Determination of polymeric pigments in wine

Wine stability is a key factor in ensuring its sensory quality and consumer acceptance over time. Among the various factors that influence this stability, temperature, dissolved oxygen and changes in the matrix play a fundamental role, since, for example, high temperatures accelerate undesirable chemical reactions that can cause colour loss, premature oxidation and aromatic alterations. In particular, phenolic compounds, which are responsible for the colour and part of the structure of wine, are highly sensitive to thermal conditions during storage and marketing.

In this context, the **determination of polymeric pigments** has become an essential analytical tool for assessing the colour stability of wine. Unlike monomeric anthocyanins, polymeric pigments are more resistant to discolouration, pH and the action of SO_2, making them reliable indicators of wine colour evolution and ageing. Quantifying them provides a better understanding of the impact of heat and other factors on the phenolic structure and allows us to predict the wine's ability to maintain its colour over time.

Therefore, the evaluation of polymeric pigments is essential for quality control, the optimisation of storage conditions and the development of oenological strategies aimed at improving the longevity and stability of the final product.

Automated biosystems reagent for the determination of polymeric pigments in red wine

The **colour of red wine** is one of the sensory aspects most valued by consumers and is often directly associated with its quality. This colour is mainly due to **anthocyanins**, whose basic structure is shown in *Figure 1*. These molecules are coloured because their positive charge is delocalised in the flavilium form, which allows them to absorb light in the visible region of the spectrum.

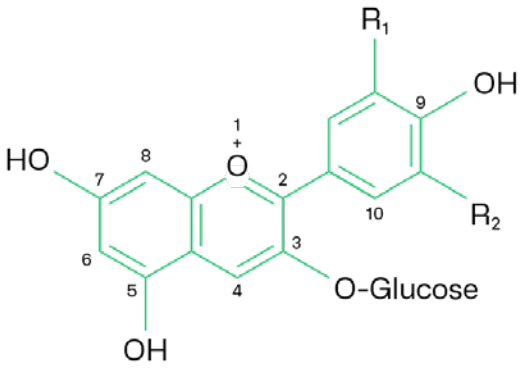

Figure 1: Anthocyanin structure

Colour changes in wine are closely related to the position of this charge and the different resonant structures that anthocyanins can adopt. Therefore, in red wine, different structural forms coexist simultaneously, responsible for variations in colour tone and intensity (Castañeda-Ovando et al., 2009). In addition, **sulphur dioxide** (**SO_2**), widely used in winemaking, plays an important role in this balance, as it can bind to anthocyanins and cause visible changes in the colour of wine (Pelonnier-Magimel et al., 2023).

The **copigmentation interactions** of this molecule promote the formation of **coloured tertiary structures**, which contribute to the intensification and stability of wine colour through various stabilisation mechanisms (Boulton, 2001).

The red colour of **monomeric anthocyanins** is particularly sensitive to discolouration caused by the bisulphite ion, while **polymeric pigments** are more resistant to this effect and therefore maintain their absorbance at 520 nm. This difference in behaviour allows for their analytical quantification.

Polymeric pigments are determined by decolourising the wine at pH 4.9 using a concentrated sulphite solution. Under these conditions, monomeric anthocyanins lose their colour, while the residual colour, measured at 520 nm, is directly proportional to the concentration of polymeric pigments present in the sample. The results are expressed as **mg/L equivalents of malvidin-3-glucoside**. Taking the Adams–Harbertson method as a reference.

These pigments are formed by condensation processes in which anthocyanins (A) and tannins (T) can interact directly or through intermediate substances such as acetaldehyde (Wang et al., 2023).

In these cases, we will distinguish between different forms of bonding and compounds:

- Direct reactions of TA and AT.
- Through a bridge with acetaldehyde TA and AT.

However, there are some polymeric pigments that are sensitive to the addition of bisulphite, which contrasts with the considerations detailed in this study. Based on current scientific knowledge, only AT polymeric pigments, directly or indirectly through acetaldehyde bridges, are insensitive to discolouration by the addition of SO_2 (*Figure 2*). Therefore, the proposed polymeric pigment fraction does not estimate all polymeric pigments present in wines, but only those of the AT type. These colourless compounds were produced by the reaction of SO_2 with anthocyanins in the C-4 position. In the case of TA, this position is free, which is why they are susceptible to discolouration.

