Chemometrics and Intelligent Laboratory Systems 203 (2020) 104067

Contents lists available at ScienceDirect

Chemometrics and Intelligent Laboratory Systems

journal homepage: www.elsevier.com/locate/chemometrics

A chemometric approach to the evaluation of the ageing ability of red wines

Jose Luis Aleixandre-Tudo *, Wessel du Toit

Department of Viticulture and Oenology, Stellenbosch University, Private Bag X1, Matieland, 7602, South Africa

ARTICLE INFO

Keywords:
Ageing ability
Ageing potential
Phenolic compounds
Tannins
Anthocyanins
Chemometrics

ABSTRACT

One of the most important quality attributes of red wines is its ability to withstand and ageing process. The multidimensionality of the ageing ability concept, which includes a combination of colour, taste, mouthfeel, and aroma was reported in previous studies. Phenolic compounds are largely or partially involved in most of these wine attributes and have been proposed as potential candidates to evaluate the ageing ability of red wines. The phenolic and colour properties of a large number of wines were measured during a barrel and bottle ageing process of 24 months. To our understanding, a wine that needs the longest time to reach optimal phenolic quality is considered a wine with higher ability to age (concentration assumption). Moreover, a wine that is able to maintain its optimal phenolic quality for longer will also be a wine with high ageing ability (stability assumption). Based on the formulated assumptions a scoring system was used to identify those wines with theoretically high ability to age. As expected, these wines contained initial high levels of tannins, total phenols and anthocyanins, including high polymeric pigment presence and enhanced colour properties. Interestingly, high ageing ability wines showed a smaller change in the colour properties over time which might be indicating slower pigment formation rates. In addition, a chemometric attempt was undertaken to explore an ageing index based on initial phenolic content. The evolution of the index over time using a multi-block approach showed stability for the index values, in line with the short term stability of tannin and total phenol levels. Finally, promising results were obtained as two thirds of the wines were correctly classified when a validation task between the ageing index and the score values was attempted.

1. Introduction

Red winemaking entails a fermentation process in which the solid parts of the berries remain in contact with the juice/must. The purpose of maceration is to promote the diffusion of compounds associated with the skin and seed into the eventual wine matrix [1,2]. In white winemaking, maceration, if applied, is limited to a few hours before alcoholic fermentation and it is mainly directed towards enriching the juice with aromas or precursor compounds [3]. On the contrary, the main purpose of maceration in red wine is to promote the release of phenolic compounds. Phenolic compounds provide red wines its characteristic colour and mouthfeel attributes and are therefore crucial for the red wine organoleptic properties [4,5].

Once a red wine fermentation is completed, an ageing process is commonly followed, which often leads to an improvement of the final wine quality. The first part occurs generally in wooden casks or barrels, whereas the second part of the process will take place in bottles. During barrel ageing wines are exposed to a more oxidative environment as oxygen permeates trough the wood into the wine [6,7]. In addition, the diffusion of wood components also takes place. Wood barrels contribute mainly to wine flavour and aroma in addition to phenolics, such as hydrolysable tannins, also being released [8]. Alternatively, during bottle ageing wines are exposed to a more reductive conditions, as only the dissolved oxygen at bottling or the low levels of oxygen that permeates though the closures will be present. The development of the wine during bottle ageing is not due to external factors as the wine composition is not modified by the incorporation of other components.

As mentioned, the changes in the organoleptic properties often happens during wine ageing. Additional to development of new and more complex flavour and aroma compounds, positive changes in the mouthfeel properties may also occurs [9–11]. The ageing ability, or ageing potential as it is also commonly referred to, may therefore indicate the ability of a wine to withstand an ageing process. However, the definition of this concept was found vague and unclear with limited attempts to elucidate it further being reported [12–14]. Based on literature and our own understanding, two practical definitions are here formulated. A

* Corresponding author.
E-mail address: joaltu@sun.ac.za (J.L. Aleixandre-Tudo).

https://doi.org/10.1016/j.chemolab.2020.104067
Received 30 September 2019; Received in revised form 23 May 2020; Accepted 28 May 2020
Available online 1 June 2020

wine that reaches its optimal organoleptic properties, or optimal quality, after a longer period of time is therefore assumed to have higher ageing ability. In other words, a wine that needs 30 years to reach optimal quality has a higher ageing ability than another that needs 5 years. An alternative definition would be: a wine with ability to age is a wine that will keep optimal organoleptic properties during a longer period of time before quality perception starts decreasing.

The reported studies lack of a clear definition or even attempt to define, quantify and confirm wine ageing ability or ageing potential. In most cases, the purpose is not to evaluate the ageing ability of the wines. The terms are just included as keywords or vaguely used to speculate on the projected outcomes of the results reported [15–19]. However, a few sensory studies have tried to shed light onto the ageing ability concept with interesting results being reported [12–14]. Wines with ageing ability were defined by a group of winemakers as astringent with a saturated colour. The results also showed that a combination of visual and olfacto-gustatory assessments was needed to provide consensus on wine's ageing potential [12]. These findings were in agreement with another study indicating that the ageing ability includes a complex mixture of colour, aroma, taste and mouthfeel perceptions [13]. In a different study wine complexity was evaluated in relation to red wine perceived ageing ability. The results showed the multidimensionality of the concept, but most importantly highlighted structure and mouthfeel as the predominant words used by wine professionals when defining ageing ability. The authors also observed less emphasis on visual aspects such as colour [14].

When the ageing ability of a young wine needs to be evaluated its aroma, taste, mouthfeel and colour attributes should thus be taken into account. Phenolic compounds are directly responsible for wine mouthfeel and colour properties [4]. Anthocyanins are responsible for the red wine colour and their combinations with grape and wine components give rise to a wide variety of pigments with varying colour properties [20,21]. Moreover, proanthocyanidins or tannins are causing wine astringency [10]. The tannin content and composition defines wine astringency intensity and sub qualities [22]. Phenolics, also influences wine taste such as bitterness [23]. It can therefore be speculated that phenolic compounds are good candidates to evaluate the ageing ability of wines as they are largely or partially involved in several of the parameters deemed to influence the ability of red wines to age.

Currently only sensorial evaluation is used by winemakers to define the ageing ability of their wines. The outcome is then normally used to define the ageing strategy. However, sensorial evaluations only might be subjective. A chemical approach to the evaluation of the ageing ability of red wines will therefore benefit winemakers in their everyday decision-making tasks. Based on the relevant role played by phenolic compounds on wine ageing, the measurement of some of the relevant phenolic wine's chemical and physical (colour) properties may provide a valuable addition to the evaluation of the ageing ability of red wines. The main aim of this study was thus to evaluate the ageing ability of several wines that have been exposed to an ageing process of two years (12 months in barrel followed by 12 months in bottle). Phenolic and colour measurements were used to monitor the evolution of the wines during ageing. A chemometric approach using multivariate data analysis is presented here to propose an ageing ability index, based on phenolics, that estimates the ability of red wines to age.

2. Materials and methods

Wine samples. Eighty-two red wines (2016 vintage) including cultivars such as Cabernet Sauvignon (23), Shiraz (19), Pinotage (13), Merlot (11), Ruby Cabernet (2), Cabernet Franc (4), Cinsault (1), Grenache noir (1), Malbec (1), Mourvedre (1), Petit Verdot (4), Pinot Noir (2) were used to evaluate the phenolic evolution during the ageing process. The selection of samples was done with the objective of including a wide range of phenolic levels and composition. The winemaking as well as the one-year barrel ageing took place under an unsupervised approach i.e. winemaking practices applied were individually decided by the winemakers and barrels used to age the wines were from different origin, toasting intensities and/or number of fills. After barrel ageing, the wines were sampled and bottled under screw cap where an additional bottle ageing period of one year was undertaken under controlled temperature (15 °C). To evaluate the phenolic changes occurring during ageing, the wines were analysed after malolactic fermentation (T0), as well as after a year of barrel ageing (T1) and after a year of bottle ageing (T2) (two years of ageing in total).

