

COLOUR EXTRACTION FROM RED WINES

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Colour: foremost a matter of potential

The pigments which ensure the colour of red wines, also in terms of intensity and tone, are the anthocyanins derived from the grapes and the resulting products formed from reactions, during the vinification. With the exception of the grape varieties said to be "teinturiers", the anthocyanins are located in the vacuoles of the cells making up the grape berry skin. The tannins, which play a role in the stability of this colour, are found mainly in the seeds and skins. Recent studies by the INRA indicate the presence of tannins in low concentrations even in the pulp.

All these compounds are biosynthesized from sugars. They evolve quantitatively in a different manner during the maturation phase, starting from the veraison:

- The anthocyanins accumulate more or less regularly up until they reach a plateau. In 2007, the measurements completed on grapes with the Glories method, showed 3 main kinetic types: rapid accumulation followed by a prolonged plateau (ex : Syrah 340506), very high levels very early on, with a following limited accumulation, a short plateau and a tendency to then decrease (ex : Syrah 300501, 340503), a slow and continuous accumulation (ex: Syrah 340501).
- The tannins evolve very little: it is possible to note differences between parcelles according to their potential, but the levels do not vary in a significant manner during the maturation phase after veraison.

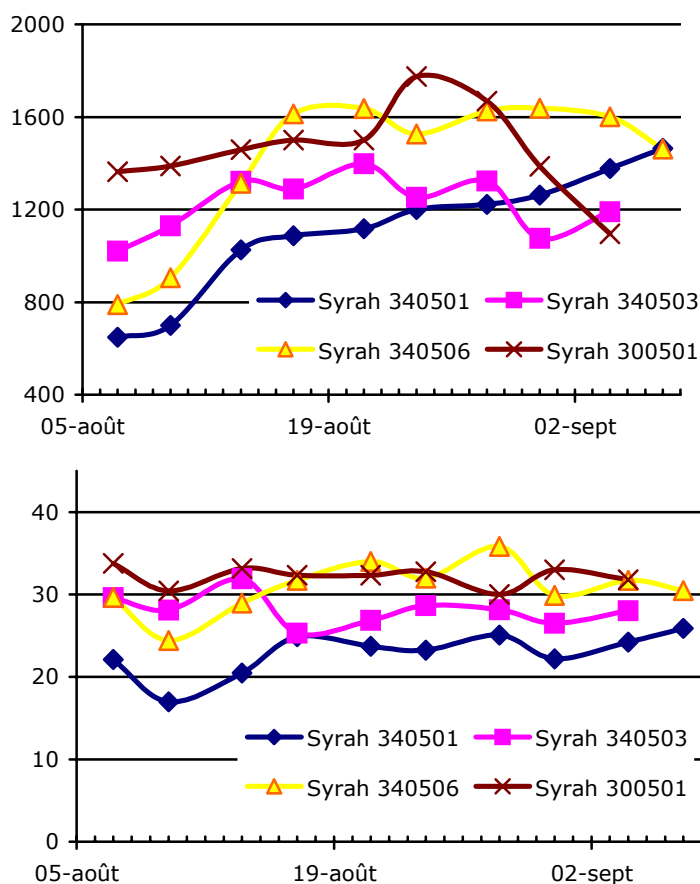


Figure 1 : Evolution of the total anthocyanins (ApH1 mg / L, graph on left) and of the total polyphenol index (DO280, graph on right) on several Syrah of the Observatoire du Millésime in 2007 – Glories Method.

The measurable levels in the berries at the harvest depend essentially on:

- The **grape variety**: Cabernet sauvignon and Syrah, have a high colour potential, Merlot, Mourvèdre and Carignan, medium, Grenache, medium to poor, Cinsault, poor.
- The **physiological state of the vine** during the biosynthesis phase. An excess of vigour, or also an excess of water restriction are unfavourable for the accumulation of anthocyanins.
- The **climatic conditions**: cool nights and the absence of excessive temperatures during the maturation are favourable for the accumulation of anthocyanins.

