates the wine styles, which are to be made. For instance, she says that the general market prefers a wine to have a consistent flavour from vintage to vintage. An example of this is the KWV Roodeberg wine, which is blended essentially to taste the same vintage after vintage. Hence she once again emphasised that the study of phenolic ripeness should be linked to the flavour and mouth feel study.

Francois Naude (Winemaker and wine consultant)

Francois's comment on phenolic ripeness was that "the more you know, the less you know". It is very much like micro-oxygenation. He is of the opinion that South Africa has not scratched the surface of phenolic ripeness yet and he also believes that the more research put in the more the deductions will change. His opinion is that phenolic ripeness is a major part in the practice of making good wine. He says that drinking patterns have changed in the last couple of years, and the public is now demanding a wine that can be drunk immediately after release, and thus does not require storage. Hence it is important that the manipulation of softening tannins is understood. He believes the winemaking style of the old days where a wine required 10 to 15 years to soften the tannins is really not applicable at the moment. He also emphasises that science in winemaking is changing continuously. He gave an example of wood barrels: he said that many factors in the manufacture of wood barrels were not fully understood yet they led to a better wine product. As in the case of wood barrels, research is very necessary to understand the wood process.

He believes the Australians have a very good understanding of softening wine tannins. The addition of tannin to complex wine was introduced to stabilise the colour and thus yield a more market friendly wine. This type of wine started selling exceptionally well in Europe and thus caused the French to lose market share. Further, the Australians carried out a market survey to determine what type of wines were in demand. The types of wine required by the general public

were to be of beverage quality and hence easy drinking. The French on the other hand were losing market share because their wines could not be drunk young and they were reluctant to manipulate their winemaking style like the Australians, and hence Glories became popular.

Francois believes that the Portuguese understand the phenolic ripeness far better than any other nation. They produce wines that are phenolically ripe and manipulate their winemaking process accordingly. To the Portuguese it does not matter what the alcohol level is as they were essentially producing Port which was fortified anyway. The most important objective to the Portuguese is to obtain a dense colour that will complex with tannins. Francois also mentioned that the tannin to anthocyanin ratio used by the French is in principal an excellent method, however this has to be modified so that it can be used in other regions of the word. He therefore believes that research in South Africa is very important.

Francois believes that the most important aspect of phenolic ripeness is first of all the collection of the samples and secondly to establish consistent methods of evaluation so that results can be compared.

Hannelie Smit (Owner of VinLab [60])

Hannelie said that phenolic ripeness is vineyard specific and that we can't compare the ripeness study with overseas as it comes back to what is carried out in the vineyard. The analysis also assists in decision making with vinification, she emphasized that most users used the results as confirmation of what was carried out in the vineyard.

In South Africa we don't really know enough, however, we are improving and VinLab believed that they were definitely better equipped to comment on phenolic ripeness in comparison with three years ago. With regard to a question whether hotter areas showed a lower potential anthocyanin level, Hannelie responded that they offered a laboratory service rather than carry out specific research into certain areas.

She believed that the young wine makers were especially interested in new techniques and that the demand for phenolic ripeness analysis was increasing.

Hannelie also mentioned that because of the various laboratories using their own techniques it would not really be possible for a client to compare results from different laboratories and reach a conclusion. A client should stay with a laboratory of choice and continue with them for the entire season.

In summary Hannelie mentioned “that, until such time as a vast database of the history of the vineyard has been developed, the real value of phenolic ripeness numbers are as follows:

- To compare vintages
- To compare vineyards
- To compare the effect on the phenolic profile of different vineyard management techniques”.

Christiaan Eedes (Deputy Editor of Wine Magazine [89])

A Cape Town wine retailer related to me that after the 2006 Old Mutual Trophy Wine Show results were announced, she was asked by a regular customer to make a selection from the top performing red wines for his cellar. There was no cap on how much was to be spent, the only condition being that the wines should have the potential to improve in bottle for at least 10 years. Along came the public tasting of the trophy, gold and silver medal-winning wines, which provided said retailer with the opportunity to review the line-up in accordance with her customer's requirements. In the end, she decided that there was nothing on show that she could buy on behalf of her customer in good faith, and I was forced to concur with her. It's not that any of the wines were undeserving of the honours that they received, for they were all very good in a particular style, that being soft and accessible. Nevertheless, it is difficult to have any conviction that they will mature to any real advantage.