Phenolic analysis. The modified Somers assay was used to quantify chemical age 1 and 2, ionized anthocyanins (%), total anthocyanins (mg/L), SO_2 resistant pigments and the total phenolic content [24]. The parameters chemical age 1 and 2 indicate the proportion between monomeric and polymeric forms of the anthocyanins. The ionized anthocyanins indicate the amount of these compounds found in the ionized red coloured form (flavilium cation). Finally, the SO_2 resistant pigments measure the polymeric pigments not bleached by SO_2 additions. The total tannin content was in this case obtained through a PLS calibration for methyl cellulose precipitable (MCP) tannins [25]. Finally, the proportion of the colour corresponding to the yellow (420%yellow), red (520%red) and blue (620%blue) wine colour components was measured in addition to the total colour intensity (colour density) from the addition of the aforementioned wine colorations [26]. The hue was also calculated as the ratio between the red and yellow wine colours. CIElab coordinates were also collected, luminosity (L*), a* and b* components, chroma (Cab*) and tonality (hab*) were measured [27]. Individual phenolic content was quantified using a high liquid chromatography (HPLC) method as reported elsewhere [25,28]. Some of the individual phenolics were grouped per phenolic family. The total content of phenolic acids (sum of hydroxybenzoic and hydroxycinnamic acids), flavonol content and monomeric anthocyanins were calculated. The individual phenolics quantified from the HPLC analysis were added together as total HPLC phenolics. Moreover, to further investigate the phenolic evolution during ageing new variables were calculated. The percentage of the total phenol content corresponding to the anthocyanins, phenolic acids, flavonols and proanthocyanidins were included. HPLC data was used for the calculation of these parameters. Two tannin/anthocyanin ratios were also included. These corresponded to the MCP tannin content and total anthocyanin content (Somers assay) and the polymeric phenols to monomeric anthocyanins quantified with HPLC. Finally, the ratio polymeric to monomeric anthocyanins was also included. These newly created variables were only used to obtain the phenolic profile of those wines identified with high ability to age.

Multivariate data analysis of the data. Principal component analysis (PCA) is an exploratory technique that transforms an original set of correlated variables into a new set of uncorrelated variables known as principal components. It reduces the dimensionality of the data into a set of scores and loading vectors. The scores plot in combination with the loadings plot indicates the responsive variables and their correlation with a group of observations [29]. Orthogonal-PLS (OPLS) is a modification of the PLS method that evaluates the unidirectional variation in the X variables that is orthogonal to the Y predictive variable. The systematic variation of the X data set is separated in linearly related or predictive to Y and orthogonal non-correlated to Y variation [30,31]. OPLS provides enhanced model transparency and interpretability. Discriminant analysis can also be used if different classes are assigned. S-plots are used to visualize the predictive component loading by plotting the covariance and the correlation structure between the X variables and the predictive scores. After Pareto scaling the plot takes and S shape with X variables situated in the external parts of the S combining high model influence with high reliability.

In multi-block analysis, score values of base level models can be used as variables in higher level models. This hierarchal modelling is used to analyse data sets obtained from different analytical procedures or even to process data over time, evaluating overall process performance. Hierarchal modelling is also suitable for data sets with varying size in

variables and observations, allowing variables from the different data sets to equally influence the model [32–34]. In this case data at time 0, 1 and 2 were used as low level PLS models. The scores values were used in a higher level model to investigate the evolution of the ageing index over time. A permutation test was also performed to evaluate the ability of the model to predict new observations, making sure that the model is not just fitting the training set. The goodness of fit (R^2 and Q^2) of the original model is compared against the goodness of fit of several models where the Y predictive values are randomly permuted while the X matrix remain the same. Finally, to further validate the prediction accuracy of the models, a classification task was performed to evaluate the correctly classified observations in the prediction set. Data analysis was performed using SIMCA 14.1 software from Sartorius Stedim Biotech (Gotinga, Germany).

3. Results and discussion

Phenolic profiling of high ageing ability red wines. In our definition of ageing ability, a wine that needs the longest time to reach optimal phenolic quality is considered a wine with higher ability to age. In combination to this, a wine that is able to maintain its optimal phenolic quality for longer will also be a wine with high ageing ability. The ideal scenario will thus be a wine that needs the longest to reach optimal phenolic quality and at the same time a wine that maintains phenolic quality the longest. A wine with high ability to age might therefore be a wine with high phenolic content that is relatively stable over time. Two assumptions are therefore formulated: the first assumption accepts that the higher the phenolic content, the longer a specific wine will need to reach optimal phenolic quality (concentration assumption); the second assumption entails that a wine with stable phenolics (limited change of phenolics over time) will be also a wine that maintains its optimal phenolic quality for longer (stability assumption). Quality is thus defined here in terms of phenolic concentration and stability. It can therefore be suggested that if both assumptions are accepted, a wine will have increased ability to age.

To evaluate the above-mentioned, the change in phenolic content during 24 months was calculated (the levels of a given phenolic measurement at time 24 months (T2) were subtracted from the levels at time 0 (T0), that corresponds to the initial time point). As the phenolic levels can increase (e.g. pigmented polymers) or decrease (e.g. anthocyanins) the absolute value of that difference was calculated. The average of the variation was also calculated for each phenolic measurement and used as a threshold to identify if a wine contains stable phenolics. A variation lower than the average indicated relative stability for a particular phenolic measurement in a wine. On the other hand, the phenolic content at time 0 was used to identify the highly phenolic containing wines. The average for a phenolic measurement was calculated and those wines with phenolic levels higher than the average were considered as high ageing phenolic content wines. The target wines were therefore those that had minimal phenolic change over time and started off with a high phenolic content. The phenolic levels were thus individually evaluated in terms of both conditions (stability and concentration) to identify the wines with theoretically higher ability to age. Moreover, as the study also included some phenolic parameters, a careful evaluation of the meaning of those in relation to ageing ability was undertaken. For example, in the case of the chemical age 1 and 2, values lower than the average were found appropriate to meet the concentration condition as the incorporation of monomeric anthocyanin into polymeric structures is a sign of wine ageing [21]. The same reasoning was applied for luminosity (L*) and Hue were lower values were considered an indication of higher ageing ability.

Consequently, a scoring system was attempted to provide an overall ageing score for each wine and to identify those wines with higher ability to age. If the variation was lower than the median and the levels for that phenolic measurement were also lower than the median a 0 score was given. If one of the two conditions (stability or concentration) was met a score 1 was allocated, Finally, if the wine was stable and the initial phenolic content was high a score of 2 was given. The sum of the scores obtained for the phenolic measurements provided a ranking, with higher scores theoretically indicating higher ageing ability. Due to the unsupervised approached followed in the study, only 50 wines were monitored during the two years of ageing as some of the samples were lost during the experiment for various reasons, included blending by the winery, missing samples, faulty wines etc. After the ranking process was performed, the first 10 wines with the highest scores were targeted. Samples 5, 8, 9, 16, 23, 24, 25, 27, 44 and 51 were therefore selected. These wines were single cultivar Cabernet Sauvignon (2), Merlot (2), Pinotage (3), Ruby Cabernet (2) and Mourvedre wines and were provided by six different cellars. Once the theoretically high ageing ability wines were targeted the objective was to profile those wines to understand which were their phenolic features. The complete data set (82 wines) and the phenolic data collected at time O (T0) was used for this purpose. PCA and OPLS-DA were then evaluated to identify the phenolic features characteristic of this wines. Fig. 1 shows the contributions plot for the group to average comparison of the selected wines. The PCA model obtained had a $R^2 = 0.671$ and $Q^2 = 0.51$.