There are many methods to analyze the colour of the grape berries which can be used as tools to help with decision making. The ICV evaluated a certain number of these methods. You can turn to your oenologist- for advice in order to have more information about one or another of the methods. Whatever be their accuracy, certain points are particularly important for the quality of the results:

- analysis of intact grapes: the trials completed on IRTF in 2001 showed that several hours of maceration of partially crushed grape berries were sufficient to give an increase of the values said “anthocyanins” comparable to the maximal amplitude observed for a given grape.
- always follow the same colour extraction procedures (material, extraction surroundings, maceration duration...): none of the current analysis methods measure the total anthocyanins and polyphenols of a grape berry, but measure those extracted in liquid phase following a defined protocol,
- do not compare the values obtained by different methods: given the differences in analytical protocols, there are very weak correlations between the values given by different methods for the same sample (ICV trials 2000)
- Following accumulation dynamics: measuring a value at a given time (for example upon reception at the winery) gives very limited information about the maturity. Is it – in an accumulation phase? On a plateau? In a decreasing phase? Only a regular following during several weeks after veraison allows for the evaluation of the potential, its availability and its evolution stage.

Extracting: a large diversity of situations

Since the compounds responsible for the colour are localized in the cells of the skin, the vinification and the choice of the techniques applied aim to **open a path for the passage through the pulp**. In fact, no extraction is possible through the “pruine”.

If we reason simply, to extract, it is necessary to access the resource (in this case the skin cells) and allow for the compounds which they contain to pass into solution.

The factors which determine the access to the resource are mainly:

- **Crushing** which opens the grape berries and liberates the juice. This operation liberates the solvent in which the extracted compounds will be found and opens the path for the transfers from the skin,
- **Enzymatic treatments** which weaken the cell walls of the pulp, accelerate and facilitate the liberation of the pulp juice and the coming of contact of this juice with the skin cells: the extractions start earlier. The grape berries also release an endogenous enzymatic activity, but in a staggered manner in relation to the start of the vinification. The initial enzymatic treatments therefore very strongly influence the extraction order and the stabilization.
- **SO₂** which destroys the cellular walls, does so in a continually greater manner as the dose is increased. This property is the origin of the “sulfitic maceration” (SM). As apposed to the enzymatic treatment, the action of SO₂ is not specific.
- **Mechanical or physical actions**: pumping over, “delestages”, “pigeages”, pressing but also pressure and vacuum (flash – detente, thermo – detente) on whole harvests.

The **temperature** is a predominant physical factor but indirectly. It intervenes to favourize or create the extraction conditions by weakening the various elements which assure the resistance of the grape berry cells. This is the case in the thermo vinification with or without application of détente or pressure *a posteriori*: the heating temperature of the harvest destroys the enzymatic activities very quickly but increases the internal pressure (at least partial vaporization of the water of the cells) leading to a mechanical rupture of the walls and membranes. In the end, it is the **combination** between application of time- temperature- complementary methods (suction for example)- extraction methods completed

(maceration, pressing, draining...), that will determine the quantity of anthocyanins liberated. In addition, this is also the case for classic fermentations: in this situation, given the values of habitual tasks, the temperature accelerates the enzymatic processes. Furthermore, the temperature is a regulator of the alcoholic fermentation speed, and hence the speed of alcohol accumulation in the must. Although, the alcohol also relies on the solubility (cf. below)

The kinetics and the extraction levels depend on the **controlling of all the factors**. Certain winemakers think that it is obligatory to heat in order to extract and thus want to macerate at 30°C or even higher. This is a mistaken shortened and simplified reasoning: by crushing, increasing the enzymes doses, more frequently doing delestages and staying at temperatures which allow for the management of fermentation risks and aromatic style, it is possible to attain without difficulty equivalent if not better results.