In the modern era, South African red wine has been much berated for being astringent and green by international critics. In reaction to this, local winemakers have become obsessed with "full phenolic ripeness", adopting ever longer hang times for their grapes before picking.

There can be no doubt that South African reds, in general, now display better ripeness and concentration levels than they did 10 or 20 years ago, but this trend has not been without its concomitant problems. Alcohol levels have risen dramatically which does not make for easy drinking, whether the wine is young or old. In addition, residual sugar levels are higher, acids less fresh and tannins softer now, all mitigating against the wines’ ability to mature well.

Whatever the shortcomings of the top performing reds at this year's Trophy Wine Show, the general consensus seems to be that the whites were truly excellent. Far from being a random outcome, I think this is indicative of a sea change that is occurring in the industry.

Most of the South African winelands have a very temperate and essentially Mediterranean climate. Conventional wisdom has therefore maintained that this suits red varieties more than white

varieties on the basis that the former tend to be more robust and ripen later than the latter and will therefore benefit from the extra sunshine.

However, there is a growing body of thought that it is South Africa's white wines that are our best vinous offering in world terms. One hypothesis as to why this might be so is because the grapes involved are picked at the beginning of the summer; they escape the searing heat that comes in later months leading to ripening conditions that are too severe for optimal flavour development in the red grapes. Of course, the situation is made worse by global warming.

Dagi Schmidtke (Owner and winemaker of “Olyvenbosch Cabernet Sauvignon” [90|)

Dagi states on his back label that the wine is harvested at “optimum ripeness”, the following was posed to him: “Dear Sir, I was recently given one of your bottles of wine and noticed that the back label stated the grapes were harvested at "optimum ripeness". I have a question, what in your terms is optimum ripeness, in other words how is it defined, was it measured or is it purely on a taste perception?”

His answer was “Optimum ripeness for our cultivars is 24 - 25 Brix, as well as taste.”

Charles Back (Owner of the Fairview and Spice Route operations [56]) [91], reflects as follows: "About 25 years ago, we used to pick at a sugar level of 23° Brix, regardless. Now if the grape has reached 26° or 27° Brix, then so be it." One potential solution would be to plant varieties that reach full phenolic ripeness at lower sugar levels. Back points to another wine from Fairview, the Shiraz Mourvèdre Viognier blend. Red variety Mourvèdre reaches phenolic ripeness at relatively low sugars, and by including it as a component in the mix, an extreme alcohol level is avoided.

Bruce Jack (Flagstone Winery [92]) [91] and one of the most progressive young winemakers around, is adamant that the best wine depends on optimally ripe fruit, but instead of referring to phenolic ripeness, he speaks of vine ripeness.

His take on the matter is instructive: the grape is no more than the vine's way of reproducing itself in basic biological terms. So the more succulent and tasty the berry, the more likely some bird or animal will consume it and so disperse the seeds. When the vine is flourishing, Jack argues, it is not inclined to produce fruit. But when it is stressed, it will stop vegetative growth and focus on fruit production to ensure survival. As far as Jack is concerned, the winemaker's role in the vineyard is to manage the vine so that it concentrates its energies on producing grapes of optimal quality.

David Trafford (Winemaker De Trafford wines [93]) [91]

David is also convinced of the merits of picking at optimum ripeness. "A longer hang-time," he says, "means softer, but also richer, more plentiful tannins." He points out, however, that there are many factors other than phenolic ripeness that determine when to pick. Sugar, acid and pH remain important and the general state of the vineyard must also be considered. "You might still have green seeds, but if the leaves are shrivelled, you must pick." The judgement of the winemaker remains crucial in the whole process.

