QCL WINE SCIENCE

WINELab®

Phenolic Maturity of Grapes

The stabilization of polyphenols and their extraction from the grapes are among the most important aspects that the oenologist must manage during the vinification of red wines. Thus it is essential to identify the moment when the grapes reach the maximum phenolic content to start the harvest. Obtaining the highest concentration of polyphenols in the grapes is in fact one of the main agronomic objectives that has a positive influence on the entire process of winemaking, giving the oenologist the possibility to obtain a wine of higher quality. Is it possible to quickly and easily determine when to harvest the grapes so as to maximise the extraction of phenolic compounds?

Phenolic Compounds in Grapes

In grapes there are a number of phenolic compounds, located in the various parts that make up the bunch; among these, the predominant ones are anthocyanins and tannins. Anthocyanins represent the red pigments of grapes. They are found primarily in the skin, exceptionally in the flesh in some varieties, but they are also present in the leaves, in greater quantities the closer the vine reaches the end of its vegetative cycle. Tannins are substances capable of producing stable combinations with proteins and other vegetal polymers. They react with the proteins and glycoproteins of saliva, determining the sensory sensation of astringency. Tannins are found in the skin and in grape seeds, the seeds of the berry. From a chemical point of view, tannins are relatively voluminous phenolic molecules derived from the polymerization of monomeric molecules containing phenolic functions.

The Oenological Maturity of Grapes

The oenological maturity is determined by an appropriate balance of the composition of the grapes in order to obtain the best possible wine, depending on the climatic situation, the vintage and the oenological objective. This parameter can be assessed through the separate determination of three other parameters:

- Technological maturity, which corresponds to the moment of maximum sugar to total acidity ratio
- Aromatic maturity refers to the aromatic potential of the grape; it can be determined essentially by tasting the berry
- Phenolic maturity

The phenolic maturity of the grapes takes into account the overall concentration of phenolic compounds (anthocyanins and tannins), their structure and their extractability, i.e. the percentage of anthocyanins and tannins that can be extracted from the grapes and then found in the must and then in the wine. The importance of determining the extractability of phenolic compounds is given by the fact that, under the same environmental and cultivation conditions, a wine obtained from ripe or slightly overripe grapes contains more phenolic compounds than a wine obtained from unripe grapes.

The Evolution of the Concentration of Anthocyanins and Tannins During Grape Maturation

During the ripening period of the grapes the concentrations of anthocyanins and tannins in the skins of the berries are subject to variations. It is essential to determine the moment when the highest concentration of phenolic compounds is present so that the harvest can be carried out at that moment, thus ensuring the highest transfer of these substances into the must. From such perspective, it is important to know the development of the concentration of the main phenolic compounds of the grapes during their ripening period. From veraison to so-called technological maturity, the grape skins are enriched with phenolic compounds. In particular, anthocyanins appear at veraison and continue to increase throughout the course of ripening, reaching their maximum concentration near technological maturity, only to decrease during the over-ripening phase of the grapes. The tannins present in the skins show the same behaviour, with the difference that at the time of veraison they are already present in significant quantities.
As far as the tannins present in the grape seeds are concerned, there is an opposite behaviour: their concentration decreases from the moment of veraison and throughout the period of ripening of the grapes. This decrease seems to be related to the accumulation of anthocyanins in the skins. Depending on the environment, the maximum concentration of anthocyanins and tannins present in the grapes may coincide with the maximum ratio of sugar to total acidity, but it may also be prior or following. It is for this reason that it is considered important to identify the phenolic maturity of the grapes, as well as the technological maturity, in order to establish the optimal moment for the harvest.

The Official Method (Glories, 1990)

In order to determine the phenolic content of grapes, several methods have been studied and proposed over the years, but they have not proved adequate to determine the concentration of anthocyanins and tannins present in the grapes and to determine how many of these phenolic compounds can be transferred from the grapes to the wine during fermentation.
In 1990 Glories proposed a first valid method that makes it possible to determine the optimal harvest date to maximize the extraction of polyphenols from the grapes.
The method involves sampling about 200 berries, which are then homogenized using a mixer. In this way the seeds present in the berries are also fragmented, thus inducing the partial extraction of the tannins they contain, necessary to define the exact phenolic content. From this mixture, divided into two parts, the anthocyanins and tannins are extracted by dilution with an acid medium. Therefore a 1:1 dilution of one part of the homogenized product is carried out with an acid solution at pH 1, and of the other part with a solution at pH 3,2.
The addition of the solution at pH 1 is intended to exaggerate the extraction of anthocyanins and tannins, considering that such an acidic solution is able to alter the membrane of the skin cells and consequently release all their contents; all the anthocyanins and tannins present are therefore extractable and soluble at pH 1. The solution at pH 3.2 is intended to simulate what actually happens during grape maceration when vinification takes place. The riper the grapes are, the more the cell membrane of the berries is degraded by enzymes. In other words, the riper the grapes are, the more the extraction of anthocyanins tends to be similar to that obtained by adding the pH 1 solution.