The passage into solution depends on:

- The form, the size and the positioning of the openings in the cellular walls or membranes. This is what explains in part, the sensorial differences according to the different enzymatic preparations which can be put in place starting at the grape reception but also why the dosages are increased for grapes which are not completely mature: the cells are more resistant and liberate more pectins, which are two reasons for the increased dose.
- The concentration level of the juice in contact with the compartments containing the resource. **The more concentrated the juice, the less apt it is to solubilize the components of the grape berry**. In this sense, delestage and pumping over are not equivalent, even if we work on the same apparent volume of juice. The delestage renews almost entirely the juice in contact with the skins (where the resource is found) whereas the pumping over is completed on only a limited part.
- For the tannins, the alcohol plays a non negligible role. The tannins in the skins are more accessible than those in the seeds and are more water soluble, thus are extracted more easily. With the progressive increase in alcohol concentration during the alcoholic fermentation, the tannins of the seeds are more and more easily extracted. Furthermore, without being able to make a founded link with these mechanisms and the physical-chemical characteristics of the different tannins, in practice it has been shown that early extractions lead to wine which are often less dry, less astringent and less bitter than those with late extractions.

For that which concerns the colour, the kinetic are relatively rapid: a few hours suffice in thermovinifications or high temperature pre-fermentative macerations (i.e around 60°C) and a few days suffice for classic fermentations (of 3-4 in small R&D tanks to 7-8 in wineries).

The techniques and their variants

The techniques also jointly play on many extraction factors: for example the enzyme treatments-crushing- heating- flash détente- pressing combine 5 extraction factors. It is thus difficult, in a multi-parametric situation, to anticipate the consequences and all the possible control methods.

We can however consider a global characterization of the techniques available today used in wineries.

Next we will talk about instant colour as the measurement of the colour intensity (CI) at the time of vinification, which is essentially to say the extraction result. The techniques and conditions for the stabilization of this colour will determine the final colour, measured several weeks or months after the vinification.

The classic techniques

The grapes are placed in the tanks after crushing and enzymatic treatment. The extraction is completed mechanically by pumping over, pigeage or delestages. The **instant colour reaches a maximum at around 4 to 10 days of the maceration** in accordance with the intensity of the working of the cap, the pulp maturity, the enzyme dose and the temperature. As a reminder, we use enzymes at a base dose, either 1g/hL or 1,5g/hL (respectively of KZymplus® and FlashZym® or AlphaRouge® in our experiments) when the grapes are at pulp maturity (generally a potential of 13.5% and above) and at a double dose when the maturity is not reached.

It is still the most widespread technique in the world.

In these conditions, the maximum Total Polyphenol Index (TPI), a rough indicator of the tannic concentration, is reached between 8 and 12 days.

Many variants exist, depending on the type of vinification equipment installed:

- Pigeage tanks equipped with a mechanism which pushes the cap until it is submerged below the fermenting must,
- Rotative tanks which plunge the cap by regular programmable rotation (similar to pigeage)
- Rake tanks which break up the cap allowing for exchanges between the juice and the skins,
- Tanks with superior compartments with automated pumping over for a part of the fermenting must,
- Tanks with pigeage “from the bottom” which send air or a gas under pressure to break up the cap...

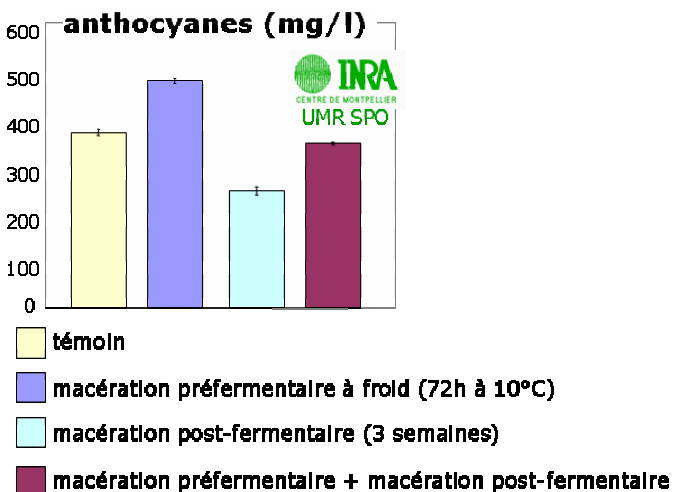
In all cases, it is the renewing of the contact between the juice or wine with the skins which determines the quantitative aspects of the extractions. As the volume of juice or wine is increasingly renewed, it is more susceptible to pick up new components from the grape berries which pass into solution.