Pieter Ferreira (Cellarmaster Graham Beck Wines [94])

Pieter was asked on the web "What is phenolic ripeness and how does it affect wine?" by Brooke Pieter Ferreira answers [95]: "First of all phenolic ripeness is associated with grapes that have tannin. Normally it is related to red grape varieties but we also know that there are certain white grapes that also contain some phenolics, i.e. Viognier. There are basically two levels of ripeness that we follow before we pick the grapes. One is sugar ripeness and the other phenolic ripeness. In South Africa sugar ripeness is easily achieved because of the amount of sunshine. Phenolic ripeness is a little more difficult to achieve. The effect of phenolic ripeness will determine whether the wine tastes "green" and aggressive (picked to early) or that it has nice roundness on the palate with no astringency. Should you need more info please let me know."

Wine Magazine poll. The most recent poll in Wine magazine, May 2005: As winemakers pursue full phenolic ripeness, the resulting wines have increasingly high alcohol levels. What do you think about this?

Result: 56% Rather rich and ripe than thin and weedy
44% Elegance and finesse have been lost.

8.2. International

8.2.1. USA, California

Moderator David Graves of Saintsbury noted that [96] "wine styles are very much a human creation, and we make a huge number of choices to influence style", he then asked a group of six winemakers from Carneros, "Why are alcohol levels rising, and why is fruit picked at an ever riper level?"

"We do look for richness that comes with a certain alcohol," answered **Anne Moller-Racke**, president of the Donum Estate and viticulturist for **Robert Stemmler** winery. "You want flavour development at lower sugars if possible, but there is a sweet point you want to hit."

To make luscious, intense wines that are not alcoholic, she explained, “We work on the edge, because if you wait at 24° Brix sugar and it gets warm, even with 5% to 10% dehydration that you can’t feel, you are quickly at 26° or 27° Brix.”

Ripeness decisions begin at pruning, she said. “Pruning and suckering may sound like a recipe, but each time you must vary the ingredients depending on the vintage.” Her biggest challenge is to understand the vintage as early as possible, then advise the winemakers. With attention to detail and knowledge of the vineyard’s history, “you can predict and make good decisions.”

Cooler years present a different challenge, Moller-Racke stated. “In 1999, we had all the hang time in the world and wonderful flavours at only 23° Brix, but that doesn’t give richness in the mouth.”

Wayne Donaldson, winemaker at **Domaine Chandon**, agreed that in “just about every season I’ve had in California (we’re) sitting at 23.5° or 24° Brix and flavour profiles (are) right there and then, slam, we get hit.” Coming from Australia’s Yarra Valley, he has had to deal with California’s “incredible sunshine.” For whatever reason, Donaldson remarked, the consumer palate “is being guided towards bigger, richer, viscous, unctuous, fat, gooey wines,” and the sun helps make them, but it doesn’t necessarily help achieve physiological ripeness.

Sugars, flavours and tannins “are all linked…but they do have different ripening paths,” Donaldson said. “That’s the conundrum, trying to make wines with all these things in balance, yet we’re being hammered with alcohol.”

“And is climate changing, is it getting warmer?” he asked. “Maybe assuming that our terroir is always going to be static is flawed.” Donaldson says long-term strategies should focus on the vineyard – on clones, rootstocks and cultural practices. For example, with vertical canopies, he thinks orienting rows into the sun can shade fruit and keep it cooler, “stretching that (hang time) window out a bit.”

Graves agreed that “it’s easy to go too far in the world of sun exposure in the vineyard canopy,” suggesting that “maybe the pendulum is swinging back a little towards open shade rather than full sun.”

James Hall, winemaker at **Patz & Hall**, said that in making the most important decision of the year – when to harvest – he prefers the term “ripeness,” implying that before it is reached, “there’s a state of un-ripeness.”

“Over the years,” Hall said, “I’ve learned that grapes higher in sugar and with riper tannins, particularly riper seeds, allow for fuller extraction in the winery.” He concurred that fall heat waves are frustrating and “a logistical nightmare to get all the fruit in. That said, it doesn’t necessarily mean the vintage is a failure or that the wines are unbalanced. It just means it’s necessary to address that in the winery.”

Hall recalled that, in the 1980s, “people were very obsessed with…total acidity and…picking based on pH and those wines really didn’t have the flavour profile or depth of character that I think wines have these days. Alcohol is the inverse of that and too much of any one component is clearly not desirable.”