High ageing ability wines were characterized by having high levels of the following variables: SO_2resist, 620%blue, 420%yellow, CD, Tannins (mg/L) and hab* in a first order. Other variables with relevant contributions were Tanth (mg/L), TP, 520%red, Pphen (mg/L), Flavon (mg/L) and TP-HPLC (mg/L). Moreover, the identified high ageing ability wines had lower values of L*, a*, Cab* and PhAcids%. For the discriminant analysis, two classes were allocated, with class 1 corresponding to the targeted high ageing ability group, whereas group 2 corresponded to the remaining wines. The OPLS model obtained had an $R^2 = 0.708$ and a $Q^2 = 0.0129$. A S-plot was in this case used to further identify those variables explaining the differences between the two groups. Fig. 2 shows the S-plot of the OPLS-DA model obtained. The variables Tannins (mg/L), PPhen (mg/L), TP-HPLC (mg/L) and Tanth (mg/L) were the most influential when the discrimination of the two groups was attempted. On the other side of the S-plot the CIElab colour variables L*, a* and Cab* were representative of class 2, however these variables seem to explain less model variance due to the small p1 values.

Interestingly, the contributions plot shows some of the colour variables (620%blue, 420%yellow, CD, hab*, L*, a* and Cab*) and the anthocyanin parameters (SO_2resist) as most explanatory for the differences between high ageing ability wines. The total tannin content (Tannins (mg/L)) was also found as an important explanatory variable. This seems to be in agreement with previous studies where wines with ability to age were defined as astringent with a saturated colour [12,13]. The MCP tannin assay reported here is based on the precipitation of the tannin compounds with a cellulose polymer [24,35]. This method relies on the same protein-tannin aggregation principle that leads to the astringency perception taking place in the oral cavity when salivary proteins interact with wine tannins. A positive correlation between precipitation based tannin methods and sensorial astringency intensities has been reported in the literature [36–40]. The MCP tannin assay can therefore be understood as an indirect estimation of the wine's astringency. Moreover, the colour parameters might explain the colour saturation.

In addition, the OPLS-DA S-plot showed the variables MCP tannin and total phenol as highly reliable (large p(corr)) and accounting for high model variance (p). The anthocyanin content also showed high reliability but lower explained variance. From the discriminant analysis it thus seems that the high phenolic and tannin content combined with high anthocyanin levels are the most influential variables that characterize high ageing ability wines. These results are in agreement with other phenolics measurement also found relevant in the contributions plot such as Tanth (mg/L), TP, PPhen (mg/L) and TP-HPLC. Interestingly the total content of flavonols (Flavon (mg/L)) was also observed to be influential. Flavonols are known to have high copigmentation ability and higher levels of these compounds might have contributed to enhanced colour properties [41,42]. Copigmentation has also been proposed to serve as a

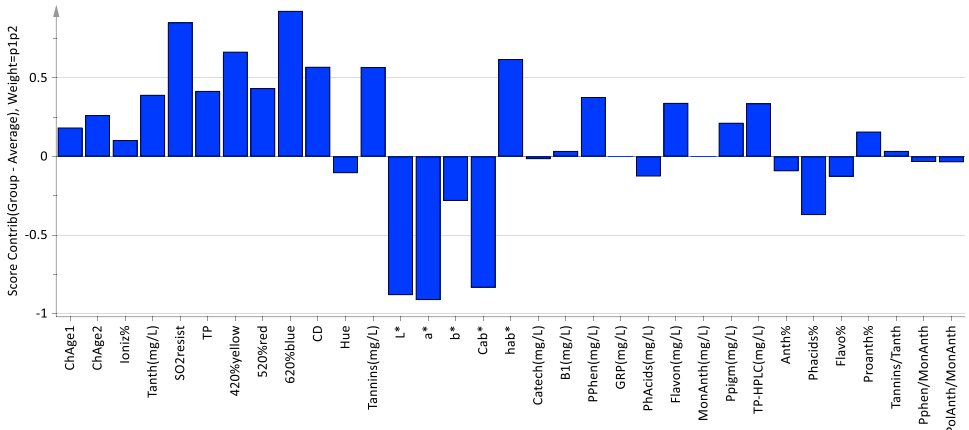

Fig. 1. Group (high ageing ability wines) to average comparison contributions plot. Initial (time 0) phenolic levels used as explanatory variables ChAge1: chemical age 1; ChAge2: chemical age 2; Ioniz%: ionization percentage; Tanth(mg/L): total anthocyanins; SO2resist: SO2 resistant pigments; TP: totap phenolics; 420%yellow: yellow coloration; 520%red: red coloration; 620% blue: blue coloration; CD: colour density; catech(mg/L): catechin; Pphen(mg/L): polymeric phenols; PhAcids(mg/L): phenolic acids; Flavon(mg/L): flavonols; MonAnth(mg/L): monomeric anthocyanins; Ppigm(mg/L): polymeric pigments; TP HPLC(mg/L): total phenols HPLC; Anth%: anthocyanin percentage; PhAcids%: phenolic acids percentage; Flavo%: flavonols percentage; Proanth%: proanthocyanidins percentage. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

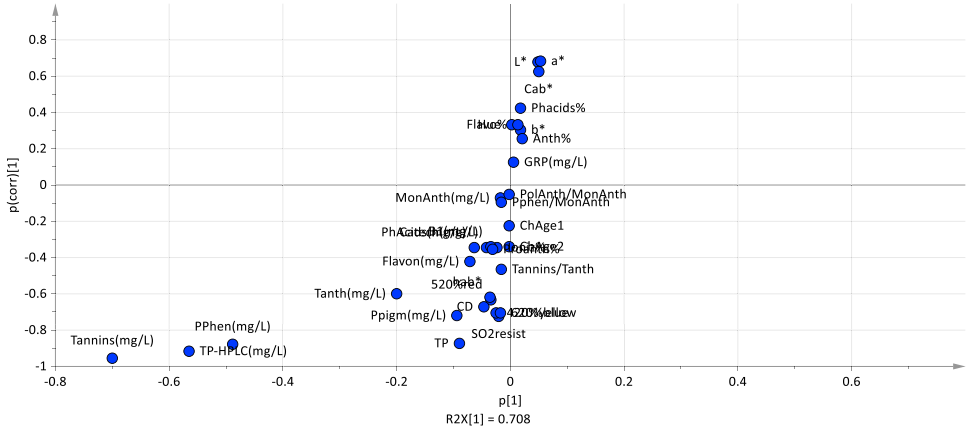

Fig. 2. OPLS-DA S-plot for the targeted high ageing ability wines (class 1) versus the rest (class 2)ChAge1: chemical age 1; ChAge2: chemical age 2; Ioniz%: ionization percentage; Tanth(mg/L): total anthocyanins; SO2resist: SO2 resistant pigments; TP: totap phenolics; 420%yellow: yellow coloration; 520%red: red coloration; 620%blue: blue coloration; CD: colour density; catech(mg/L): catechin; Pphen(mg/L): polymeric phenols; PhAcids(mg/L): phenolic acids; Flavon(mg/L): flavonols; MonAnth(mg/L): monomeric anthocyanins; Ppigm(mg/L): polymeric pigments; TP HPLC(mg/L): total phenols HPLC; Anth%: anthocyanin percentage; PhAcids%: phenolic acids percentage; Flavo%: flavonols percentage; Proanth%: proanthocyanidins percentage. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

first step towards the protection of the anthocyanins [43,44]. On the contrary, the phenolic variables created were found to have little to non-significant explanatory power as only the variable PhAcids% was found to contribute to the explained variance (Fig. 1). High ageing ability wines were found to have a lower percentage of these compounds. Phenolic acids are involved in mouthfeel (e.g. gallic acid) and colour properties (anthocyanin acylation with *p*-coumaric or caffeic acids) and lower levels might be indicating their participation in more complex phenolic structures, rather than being found in its monomeric form that is not combined to another phenolic moiety [4]. Interestingly, the tannin-anthocyanins ratios were not relevant for the differences between wines. Previous literature suggested that a certain ratio between tannins and anthocyanins is needed if wines are made to stand and ageing process [45]. However, this hypothesis needs further investigations and an optimal ratio tannin/anthocyanin could therefore not be assessed or proposed.

