ARTICLE

Study of the evolution of colour during the maceration process of cherries in liquor: an application of visible spectroscopy

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Introduction

Liquor with macerated cherries (*Prunnus avium*) is a popular hard spirit in several countries. There is increasing industrial production of this and other analogous liquors made by soaking different fruits (blackberries, peaches, mulberries, strawberries, dry figs, sloe berries and others) in several spirits, usually with a certain amount of sugar and other flavourings such as cinnamon or grains of coffee.[1]

During the maceration process, the ethanol softens the fruits and promotes the extraction of several substances that give the liquor its characteristic colour, flavour and smell. Sometimes there is also a distillation from the product of maceration (for example, Kirsh is a well-known white brandy distilled from cherries).

Colour evolution during the soaking process of fruits in liquors is of major interest for quality control, since it is related to the organoleptic properties developed. The appearance of an alcoholic drink can greatly influence the decision of a consumer to purchase. In a previous investigation[2] we studied experimentally the influence of temperature on the kinetics of pigment extraction during the maceration of cherries into a hard spirit. We concluded that, for the range of temperatures studied (5 to 30°C), the kinetics of pigments (essentially anthocyanins) extraction has an apparent activation energy of 78.2 ± 5.0 kJ mol^{-1}. The main objectives of the work discussed here are to study the evolution of the colour during the maceration process and to determine the convenience of using a simplified method for evaluating this parameter.

The ways in which colour changes occur in red wines have been investigated by several authors,[3,4] because of the economic importance and magnitude of production of this product worldwide. To our knowledge, little or no published information exists in the literature reporting on the evolution of colour in the soaking process of cherries into liquors. Nevertheless such studies can lead to a better industrial control of this process, which until today has been characterised by skilled craftsmanship, since extracting the liquor involves a certain "art",[1] based on experience rather than precisely measured amounts of components or properties.

Negueruela and Echávarri[5] reported a study on the evolution of colour during the soaking process of sloe berries in several liquors, with different amounts of fruits per litre of liquor. The process is used to produce the liquor known as *pacharán*, which is very popular in Spain. The evolution of the colour during the maceration of cherries into *orujo* was measured in our study. *Orujo* is a typical Spanish eau-de-vie made from the marc of grapes, and it consists mainly of a hydroalcoholic solution containing about 40% ethanol (v/v). In order to simplify the study, the other ingredients such as sugar and, occasionally tea, cinnamon or grains of coffee used in cherry liquors were not considered.

Colour expression is a psychophysical property that involves a certain degree of complexity, because it is a matter of perception, i.e. of subjective interpretation. As is well known,[6] colour measurement by colour coordinate determination is an attempt to assign three coordinates to a colour, which correspond to the amount of each of the three primary colours—red, green and blue—which the colour contains. These values are determined by collecting photometric data from the sample and then applying both a standard illuminant function and a standard observer function to arrive at the three colour coordinates. Colour can be expressed in different systems (L*a*b*, *XYZ*, *Yxy*, Munsell notations, and others).[7]

The CIE (*Commission Internationale de l'Éclairage*, International Commission on Illumination) values *X*, *Y* and *Z* are calculated from tables of the standard observer colour-matching functions $\underline{x}(\lambda)$, $\underline{y}(\lambda)$ and $\underline{z}(\lambda)$, the standard illuminant function and the transmittance (or more usually reflectance) values.[8] The tristimulus equations for measurement by means of transmittance, $T(\lambda)$ are:

$$X = k \cdot \sum_{400}^{700} T(\lambda) \cdot S(\lambda) \cdot \underline{x}(\lambda) \qquad (1)$$

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$$Y = k \cdot \sum_{400}^{700} T(\lambda) \cdot S(\lambda) \cdot \underline{y}(\lambda) \qquad (2)$$

$$Z = k \cdot \sum_{400}^{700} T(\lambda) \cdot S(\lambda) \cdot \underline{z}(\lambda) \qquad (3)$$

where the normalisation factor is:

$$k = \frac{100}{\sum_{400}^{700} S(\lambda) \cdot \underline{y}(\lambda)} \qquad (4)$$

and the other parameters are: $T(\lambda)$: transmittance of sample at wavelength λ; $S(\lambda)$: relative spectral power of illuminant from the relevant table[6] (in our case we proceeded with the illuminant C); $\underline{x}$ (λ), $\underline{y}$ (λ) and $\underline{z}$ (λ): CIE observer colorimetric functions.

The wavelength interval selected in the measurement will determine the table to be used for both the illuminant and the observer. In our case we selected an interval of 1 nm, which yields the most accurate results for most practical applications.[8] We refer to this rigorous method as method B, since we also used a simplified method referred to as method A, which is outlined below.