Once these dilutions have been completed, both solutions are allowed to macerate for 4 hours at room temperature, and then it is necessary to filter them on glass wool in order to eliminate turbidity. Anthocyanins are determined in both solutions using the SO2 discoloration method (Ribereau, Gayon and Stonestreet). The difference between the two results is an indication of the fragility of the grape membrane at the time of sampling and consequently an indicator of the ease of extraction of tannins and anthocyanins and thus also an index of the phenolic maturity of the grapes. The percentage of anthocyanin extractability (EA%) is calculated as follows:

$$EA\% = \frac{A_{pH1} - A_{pH3.2}}{A_{pH1}} \times 100$$

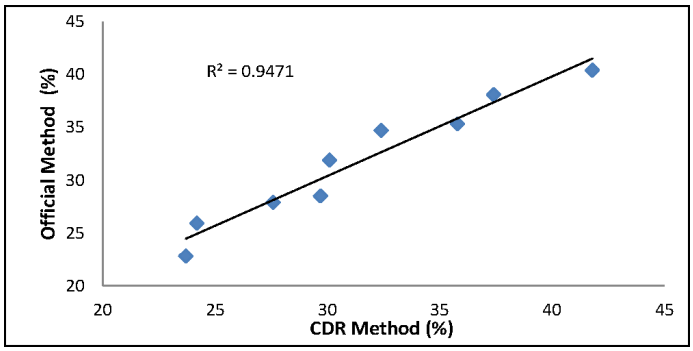
where A_{pH1} is the anthocyanin content of the solution at pH 1 and $A_{pH3.2}$ is the anthocyanin content of the solution at pH 3.2. The smaller this value, i.e. the difference between the two measurements of anthocyanin content, the more easily these compounds can be extracted. The values can vary between 70% and 20% depending on the ripeness of the grapes and decrease as they ripen. With this method it is also possible to measure how much seed tannins contribute to the total phenolic content of the extract (MP%), with the following relationship:

$$MP\% = \frac{DO_{280} - (A_{pH3.2} \times 40}{DO_{280}} \times 100$$

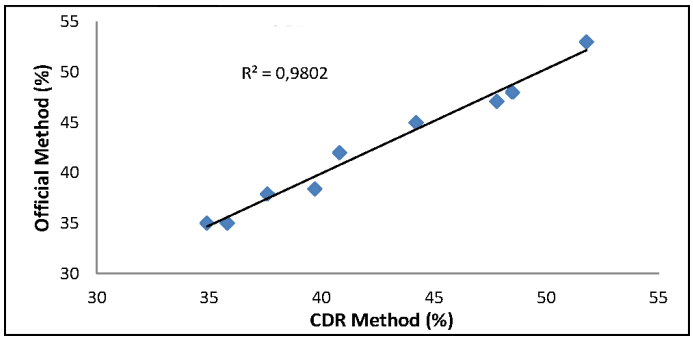
where DO_{280} is the optical density of the solution at pH 3.2 read at 280 nm, index of total polyphenols present. MP% decreases during ripening and assumes values ranging from 60 to 0 depending on the variety, the number of seeds in the berries and the ripening conditions. The Glories method described above is therefore an effective but very long method, considering the 4 hours of maceration.

The CDR Method

CDR has optimized this method to make it even more performing, fast and accurate. The sample treatment remains the same, with the difference that in the CDR method the maceration time has been optimized and reduced to only 30 minutes. The sample is then filtered or centrifuged. A small quantity of sample thus obtained - 0.5 mL - is sufficient for the CDR WineLab system to analyse the anthocyanin content, guiding the operator step by step throughout the entire sample treatment phase and during the analysis itself, developed by optimizing the official method “Dosing of anthocyanins by SO2 discoloration (Ribereau, Gayon and Stonestreet)”.
The CDR method, in addition to considerably reducing the time for the treatment of the sample, allows the determination of phenolic maturity even by personnel not specialized in laboratory techniques, unlike the official method that requires experienced and qualified personnel. The WineLab also allows the optical density to be read at 280 nm, and therefore also allows the contribution of seed tannins to be determined.
Below are the conclusions of a study carried out by CDR on two types of grapes, a Sangiovese and a Petit Verdot from two Tuscan estates. Accurate samples were taken every 2 days, for a duration of about 20 days, and a comparison was made between the official method and the data obtained with the CDR method. As can be seen from the graphs, for both types of grapes there is an excellent correlation between the official method and the CDR method. As previously mentioned, with the WineLab tool, in addition to the phenolic maturity analysis, it is also possible to determine the contribution of seed tannins to the total polyphenolic content. Without having to resort to further



Calibration curve, grape phenolic maturity - Sangiovese Estate 1



Calibration curve, grape phenolic maturity - Petit Verdot Estate 2

equipment, the WineLab alone also provides the complete panel of parameters dedicated to quality control on must and wine, including, among others, the sugar and total acidity tests necessary to evaluate the technological maturity, which is fundamental in conjunction with phenolic maturity to determine the ideal time for the harvest.

Conclusions

In the case of a red wine it is important to take into account the phenolic maturity as phenolic compounds directly determine the colour of red wines and strongly influence their stability during ageing. In order to obtain maximum extractability of phenolic compounds during vinification, it is not sufficient to check the technological maturity, but it is necessary to measure the concentration of anthocyanins in the proximity of maturation. The method considered to be the reference method for the determination of phenolic maturity is the Glories method based on the extraction of anthocyanins from a sample of must, partly under conditions simulating the wine-making process (extraction by means of a buffered solution at pH 3.2), and partly under extreme conditions, capable of completely eliminating diffusion barriers (acid solution at pH 1). This method is very time-consuming because it requires a long extraction and sample preparation phase. In addition, the analyses must be carried out by an operator specialised in laboratory techniques. CDR has optimized the Glories method in order to make it even more efficient, fast and accurate and has implemented it on WineLab, the wine analysis system with which it is possible to measure, in addition to the phenolic maturity, a large analysis panel for the complete control of winemaking including the determination of sugars and total acidity, fundamental parameters to determine the technological maturity of the grapes.

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