Furthermore, the different variants causing **mechanical breaking** up which is more or less prominent, can extract in a more or less marked manner the vegetal components that favourizes vegetal notes and mask the fruit, all while also determining the short term turbidity of the juice and the future levels of lees. This is not neutral for the colour: adsorbent particles, reactivity to oxygen and precipitation cores are largely generated during these extraction phases. The technique choice (dosage and redaction of added enzymes, winery equipment, extraction techniques, earliness and extraction rhythm) are hence predominant for the colour stability and for the aromatic and taste sensations.

To this end, the delestage, and even more so when we take the juice or wine from the bottom, is the technique which remains globally favoured.

Cold pre-fermentative maceration

The de-stemmed – crushed grapes are cooled via an exchanger to be brought to a temperature < 15°C and even generally < 10°C. It is maintained by one or more flags or by pumpings protected with CO₂ during 2 to 6 days.



There is thus a dynamic extraction phase (pumping over or delestages) or static phase (crushing of berries in the bottom of the tank) at a low temperature and in the absence of alcohol (or for the least a very low concentration): it is this that allows for this technique to be judged as different from the last.

The instant colour increases rapidly up to reaching a high value at the end of 3 to 5 days. The lengthening of the pre-fermentative maceration beyond this length of time leads to a poor increase in the instant colour: in pushing up to 20 days, the gain is 10% relative to a pre-fermentative maceration of 4 days (results on Cabernet sauvignon, Virginia Tech University). Some trials completed by the INRA (cf. below, results

published by the *American Journal of Enology and Viticulture* : *Cheyrier et al., 2006, n°57, pp 298 – 305*) demonstrated a gain of free anthocyanins linked to the practice of pre-fermentative maceration.

Other trials, notably in the USA where this type of vinification is very frequent, have not always shown colour gain in comparison to controls: it would seem that for grape varieties which are relatively “poor” in colour as for Pinot Noir, gain little in this point of view whereas those which are more “rich” gain a little, at least over the short term. These results are not contradictory with those of the INRA since **the extraction of free anthocyanins determines only in part the colour of the final wine** (cf. “Stabilization” part).

Carbonic maceration

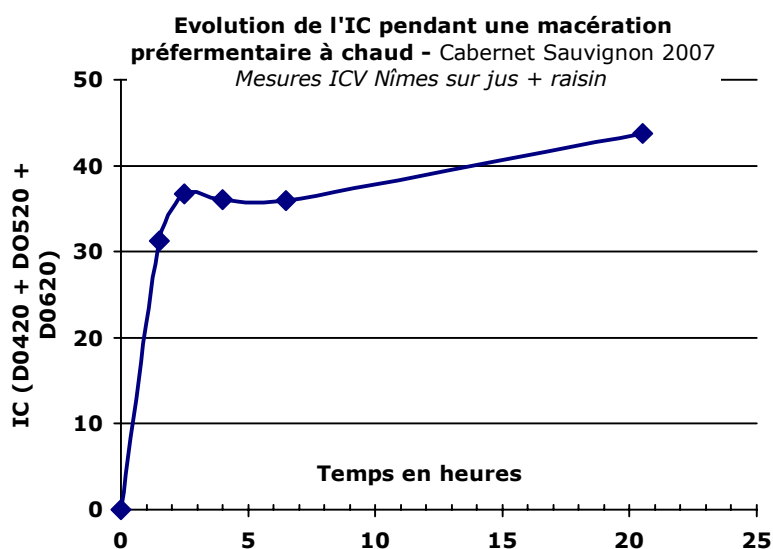
This technique consists of placing whole grapes into tanks saturated with CO₂. Yeasts are added to the juice at the bottom of the tank and via the fermentation, the levels of CO₂ are maintained all while maintaining a temperature above 25°C.