Alternatively, and to better understand the change in phenolic content and composition of the identified high ageing ability wines over time a new PCA was attempted. In this case the phenolic variation over time were used as explanatory variables. The value for a specific measurement at time 2 (24 months) was subtracted from the levels at time 0 (0 months). For interpretation purposes the absolute values of the variation were used. The high ageing ability wines identified from the scoring exercise were compared against the remaining group. Fig. 3 shows the contributions plot for the group to average comparison. Interestingly the results highlighted the colour variables (420%yellow, 520%red, 620% blue, CD, L*, a*, b*, Cab* and hab*) as the most explanatory of the differences between wines. It seems that the identified high ageing ability wines are characterized by a limited change in colour properties when compared against the average wine on the data set. Overall a positive increase in colour was observed during the ageing process (unpublished data), however the targeted high ageing ability wines seem to have a limited change in the colour properties which might be translated into smaller reaction rates during ageing. These results might be supported by the ChAge1 parameter, indicating the extent of the anthocyanin monomer to polymer transition, for which the targeted wines showed also lower variation (i.e. lower incorporation of monomeric anthocyanins into polymeric structures). These newly formed pigments differ in chromatic attributes when compared against the simpler monomeric forms, often leading to enhanced colour properties [21].

Establishment of an ageing ability index. One of the objectives of this research is to propose and evaluate an ageing index for new wines based on its initial phenolic content and composition. For this purpose, an OPLS calibration was attempted using the scores obtained from the concentration and stability exercise as reported in the previous section. The 50 wines that completed the whole process were included with the

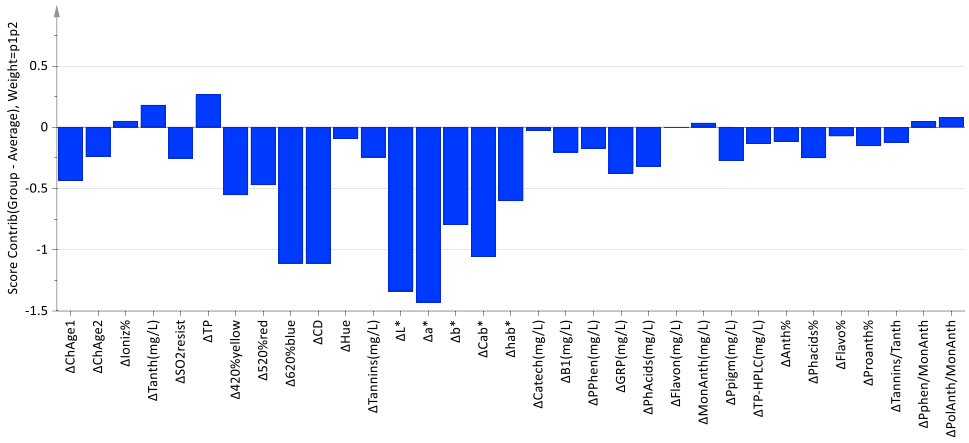

Fig. 3. Group (high ageing ability wines) to average comparison contributions plot. Change in phenolic levels (time 0 – time 2) used as explanatory variablesChAge1: chemical age 1; ChAge2: chemical age 2; Ioniz%: ionization percentage; Tanth(mg/L): total anthocyanins; SO2resist: SO2 resistant pigments; TP: totap phenolics; 420%yellow: yellow coloration; 520%red:red coloration; 620%blue: blue coloration; CD: colour density; catech(mg/L): catechin; Pphen(mg/L): polymeric phenols; PhAcids(mg/L): phenolic acids; Flavon(mg/L): flavonols; MonAnth(mg/L): monomeric anthocyanins; Ppigm(mg/L): polymeric pigments; TP HPLC(mg/L): total phenols HPLC; Anth%: anthocyanin percentage; PhAcids%: phenolic acids percentage; Flavo%: flavonols percentage; Proanth%: proanthocyanidins percentage. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

scoring values used as predictive Y variable. Only the explanatory variables contributing to the differences of high ageing ability wines were included as X variables (see previous section). An OPLS calibration with $R^2 = 0.4875$ and RMSECV = 4.48 (SD = 5.9) was obtained. These results showed that the phenolic variables measured at initial time point (time 0) were not able to accurately predict the scores obtained from the proposed ageing ability assumptions. The absence of stability information as only concentration data at time 0 was used in combination with the simplicity of the scoring system used (0-1-2 scores were allocated) could be the reason to explain the results obtained.

A different approach was then evaluated to obtain such an index. A PCA bi-plot of the 82 initial wines using the most influential variables explaining the differences between both ageing ability groups was in this case used (Fig. 4). The wines appeared mostly distributed alongside principal component 1. The variables positively correlated (higher values of those variables) with high ageing ability wines were located in the positive part of PC1, whereas the colour variables (L*, a* and Cab*) and the Phacids% were located in the negative part of PC1. It is also important to mention that the tannin related variables (PPhen (mg/L), TP, Tannins (mg/L), TP-HPLC (mg/L)) are placed in the negative part of PC2, whereas the colour and anthocyanin related variables were located in the central or slightly positive part of PC2. PC1 explains 68.2% of the total variability, with 9.3% being explained by PC2.

It can thus be concluded from Fig. 4 that PC1 is separating the wines according to ageing potential. In addition, wines with a negative position in the second component are wines with higher levels of total phenols and tannins. The score values in PC1 (t1) and 2 (t2) where therefore used to calculate an ageing index. Wines with ability to age will be positioned in the positive part of PC1 and negative part of PC2 as an increased tannin content has been suggested as a necessary condition to stand longer ageing processes [12,13]. The following formula was therefore suggested:

$$\text{Ageing index} = (((t1+1)/2) * 0.682) - (((t2+1/2) * 0.093) * 10 \quad \text{(Equation 1)}$$

With the aim of giving the index an interpretable value the following was considered. First of all, the score values were made positive by adding one and dividing by two. The score range was therefore shifted from −1 to 1 to 0 to 2. t1 and t2 where then normalized by using the explained variance of the respective component. The t2 component was then subtracted from t1 as the more negative (or closer to 0 in the normalized scores) in the PCA scores space the smaller the number to be subtracted and the higher the index. Finally, 10 was used to give the index a more understandable value.