But in a vintage like 2004, or 2003 in Europe, “you have to play the hands you are dealt,” Hall pointed out. “Personally, I don’t think I have that much control over the process. The weather and the vineyard have their own trajectory and I’m along for the ride. Sure, we can irrigate a little bit, leaf strip, thin some fruit, but (that) won’t change the fundamental character of the vineyard.”

Asked if grapes jumped in ripeness in other places where he sources grapes, Hall replied, “Yes. It’s a function of the weather. In 2004, we had an offshore flow of wind out of the Central Valley, very low humidity in some cases approaching single digits and hot temperatures. That desiccated the fruit everywhere. In Russian River, Carneros, the Santa Lucia Highlands, Mendocino and the Central Coast, the same thing.”

“But it’s really 2003 and 2004,” he explained. “I hesitate to make general conclusions about terroir and climate based on two warm vintages. We’ve had some cool years, too.”

Ken Bernards, winemaker at **Ancien Winery**, said every region has its own inherent challenges. “With the Burgundy model, in some vintages you have trouble reaching sugar and physiological ripeness and the reverse is sometimes true here. In the winery, we have developed techniques to deal with what nature doesn’t give us.”

“The thing we keep talking about…the north wind…is the reversal of what we usually have. We have marine influence and the wind pushes it off. When that happens, timing is everything,” according to Bernards. “In a given vintage, James might be bemoaning the heat and low humidity and I may be picking a week earlier or later and be in a different window.”

Michael Havens, winemaker at **Havens Wine Cellars**, said his response to the question of ripeness "has been to choose varieties that I think exhibit characteristics when grown in Carneros that I find pleasing."

Havens said he "values a balance between the bones and the flesh – the tannins and acid on one side and fruit extract and alcohol on the other, because alcohol is a sweetener and the oak, which can be both a tannin and a sweet contributor. I like those things to be pleasingly balanced in the mouth to complement food."

Havens contended that most winemaking focuses on qualities easily appreciated by most people and "that means sweetness." Instead of a balance among elements, there is a domination of sweetness. "A lot of winemaking has become formulaic…focus-group winemaking," he said. "But I appreciate a balance that's different. I focused on varieties that ripen differently in Carneros – Merlot, Cabernet Franc, Syrah and…Albariño."

"Ripeness is not a single issue; it's complex," he continued. Havens spoke of four ripeness clocks running simultaneously but at different rates – sugar accumulation, acid transpiration, phenolic ripeness and fruit character. In his varieties and to some degree in Burgundian varieties as well, fruit character starts at vegetal, moves to herbal, to fruity, then jammy and finally, cooked.

According to Havens, there's no single correct place in that series of fruit characters and on the other clocks: "I think we should be able to appreciate different senses of style and balance and fruit characteristics."

David Ramey from Ramey Wine Cellars; John Caldwell of Caldwell Wines and Mia Klein from Selene Winery discuss, why does "ripe" mean higher sugar, nowadays [97]?

Ramey, "First, we have all new plant materials. We were dealing with those virused vines, so 23° Brix was a good sugar for Napa Valley Cabernet in 1966. It is no longer a good number because we have more healthy vines".

Klein, "In the past, people did a whole line of wines. Logistics used to make a big difference. People used to pick under ripe, ripe and overripe grapes, and then make a blend, but they had to do that because they couldn't get all the grapes in if they tried picking when they were ready".

Ramey, "And the change from California sprawl to vertical is a big change".

Caldwell, “And that big change started in the early ’90s with the major replanting of vineyards due to Phylloxera. Different rootstocks, closer spacing, different clones, better row spacing. It used to be 8x12, now it’s more like 5x7, and I’ve even seen as close as meter by meter. Row spacing has always been associated with equipment”.

Ramey, “It’s not like Sauternes where you go through the same block picking individual clusters. What you are doing is breaking up the block into micro harvest units, and in that instance it has to do with the foliage”.