There is no extraction during the first maceration phase except from the berries at the bottom of the tank, "crushed" by the weight of the mass overhead. The anaerobic metabolism of the whole grape berry followed by a frequent (but obligatory) extractive phase (delestage or pumping over) with the addition of enzymes leads to a higher concentration of polyphenols in the final wine and with an CI superior by 5% to 35% to the control undergoing a classic maceration.

The different variations tested, notably in temperature and enzymatic treatment, never clearly lead to a gain of colour.

Heating the harvest

The grapes are heated via an exchanger passing from 20°C to more than 65°C in 2 to 15 minutes. This process is followed by a pressing which gives very coloured juices: in comparison to a classic fermentation, the instant colour gain (measured by the some of DO420 + DO520= CI) is in the order of 30%. The clarified juices are then fermented in liquid phase.



The variations initially rest on the temperature and times of temperature increases. No studies show the specific effect of these modulations on the instant colour.

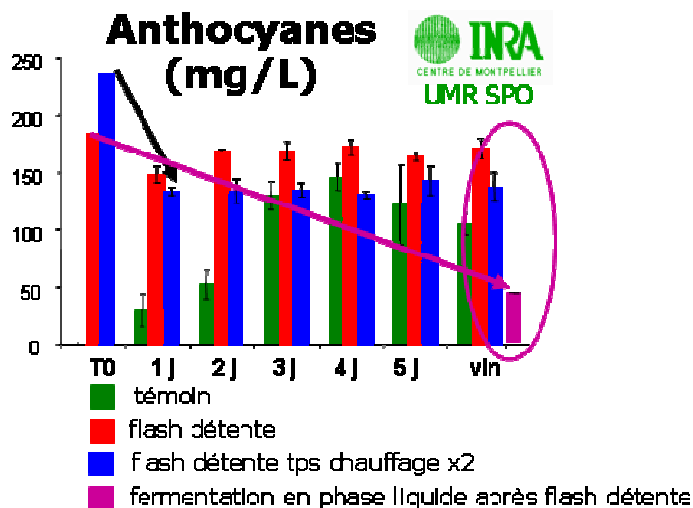
A second variation category is the hot pre-fermentative fermentation. We place the grapes in the tanks for several hours (usually 3 to 15 hours) at the temperature at which it comes out of the exchanger, assuring the heating. There is no addition of yeasts and therefore no fermentation as long as the hygiene is assured and temperature is maintained around a minimum of 55°C. This hot pre-fermentative fermentation leads to an increase of 20 to

35% of the colour obtained just at the exit from the press. Similarly to the cold pre-fermentative fermentation, a large part of the instant colour is extracted in the first hours. The total polyphenols increase also in similar proportions.

The pumping over or delestages can even start almost the next day at the beginning of the alcoholic fermentation with as a principal effect a regular increase in the crushed grape berry mass: this is closer to a classic maceration but with increasing alcohol levels and a large part of the grape berries remaining intact.

Heating of the harvest followed by flash detente

This technique consists of bringing de-stemmed-crushed grapes to a temperature close to 95°C (heating phase) and then distending it in a closed vessel. The vacuum causes the grape berries to implode in the absence of oxygen and physically bring the grapes to a temperature close to 30°C which permits: for either pressing it to ferment in liquid phase or to place it in tanks for a chosen length of time in according to the objectives for product.



The variations presented here demonstrate the quantitative impact of the heating time and of the post flash détente maceration, on Grenache noir. Parallel measurements of tannins logically showed that the post flash détente maceration enriched the wine mainly in the first three days, passing from a factor of 1 to 3!

The effects of enzyme addition posterior to the flash détente at classic doses only had a slight effect on the instant colour. On the other hand, they play their role by decreasing the pectin and hence have an effect on the clarification and thus stabilization of this colour. The increasing of the dose plays positively on the instant colour and the DO280 (industrial trials 2007 harvest).

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