Variation of the ageing index over time. Theoretically the ageing ability of a wine will decrease over time. However, some of the phenolic compounds with relevant role in the ability of wines to age are quite stable during ageing, at least on a short-term basis. For example, tannin compounds have shown relative stability during the first years of ageing, with slow decrease rates on a longer term [46–48]. Using the identified discriminatory phenolic parameters as X variables and the ageing index values from equation (1) as Y predictive variable an OPLS model (R^2 =

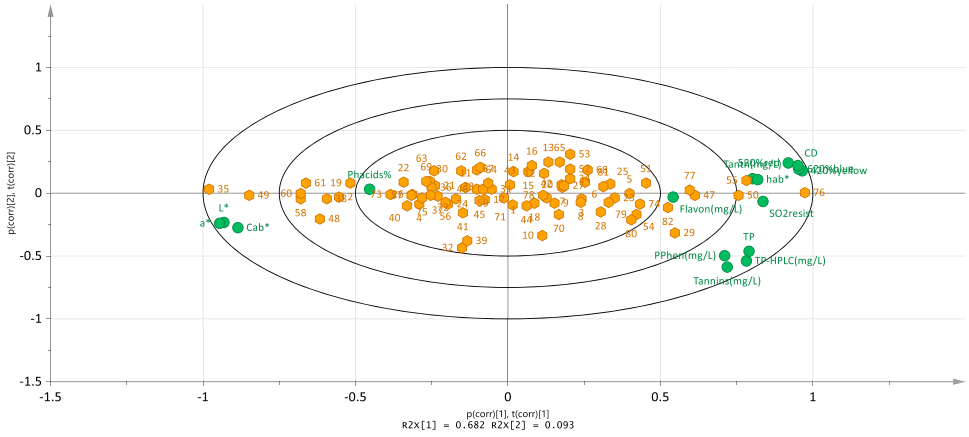

Fig. 4. PCA bi-plot of the 82 wines using the most influential explanatory variables for high ageing ability winesTanth(mg/L): total anthocyanins; SO2resist: SO2 resistant pigments; TP: total phenolics; 420%yellow: yellow coloration; 520%red: red coloration; 620%blue: blue coloration; CD: colour density; Pphen(mg/L): polymeric phenols; Flavon(mg/L): flavonols; Ppigm(mg/L): polymeric pigments; TP HPLC(mg/L): total phenols HPLC; PhAcids%: phenolic acids percentage. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

0.673 and $Q^2 = 0.997$) was used to predict the ageing index of the wines after 12 and 24 months of ageing. The ageing index values for the wines evaluated are represented in Fig. 5. As can be observed, limited variation between the three sampling times was generally observed, indicating a certain stability of the index during these two first years of ageing. However, to confirm these initial results, a multi-block analysis was also performed to evaluate the stability of the index over time.

A schematic representation of the experimental design for the multi-block analysis is shown in Fig. 6. At base level the phenolic measurements explaining the differences between the theoretically high ageing ability wines as identified in the contributions plot were used for the three time points as X variables. The ageing index values calculated from equation (1) for time 0 and using the OPLS model for time 1 and 2, were used as Y predicted values, unchanged to the top model. Score values of the predictive (p) and orthogonal (po) components were taken up to the top level.

The loading plot for the ageing index variables at the different time points can be observed in Fig. 7. The stability of the index over time can be identified from the plot as the three variables ageing index (A Index(T0), A Index(T1) and A Index(T2)) share positioning along the predictive component 1, which explains a large part of the variability contained in the data set (88.8%). It can thus be deduced that over 24 months of ageing the wines will have a similar ageing index with no decrease in the index values expected. A reason for this could be given by the phenolic measurements used to calculate the ageing index. As can be observed in Fig. 4, the calculation of the index is based on the parameters tannins (mg/L), TP, TP-HPLC (mg/L) and PPhen (mg/L) in combination with the colour measurements (CD, 420%yellow, 520%red and 620% blue) and the TAnth (mg/L) content. Several studies have observed stable total phenol and tannin content after short term ageing in varying conditions [47–51]. The limited decrease in the total phenol content is ascribed to the anthocyanin degradation which accounts for a smaller part of the phenolic content in comparison to tannin compounds [41,47,49,51]. Moreover, an increase in the colour properties of wines after ageing periods of variable durations have been reported and are ascribed to the formation of more complex pigmented structures with enhanced colour properties [2,21,51,52]. The stability of the colour properties as well as the total phenol content with the exception of the anthocyanins during the duration of the experiment is probably explaining the stability of the index over time.

In addition to further validate the OPLS model used to assess the stability of the index, a permutation test was also performed. In a permutation test the objective is to ascertain that the model is not just fitting the training set, but is able to predict new observations. For this, the test

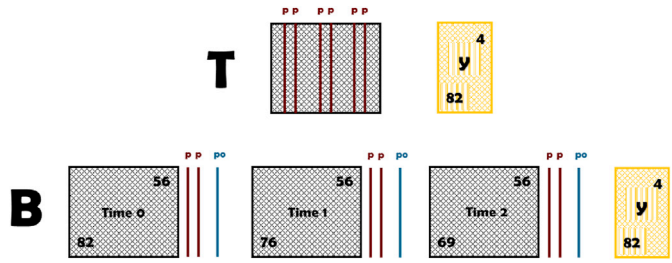

Fig. 6. Multi-block analysis to evaluate the stability of the ageing index over the aging period. OPLS was used in the base (B) and top (T) models.

evaluates the prediction ability of the original model against the prediction ability a number of models where the Y values have been randomly permuted i.e. the ageing index values are randomly assigned while the X variables or phenolic measurements are kept the same. Fig. 8 shows the permutation test with 100 permutations being performed. As can be observed the new permuted models always showed R^2 and Q^2 values lower than the original model (right side of the graph). The X axis shows the correlation between the new permuted models and the original models, with a correlation 1 between the original model with itself. Moreover, the Q^2 regression line intersects the vertical axis in −0.209 indicating absence of prediction ability in the permuted models. It can be concluded that the prediction ability of the original model is due to existing correlation between the X and Y datasets and not just spuriousness of the model. The validation of the model supports the suggested statement of stable index values during the ageing period evaluated.

Validation of the ageing index. A direct correlation between the ageing index values and the scores values obtained from the concentration and stability approach was evaluated and although a certain trend was depicted a poor correlation ($R^2 = 0.3$) was found. However, it is important to mention that the scoring system includes data of not only concentration but also phenolic stability over time; unlike the PCA approach when only concentration data at time 0 is used to obtain the ageing index. In any case, the final application should be to measure phenolic content initially before the ageing process commences in order for winemakers to make an informed based decision on the ageing strategy to apply. This reasoning justifies the selection of this approach as otherwise data collected after a period of time should be needed and an early estimation would therefore be non-viable.

As a certain trend was observed when the correlation of both approaches (scoring and PCA) was evaluated, a classification exercise was attempted to evaluate if low, medium or high ageing ability class could

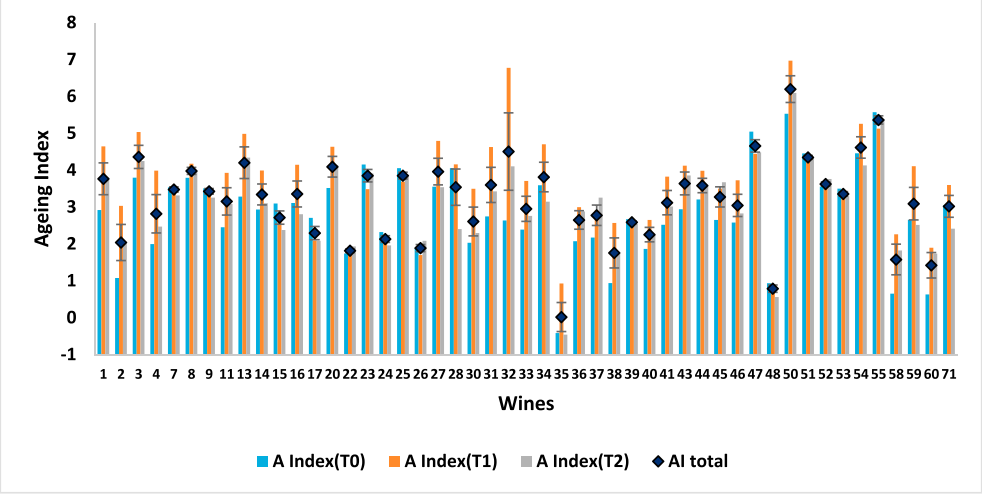

Fig. 5. Ageing index values at times 0, 1 (12 months) and 2 (24 months) for the wines that completed the ageing process. The average ageing index value for the aging period is also shown with the standard deviation of the three times.