Klein, “Especially when you’re talking about reds. The foliage will show you when it’s time to pick. We’re integrators. We look at one thing at a time, but we integrate that information to make a decision. So, I look at the weather report, to get a good idea of what it will be for the rest of the week. I know what the water status of the vines is. I know what rootstock they are on. I know what my tank space is like …so they are all there and we incorporate all of those things in making our harvest decision”.

The question; “*I want each of you to pick a variety of red grapes and tell me what you would like to do irrespective of reality conditions*” was posed to each of them.

Caldwell, “With Syrah, my buyers want ripe, ripe fruit. They want big, huge flavours. They’re looking for very, very dark fruit. My buyers don’t even come out to taste until 24.5° to 25° Brix. They are not even interested. Then vintage is important. What is the hang time? Are the vines still bright? Do they have some green left in the leaves, some spunk in them? If so, we let them hang. Like Mia said, “If it’s not getting worse, then its getting better.” At about 25° to 26° Brix the clusters start getting a little soft and loose; a little dimpling is the first sign that we are getting close. Its not uncommon that at that time some pH’s are being taken, when they get up around 3.7 or 3.9 then they start thinking about harvest. But it takes all of these different components: looking at the vines, the dimpling, tasting the fruit. It’s all part of the equation”.

Klein, “Merlot always gets stuck. You think they’re doing great and they’re close. Then you go out three days later and everything is the same: the same look of the vines, the same sugar, and the same pH. So you have to wait. It gets to about 25° Brix and then it sticks. With Cabernet at that Brix you might go look at it. With Merlot, you’d go look at it, but then you say, “it is going to be while.” You think three, four, maybe seven more days, but then three weeks go by and nothing has changed in flavour. Maybe the sugar has moved a little bit, but nothing else has changed. The pH has to go up as a sign of true ripeness”.

Ramey, “In the old days, Davis gave us a ripeness index that focused on Brix. Then we heard from France that tannins and anthocyanins in red grape skins were polymerising while they were on the vine. Above a certain molecular weight there is a soft tannic mouth feel. Below that weight it is chunky or astringent in the mouth. That’s the whole thing about waiting with red wines these days, to soften the tannins. With Cabernet, if there is not a compelling reason to pick you are almost always better off waiting. Compelling reasons to pick include entire defoliation of the grapevine or impending rains, but it is all about the phenolic ripeness. Classic examples to the counterpoint of that are certain well known wineries that are undrinkable in their youth, and undrinkable in their adulthood. These are wines that have immature tannins. And if the tannins are immature in their youth, they aren’t going to get better”.

The question; *“Can we get ripeness at less than 26° Brix? I mean there is virtually no fine red wine in California under 14 % alcohol”* was posed to each of them.

Klein, “There is no one under 14 percent who’s making “fine” wine. Sorry. Well, that’s a bit harsh, let’s just say that it’s pretty hard to get the flavours, mouth feel and extraction that we associate with great wines at less than 14 percent alcohol”.

Ramey, “There’s an interesting issue. To the extent that we compare to the great vintages of France, Burgundy will reach 15 percent naturally in great years. Why should we take mediocre French vintages as our yardstick? We have ripe grapes. Sometimes we deal with over-ripeness. That’s our issue, but its no longer green, hard undrinkable tannins”.

Caldwell, “The same is true of Bordeaux. They made a lot of that green, lead pencil undrinkable wine”.

The question; *“Okay, so if we want to maximise ripeness, explain to me how almost continuous irrigation leads to concentration, and how can amelioration in the wine NOT lead to dilution*” was posed to each of them.

Caldwell, “When I deliver grapes at 27° or 28° Brix, they are so concentrated and dehydrated, and a lot of that additional Brix is from dehydration. So as a grower, I’m delivering grapes that are sometimes 10-20 percent less weight, just in water. They’ve started to dimple and soften, at least on the sun side of the cluster. What happens at the fermentor is that they are seriously, legitimately just adding back the water that’s dehydrated to get those flavours. So we’re not diluting, were actually adding it back. We don’t care about the sugars. We care about the flavours.

Ramey, “It depends on the vineyard, because number one, my goal is to not harvest dehydrated fruit. The goal of quality farming is fresh, ripe fruit, and in my 25 years in the California business, I can say I have seen more vineyards harmed by dry farming than over watering”.