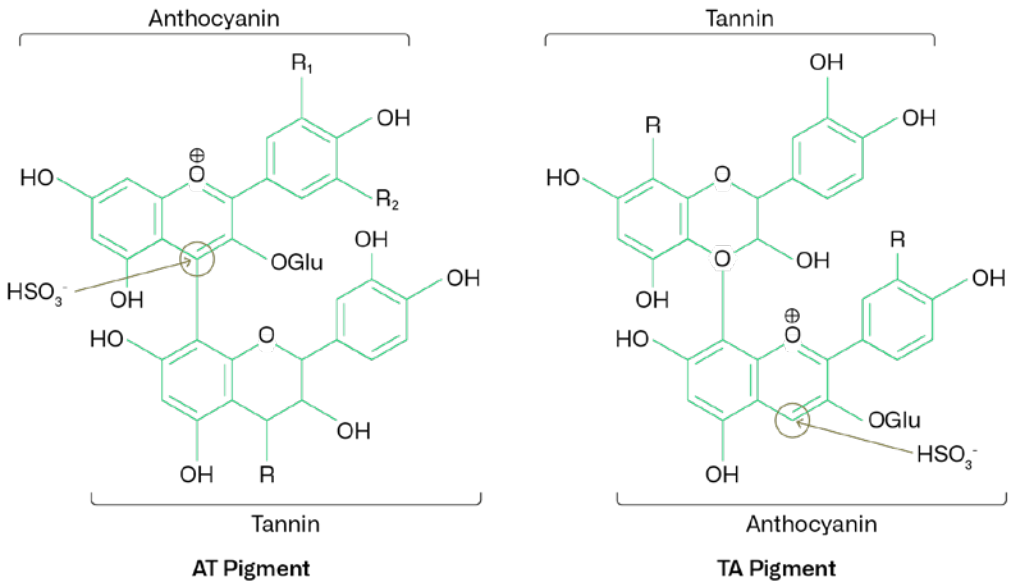

Figure 2: AT and TA pigments

However, we must not only consider AT and TA compounds for colour stability in wine; we should also take into account **pyranoanthocyanin** (*Figure 3*) which is not sensitive to bleaching by SO_2. This fraction is low in young wines and increases with ageing, being important in wines with long ageing periods, responsible for **red-orange hues**. While acetaldehyde binds anthocyanins and tannins via an ethyl bridge, producing **violet pigments**, direct associations between anthocyanins and flavanols give rise to stable **red/orange pigments**, while some other authors have described certain polymeric anthocyanin pigments with **reddish-blue and violet hues**.

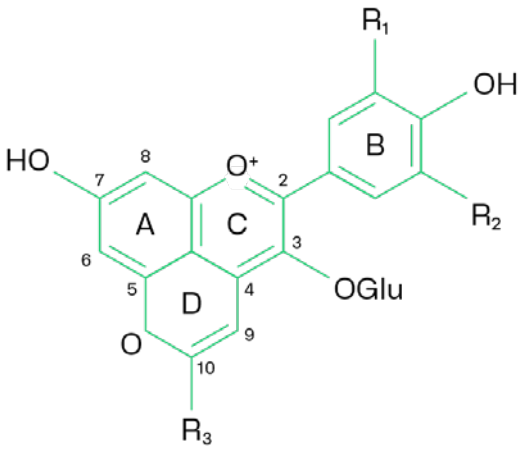

Figure 3: Structure of a pyroanthocyanidin

To calculate the concentration of these pigments, we will use the following formula:

Polymeric pigments (mg/L eqq. of malvidin-3-glucoside) = (A2 - A1) x 122.41

The factor 122.4 is obtained using the molar extinction coefficient of malvidin 3-glucoside and molecular weight, a light path length of 1 cm in the cuvette, and the dilution factor of the sample in the reaction solution.

The determination of polymeric pigments in wine allows the **long-term colour stability** to be assessed. Unlike monomeric anthocyanins, which are more unstable and sensitive to factors such as sulphite, polymeric pigments are more resistant to discolouration, and their presence indicates that the wine will have a more durable colour and be less susceptible to changes over time.

References

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