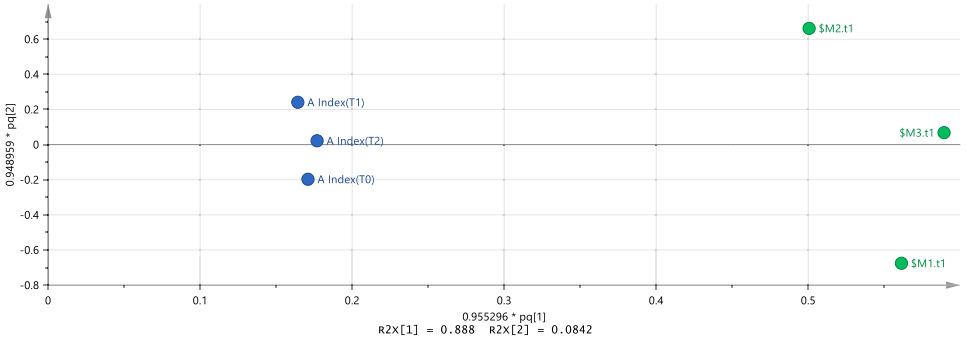

Fig. 7. Loadings plot for the top model derived from the multi-block analysis of the wines at time 0, 12 and 24 month of aging.

be predicted. For this purpose, the data set was divided into two equal calibration and validation subsets. In the calibration subset, classes low, medium or high were assigned based on the ageing index generated from the PCA approach with the three classes obtained after three equal ranges were determined. This sub set was later used to predict class of the validation subset whose classes where assigned using the scoring system obtained after the concentration and stability exercise. The results of the classification task are presented in Table 1. The equal range distribution of the samples from the scoring exercise divided the sample set in 10 samples for the low class, 6 for the medium class and 9 for the high ageing ability class. The calibration set was distributed as follows: 10 samples as low, 11 samples as medium and 4 samples as high. The results of the classification table showed some of the samples being misclassified. However, the misclassified samples were, except for one sample, always classified in some of the nearest groups i.e. 4 samples were classified as medium for the high class. The only exception was a sample with low ageing ability that was classified as being high. Having a closer look at the misclassified sample the lower L*, a* and Cab* values together with high values of polymeric phenols might have caused its allocation in the high class. This also points towards the significant variability in terms of phenolic content and composition that is observed at cultivar and wine style level, which also highlights the complexity of the topic. The results prove that despite some differences, both approaches are delivering similar ageing ability predictions, which to a certain extent validates the PCA approach as a valid alternative to the estimation of an ageing ability index with the solely use of initial phenolic composition.

Table 1
Misclassification table using 3 classes (low, medium and high ageing ability) obtained through an equal range distribution. Ageing index values is used in calibration, whereas scores are used for validation.

	Wines	Correct	Low	Medium	High
Low	10	70%	7	2	1
Medium	6	66.67%	1	4	1
High	9	55.56%	0	4	5

4. Conclusions

An approach towards an early estimation of the ageing ability of red wines has been proposed in this study. In accordance with the literature, the high ageing ability wines targeted in this study were characterized by having high levels of tannins and a saturated colour, in line with high levels of anthocyanins. In addition, high initial levels of polymeric pigments and flavonols and low levels of phenol acids were also observed in the phenolic profile of wines with high ability to age. Moreover, high ageing ability wines are characterized by smaller changes in colour properties over time or a slower transition from simple monomeric forms of anthocyanin into more complex pigments. The question of whether the different reaction rates are due to purely phenolic composition or alternatively to the influence of other wine components or external factors remains unanswered and requires further investigations.

As the scoring system required phenolic data generated over a two years' ageing period, an alternative attempt was proposed. The suitability of PCA and OPLS to estimate the ageing ability of the wines using initial phenolic properties was investigated. The variation of the ageing

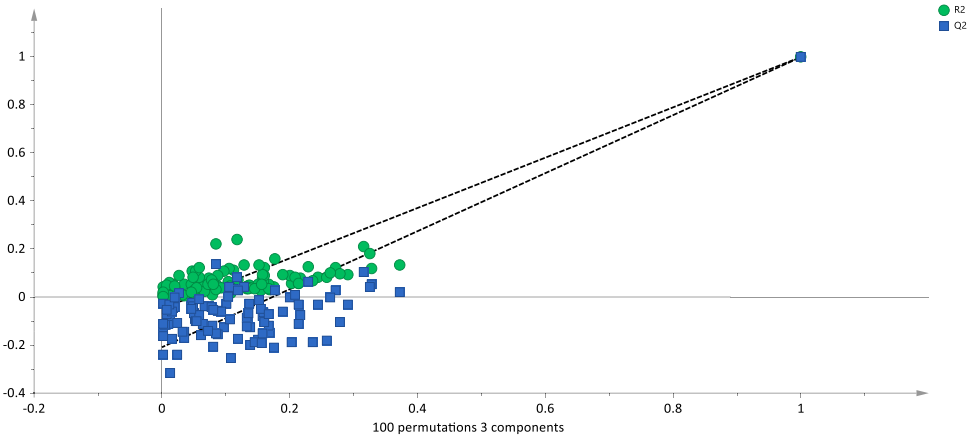

Fig. 8. Permutation test of the multi-block top OPLS model with 100 permutations.

ability over time was also evaluated with relative stability during the two years of ageing being observed. The short-term stability of some of the phenolic compounds, specially tannins and tannin related measurements, was suggested as the main reason for these results. An expected decrease in the index values is however foreseen as the phenolic content starts decreasing over a longer period. Finally, the index values were validated with a classification exercise, indicating that a similar interpretation of the ageing ability concept in both approaches is provided.

To our knowledge this study provides the first attempt to conceptually define the ageing ability or ageing potential related to phenolic compounds in red wines. A combination between wine phenolic stability and initial concentration was proposed as the two necessary conditions for wines with ability to age. Moreover, a chemical approach to the definition was also provided, in other words the conceptual definition was translated into measurable variables in terms of phenolic and colour measurements.

On the other hand, it must be kept in mind that other dimensions of the ageing ability concept such as aroma or flavour, were not considered and the attempt presented here is purely based on phenolic content. The natural progression of this research would thus be to investigate the ability of this approach to evaluate the sensorial perception of aging potential. In addition, the inclusion of other attributes influencing ageing ability of red wines would potentially provide a closer reflection of the sensorial evaluation of wine ageing ability. This might include the quantification of major wine components such as alcohols, acids and sugars or the evaluation of the volatile fraction. Finally, as this approach is purely based on phenolic chemistry a spectroscopy calibration could be attempted to predict the ageing ability by solely measuring the spectral properties of the wines. Spectroscopy calibrations are known by its simplicity, reliability and cost effectiveness and have proved successful to predict phenolic content in wines.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Jose Luis Aleixandre-Tudo: Conceptualization, Funding acquisition, Data curation, Formal analysis, Investigation, Methodology, Validation, Visualization, Writing - original draft, Writing - review & editing. **Wessel du Toit:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing - review & editing.