Caldwell, “Bingo”.

Ramey, “People want to carry the Old World methods over here, but it doesn’t work. California doesn’t get rain from April through October. So we start every season with the soil at field capacity, a technical term. It means it’s saturated. You do not need to water from bud break until, depending on the site, June, July 1, maybe August 1. Some sites with deep soil, maybe you get through without watering, but there’s nothing better about that. It’s just about the relationship between the roots, the soil and the vine. Most of the good vineyards in Napa and Sonoma are on poor soils that limit the crop naturally. That’s why thinning is a non-issue, because you’re not going to get more than 3½ tons on the site anyway. You’ve got close spacing. You’ve got maybe seven to eight pounds of fruit per vine. It appears that having less fruit per vine is a quality plus.”

9. CONCLUSIONS AND RECOMMENDATIONS

9.1. Conclusions

Phenolic ripeness measurements are offered as a commercial service by at least three laboratories in South Africa. Further more, at least five wineries are carrying out such analyses in-house. The Department of viticulture at the University of Stellenbosch has embarked on extensive research into the ripeness and phenolic ripeness of grapes as well as the influences of viticultural practices on ripeness.

Although there is an increasing awareness of “phenolic ripeness”, the term remains a buzzword; it is liberally quoted, but seldomly fully understood by winemakers and viticulturists. It is especially the chemistry aspect of this term that is very neglected, while the sensational tactility such as mouth feel and taste are readily quoted.

The Glories method of analysis of phenolic ripeness has yielded good results in South Africa and is the most common method currently used to analyse the amount of phenolic compounds within the grape. The most important use of this method is to judge the quality of the fruit from the potential anthocyanin concentration that the grape can deliver. It has categorically been shown that the amount of anthocyanins present in the grape is responsible for the quality of the wine, hence the following parameters (Table 22) have been established to categorise the various varieties of grapes. These parameters were determined by the Glories method as modified by the author based on four years of experimental data.

Table 22: Grape quality categories based on potential anthocyanin level (A1) (results as determined by the Glories method)

Variety	Quality category of grapes	
	Good	Excellent
Cabernet Sauvignon	>1600	>2000
Cabernet Franc	>1150	>1400
Merlot	>1400	>1650
Pinotage	>1000	>1400
Shiraz	>1550	>1800

The Glories method has also has been found to be an excellent tool to assess the quality of a vintage by comparing the relative concentrations of anthocyanins in the same vineyard each year.

This ties in with comments made in Bordeaux that the amount of phenolics in grapes correlates to the quality of a vintage.

The amount of anthocyanins, which are measured in the vineyard, can be directly correlated to the amount of anthocyanins that are found in the resultant wine. This shows that the method of determining the anthocyanins in a grape directly correlates to the amount found in the wine and hence the quality of the resultant wine can be determined by analysing the amount of phenolics in the grape. The correlation between the two analyses is very accurate, and surprisingly consistent.

The analysis of several South African vineyards has shown that the amount of potential anthocyanins within a grape sometimes peak far earlier than anticipated and, since this amount correlates to the amount found in the resultant wine, it is not always necessary to extend the hang-time of the grapes to obtain extremely high alcohol levels, as discussed by some Californian wine makers. It is generally claimed that picking grapes at phenolic ripeness leads to extremely high alcohol concentrations, although both Brad Gold and Andre van Rensburg have said that it should be avoided (see Chapter 7). Comments made by Californian winemakers with regards to picking grapes at higher sugar levels indicate that they may not really be necessary to obtain better quality in terms on anthocyanin concentration, depending on the pattern of anthocyanin concentration relative to growing time. Many winemakers allow the grapes to hang as long as possible to obtain maximum ripeness, which in many cases can result in overripe wines. The tendency in California is to extend hang-time. This results in wines described as “ripe fruits or jammy–flavours”, which may be considered as overripe by some people. Jancis Robinson has described some wines that she has tasted as wines made from “dead grapes” that have been allowed to pass the point of optimum ripeness. It has been shown from the author’s evaluation of phenolic ripeness that it is possible to pick grapes phenolically ripe at lower alcohol levels. Anthocyanins need to bond with phenols to prevent colour from dropping out of the wine and to temper harsh tannins. Oak, either in barrel or alternatives, such as chips and pellets, can add aldehydes to the process. Aldehydes can serve as cross links, introducing anthocyanins to tannins. Phenolic polymerization allows wines to mature faster, tempers harsh tannins, enhances suppleness, and provides maximum, lasting colour. Hence once the optimum level of anthocyanins has been achieved in a grape and the traditional factors used to evaluate grape ripeness are in place, the grapes can be harvested.