Acknowledgment

The authors gratefully acknowledge Winetech South Africa for financial support under the WdT 16/01 project.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemolab.2020.104067.

References

[1] J.L. Aleixandre-Tudo, W. Toit, Cold maceration application in red wine production and its effects on phenolic compounds : a review, LWT-Food Sci. Techol. 95 (2018) 200–208, https://doi.org/10.1016/j.lwt.2018.04.096.
[2] L.F. Casassa, J.F. Harbertson, Extraction, evolution and sensory impact of phenolic compounds during red wine maceration, Annu. Rev. Food Sci. Technol. 5 (2014) 83–109, https://doi.org/10.1146/annurev-food-030713-092438.
[3] E. Sánchez-Palomo, E.G. García-Carpintero, R. Alonso-VIllegas, M.A. Gonzalez-Viñas, Characterization of aroma compounds of Verdejo white wines from the La Mancha region by odour activity values, Flavour Fragrance J. 25 (2010) 456–462, https://doi.org/10.1002/ffj.2005.
[4] V. Cheynier, R. Schneider, J. Salmon, H. Fulcrand, Chemistry of wine, Compr. Nat. Prod. II (2010) 1119–1172, https://doi.org/10.1016/B978-008045382-8.00088-5.
[5] J.A. Kennedy, Grape and wine phenolics: observations and recent findings, Cienc. Investig. Agrar. 35 (2008) 77–90, https://doi.org/10.4067/S0718-16202008000200001.
[6] M. Del Alamo-Sanza, L.M. Cárcel, I. Nevares, Characterization of the oxygen transmission rate of oak wood species used in cooperage, J. Agric. Food Chem. 65 (2017) 648–655, https://doi.org/10.1021/acs.jafc.6b05188.
[7] M. Del Alamo-Sanza, I. Nevares, Recent advances in the evaluation of the oxygen transfer rate in oak barrels, J. Agric. Food Chem. 62 (2014) 8892–8899, https://doi.org/10.1021/jf502333d.
[8] P. Arapitsas, Hydrolyzable tannin analysis in food, Food Chem. 135 (2012) 1708–1717, https://doi.org/10.1016/j.foodchem.2012.05.096.
[9] K.A. Bindon, P.A. Smith, H. Holt, J.A. Kennedy, Interaction between grape-derived proanthocyanidins and cell wall material. 2. Implications for vinification, J. Agric. Food Chem. 58 (2010) 10736–10746, https://doi.org/10.1021/jf1022274.
[10] J.M. McRae, J.A. Kennedy, Wine and grape tannin interactions with salivary proteins and their impact on astringency: a review of current research, Molecules 16 (2011) 2348–2364, https://doi.org/10.3390/molecules16032348.
[11] J. Levengood, R. Boulton, The variation in the color due to copigmentation in young Cabernet Sauvignon wines, in: A.L. Waterhouse, J.A. Kennedy (Eds.), Red Wine Color: Exploring the Mysteries, ACS Symp. Ser. 886, Am. Chemical Society, Washington, DC, 2004, pp. 35–52.
[12] J. Jaffré, D. Valentin, C. Dacremont, D. Peyron, Burgundy red wines : representation of potential for ageing, Food Qual. Prefer. 20 (2009) 505–513, https://doi.org/10.1016/j.foodqual.2009.05.001.
[13] J. Langlois, J. Ballester, E. Campo, C. Dacremont, D. Peyron, Combining olfactory and gustatory clues in the judgment of ageing potential of red wine by wine professionals, Am. J. Enol. Vitic. 1 (2010) 15–22.
[14] W.V. Parr, M. Mouret, S. Blackmore, T. Pelquest-hunt, I. Urdapilleta, Representation of complexity in wine : influence of expertise, Food Qual. Prefer. 22 (2011) 647–660, https://doi.org/10.1016/j.foodqual.2011.04.005.
[15] Y. Qi, R. Wang, Q. Qin, Q. Sun, Soil affected the variations in grape and wine properties along the eastern foot of Helan, Acta Agric. Scand. Sect. B Soil Plant Sci 69 (2019) 494–502, https://doi.org/10.1080/09064710.2019.1611914.
[16] M. Rodríguez, J. Lezáun, R. Canals, M.C. Llaudy, J.M. Canals, F. Zamora, Influence of the presence of the lees during oak ageing on colour and phenolic compounds composition of red wine, Food Sci. Technol. Int. 11 (2002) 289–295, https://doi.org/10.1177/1082013205056597.
[17] M. Kyraleou, P. Teissedre, E. Tzanakouli, Y. Kotseridis, N. Proxenia, K. Chira, I. Ligas, S. Kallithraka, Addition of wood chips in red wine during and after alcoholic fermentation: differences in color parameters , phenolic content and volatile composition, OENO One 50 (2016) 209–222.
[18] Y. Liu, B. Zhang, F. He, C.Q. Duan, Y. Shi, The influence of prefermentative addition of gallic acid on the phenolic composition and chromatic characteristics of Cabernet, Sauvignon Wines 81 (2016) 1669–1678, https://doi.org/10.1111/1750-3841.13340.
[19] L. Lerno, M. Reichwage, R. Ponangi, L. Hearne, D.E. Block, A. Oberholster, Effects of cap and overall fermentation temperature on phenolic extraction in Cabernet Sauvignon fermentations, Am. J. Enol. Vitic. 4 (2015) 444–453, https://doi.org/10.5344/ajev.2015.14129.
[20] F. He, N.N. Liang, L. Mu, Q.H. Pan, J. Wang, M.J. Reeves, C.Q. Duan, Anthocyanins and their variation in red wines I. Monomeric anthocyanins and their color expression, Molecules 17 (2012) 1571–1601, https://doi.org/10.3390/molecules17021571.
[21] F. He, N.N. Liang, L. Mu, Q.H. Pan, J. Wang, M.J. Reeves, C.Q. Duan, Anthocyanins and their variation in red wines II. Anthocyanin derived pigments and their color evolution, Molecules 17 (2012) 1483–1519, https://doi.org/10.3390/molecules17021483.
[22] P.A. Smith, J.M. Mcrae, K.A. Bindon, Impact of winemaking practices on the concentration and composition of tannins in red wine, Aust. J. Grape Wine Res. 21 (2015) 601–614, https://doi.org/10.1111/ajgw.12188.
[23] F. Brossaud, V. Cheynier, A.C. Noble, Bitterness and astringency of grape and wine polyphenols, Aust. J. Grape Wine Res. 7 (2001) 33–39, https://doi.org/10.1111/j.1755-0238.2001.tb00191.x.
[24] M.D. Mercurio, R.G. Dambergs, M.J. Herderich, P.A. Smith, High throughput analysis of red wine and grape phenolics - adaptation and validation of methyl cellulose precipitable tannin assay and modified somers color assay to a rapid 96 well plate format, J. Agric. Food Chem. 55 (2007) 4651–4657, https://doi.org/10.1021/jf063674n.
[25] J.L. Aleixandre-Tudo, H. Nieuwoudt, A. Olivieri, J.L. Aleixandre, W. du Toit, Phenolic profiling of grapes, fermenting samples and wines using UV-Visible spectroscopy with chemometrics, Food Contr. 85 (2018) 11–22, https://doi.org/10.1016/j.foodcont.2017.09.014.
[26] Y. Glories, La couleur des vins rouges, 2eme partie, Connaiss, La Vigne Du Vin 18 (1984) 253–271.
[27] OIV, Determination of chromatic characteristics according to CIELab, Compend. Int. Anal. Methods. (2006) 1–16. http://www.oiv.int/oiv/files/6-Domaines%20scientifiques/6-4%20Methodes%20d%20analyses/6-4-1/EN/OIV-MA-AS2-11.pdf.
[28] Z. Peng, P.G. Iland, A. Oberholster, M.A. Sefton, E.J. Waters, Analysis of pigmented polymers in red wine by reverse phase HPLC, Aust. J. Grape Wine Res. 8 (2002) 70–75, https://doi.org/10.1111/j.1755-0238.2002.tb00213.x.
[29] A. Jackson, J.E. Edward, User's Guide to Principal Components, John Wiley & Sons, Inc., Hoboken, NJ, USA, 2005.

[30] J. Gabrielsson, H. Jonsson, C. Alriau, B. Schmidt, R. Escott, J. Trygg, The OPLS methodology for analysis of multi-block batch process data, J. Chemom. 20 (2006) 362–369, https://doi.org/10.1002/cem.1009.
[31] J. Trygg, S. Wold, Orthogonal projections to latent structures (O-PLS), J. Chemom. 16 (2002) 119–128, https://doi.org/10.1002/cem.695.
[32] M. Hanafi, A. Kohler, E.M. Qannari, Shedding new light on hierarchical principal component analysis, J. Chemom. 24 (2010) 703–709, https://doi.org/10.1002/(SICI)1099-128X(199809/10)12:5<301::AID-CEM515>3.0.CO;2-S.
[33] J.A. Westerhuis, T. Kourti, J.F. MacGregor, Analysis of multiblock and hierarchical PCA and PLS models, J. Chemom. 12 (1998) 301–321, https://doi.org/10.1149/ma2010-02/32/2003.
[34] S. Wold, N. Kettaneh, K. Tjessem, Hierarchical multiblock PLS and PC models for easier model interpretation and as an alternative to variable selection, J. Chemom. 10 (1996) 463–482, https://doi.org/10.1002/(sici)1099-128x(199609)10:5/6<463::aid-cem445>3.0.co;2-l.
[35] C.J. Sarneckis, R.G. Dambergs, P. Jones, M. Mercurio, M.J. Herderich, P.A. Smith, Quantification of condensed tannins by precipitation with methyl cellulose: development and validation of an optimised tool for grape and wine analysis, Aust. J. Grape Wine Res. 12 (2006) 39–49, https://doi.org/10.1111/j.1755-0238.2006.tb00042.x.
[36] A. Cáceres-Mella, Á. Peña-Neira, J. Narváez-Bastias, C. Jara-Campos, R. López-Solís, J.M. Canals, Comparison of analytical methods for measuring proanthocyanidins in wines and their relationship with perceived astringency, Int. J. Food Sci. Technol. 48 (2013) 2588–2594, https://doi.org/10.1111/ijfs.12253.
[37] J.A. Kennedy, J. Ferrier, J.F. Harbertson, C. Peyrot Des Gachons, Analysis of tannins in red wine using multiple methods: correlation with perceived astringency, Am. J. Enol. Vitic. 57 (2006) 481–485.
[38] M.D. Mercurio, P.A. Smith, Tannin quantification in red grapes and wine: comparison of polysaccharide- and protein-based tannin precipitation techniques and their ability to model wine astringency, J. Agric. Food Chem. 56 (2008) 5528–5537, https://doi.org/10.1021/jf8008266.
[39] J.C. Boulet, C. Trarieux, J.M. Souquet, M.A. Ducasse, S. Caillé, A. Samson, P. Williams, T. Doco, V. Cheynier, Models based on ultraviolet spectroscopy, polyphenols, oligosaccharides and polysaccharides for prediction of wine astringency, Food Chem. 190 (2016) 357–363, https://doi.org/10.1016/j.foodchem.2015.05.062.
[40] J.L. Aleixandre-Tudo, A. Buica, H. Nieuwoudt, J.L. Aleixandre, W. du Toit, Spectrophotometric analysis of phenolic compounds in grapes and wines, J. Agric. Food Chem. 65 (2017) 4009–4026, https://doi.org/10.1021/acs.jafc.7b01724.
[41] J. Darias-Martín, M. Carrillo-López, J.F. Echavarri-Granado, C. Díaz-Romero, The magnitude of copigmentation in the colour of aged red wines made in the Canary Islands, Eur. Food Res. Technol. 224 (2007) 643–648, https://doi.org/10.1007/s00217-006-0352-7.
[42] R.B. Boulton, the copigmentation of anthocynins and its role in the color of red wine: comments on a critical review, Am. J. Enol. Vitic. 52 (2001) 67–87.
[43] M.T. Escribano-Bailon, C. Santos-Buelga, Anthocyanin copigmentation - evaluation, mechanisms and implications for the colour of red wines, Curr. Org. Chem. 16 (2012) 715–723, https://doi.org/10.2174/138527212799957977.
[44] J. Heras-Roger, C. Díaz-Romero, J. Darias-Martín, What gives a wine its strong red color? Main correlations affecting copigmentation, J. Agric. Food Chem. 64 (2016) 6567–6574, https://doi.org/10.1021/acs.jafc.6b02221.
[45] P. Ribéreau-Gayon, Y. Glories, A. Maujean, D. Dubourdieu, Handbook of Enology, Volume 2, the Chemistry of Wine, Handb. Enol, vol. 2, John Wiley & Sons, Inc., Hoboken, NJ, USA, 2006, pp. 1–441, https://doi.org/10.1002/0470010398.
[46] K.A. Bindon, M.G. Mccarthy, P.A. Smith, Development of wine colour and non-bleachable pigments during the fermentation and ageing of (Vitis vinifera L. cv.) Cabernet Sauvignon wines differing in anthocyanin and tannin concentration, LWT-Food Sci. Techol. 59 (2014) 923–932, https://doi.org/10.1016/j.lwt.2014.05.051.
[47] J.M. McRae, S. Kassara, J.A. Kennedy, E.J. Waters, P.A. Smith, Effect of wine pH and bottle closure on tannins, J. Agric. Food Chem. 61 (2013) 11618–11627, https://doi.org/10.1021/jf403704f.
[48] J. Laqui-Estaña, R. López-Solís, Á. Peña-Neira, M. Medel-Marabolí, E. Obreque-Slier, Wines in contact with oak wood : the impact of the variety (Carménère and Cabernet Sauvignon), format (barrels, chips and staves), and ageing time on the phenolic composition, J. Sci. Food Agric. 99 (2018) 436–448, https://doi.org/10.1002/jsfa.9205.
[49] A. Gambuti, A. Rinaldi, M. Ugliano, L. Moio, Evolution of phenolic compounds and astringency during ageing of red wine: effect of oxygen exposure before and after bottling, J. Agric. Food Chem. 61 (2013) 1618–1627, https://doi.org/10.1021/jf302822b.
[50] G. Mazza, L. Fukumoto, P. Delaquis, B. Girard, B. Ewert, Anthocyanins, phenolics and color of Cabernet Franc, Merlot and Pinot noir wines from British columbia, J. Agric. Food Chem. 47 (1999) 4009–4017, https://doi.org/10.1021/jf990449f.
[51] M.J. Kwiatkowski, The impact of closures, including screw cap with three different headspace volumes , on the composition, colour and sensory properties of a Cabernet Sauvignon wine during two years' storage, Aust. J. Grape Wine Res. 13 (2003) 81–94.
[52] A.G.T. Siani, L.P.A. Rinaldi, M.T.L.M. Ugliano, Oxygen exposure of tannins - rich red wines during bottle ageing . Influence on phenolics and color , astringency markers and sensory attributes, Eur. Food Res. Technol. 243 (2017) 669–680, https://doi.org/10.1007/s00217-016-2780-3.