The Glories method is able to quantitatively detect any changes in viticultural practices that influence the amount of anthocyanins in a grape and the timing of optimum anthocyanin concentration. Water appears to be the most influential factor on the level of anthocyanins in the grape, including the amount as well as the timing of administration. It has also been shown that bunch thinning and topping have a dramatic effect on phenolic ripeness and that virused vines show different phenolic ripeness to un-virused vines. Hence the Glories method of determining

phenolic ripeness could be an excellent methodology to evaluate the effect of any viticultural practices on the grapes.

Once the potential level of anthocyanins has peaked, the extraction levels of the anthocyanins as well as the concentrations of seed tannins come into play to determine grape ripeness - and these factors can then assist in determining the harvest date. If the potential amount of anthocyanins, however, has not peaked, phenolic ripeness will not be achieved.

The Glories method takes considerable time before results can be obtained. It has been shown that results can be obtained in a five and a half to a six hour period, thus allowing results to be obtained within the same day of sampling. It also has been shown that many blocks can be analysed within day.

It was however found that the results of the Glories method were difficult to correlate with results of the Folin-Ciocalteau method and the Patrick Iland method. The advantage of the Glories method is that the percentage of extraction is an important indicator of ripeness over and above obtaining a total concentration of phenolic compounds, which is all the other two methods yield.

Reporting on the total amount of phenolic compounds remains questionable, in the author's opinion as a measuring device of quality as this values includes tannins which may contribute to bitterness of green flavours. The use of the total phenol index (TPI) may lead to erroneous expectations, as this value is a sum of all the phenolic compounds such as anthocyanins and tannins. Tannins, if not polymerized sufficiently, yield harsh flavours. Some researchers have shown that it is possible to increase the total amount of phenols present, as measured at a wavelength of 280 nm in UV spectra, by the addition of seeds [98]. This process mostly added to the harshness of wine, despite increasing the total phenol index.

The results obtained in South Africa by the Glories method correlate to results obtained in Bordeaux [6] and Sicily [53]. They do however differ from the Spanish results [50], possibly due to a variation in experimental methodology.

9.2. Recommendations

The analysis of phenolic ripeness in South Africa is presently rather 'disjointed', as institutions or laboratories are attempting to carry out their own research and analyses, and there is little or no comparison of results. A general method needs to be developed so that the various interested parties can at least compare their results and then perhaps compare possible viticultural influences

on phenolic content. The Glories method has proven to be an extremely reliable mechanism to judge grape quality and this should be developed into a possible implementation, to even influence the price that is paid for grapes. An existing formula from Australia for pricing of grapes bought-in is detailed in the section describing uses of phenolic ripeness (Chapter 6). The author has made an initial proposal has been made to KWV to assess quality using anthocyanin levels, extraction, and seed tannins. A formula for determining the grape quality has been developed. The correlation of the possible contribution of phenolic compounds towards the flavour structures should become an academic study. In the meantime, some emphasis should be placed on the influences of viticultural practises on the amount of anthocyanins present in the grape. Winemakers should also attempt to blend blocks of grapes that have high initial anthocyanin content, which can be harvested at lower Brix values, with those that achieve a higher anthocyanin concentration later in the season. The multiple harvest of white grape varieties, such as Sauvignon Blanc, to achieve a spectrum of complex flavours, should be applied to red grapes as well.

South Africa wants more information about phenolic ripeness and there is a hunger by the younger winemakers to achieve a better understanding of what it is and how it can be used. The various laboratories need to agree on a universal method to achieve better correlations between results that would strengthen the understanding of this topic. The author has optimised such a laboratory techniques.

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