In method A, the x and y chromaticity values are calculated[6] as $x = X / (X + Y + Z)$ and $y = Y / (X + Y + Z)$.

Experimental

Apparatus

The analytical method used was visible absorption spectrophotometry. Absorption spectra (over the range 400–700 nm) of solutions were recorded on a UV-260 Shimadzu spectrophotometer with 1 cm pathlength quartz cells. Spectra were also recorded on a Cary 1E Varian spectrophotometer using the same cells and computerised treatment of data, in order to obtain the chromatic coordinates and to cross-check the results.

Reagents and chemicals

The Council of El Arenal (a village of Ávila, Spain), interested in this study, provided the cherries. A commercial *Ponte Ulla* hard spirit (*orujo*) produced by Ruavieja S.A. in Santiago de Compostela (Galicia, Spain), with 42% ethanol (v/v), was used for the maceration of the cherries.

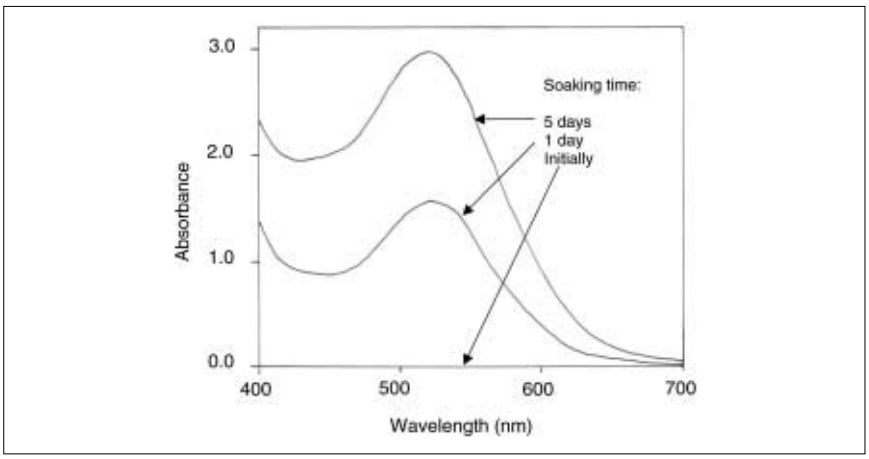

Figure 2. Examples of visible absorption spectra of the liquor with immersed cherries at 30°C.

General maceration procedure

1000 g of cherries were analysed for each run. Samples for the experiment were carefully selected in terms of weight (8.5 ± 0.5 g), size (average diameter of 2.2 ± 0.3 cm), and homogeneity of skin and colour. Samples selected for each run were immersed in a beaker containing 1.0 L of the colourless liquor, and preheated/cooled to the required temperature. The range of temperatures tested was: 5, 23 and 30°C. For the highest temperature, the experiments were performed in a thermostatic bath and for the lowest temperature the experiment was performed in a refrigerator. The solutions were kept in the dark for 20 months.

After selected times liquors were stirred to homogenise the solutions; a sample of 5 mL from each beaker was removed in order to measure the visible spectrum and, after the measurement, returned to the bulk solution to avoid any dilution effect. The reference cell used was filled with the primary hard spirit (without cherries). Before measuring its visible spectra, each sample was filtered to eliminate the presence of particles suspended in solution that would cause scattering.

Figure 1. Variation of the colour of the liquor: pure (left) and after three months with cherries immersed in it (right) at room temperature.

Results and discussion

Figure 1 shows the colour variation of the liquor as the cherries are soaked in it. The optical absorption spectra of the samples reveal that there is an absorption region, attributed to the presence of anthocyanin pigments, centred at ~525 nm, see Figure 2.

In order to quantify the evolution of colour with the time, for each temperature studied, the CIE tristimulus coordinates for illuminant C were calculated, following the simplified and standardised method proposed for wines,[9,10] according to the equations:

$$X = 0.42 \cdot T_{625} + 0.35 \cdot T_{550} + 0.21 \cdot T_{445} \qquad (5)$$

$$Y = 0.20 \cdot T_{625} + 0.63 \cdot T_{550} + 0.17 \cdot T_{495} \qquad (6)$$

$$Z = 0.24 \cdot T_{495} + 0.94 \cdot T_{445} \qquad (7)$$

where T_{625}, T_{550}, T_{495} and T_{445} are the transmittances of samples at wavelengths of 625, 550, 495 and 445 nm, respectively, through a sample of 1.0 cm pathlength.

Table 1 shows a set of the x and y chromaticity values obtained by this simplified method, method A, using only the four transmittance values at the selected wavelengths, compared with those obtained by the more rigorous method, method B. Samples 1, 2 and 3, taken as

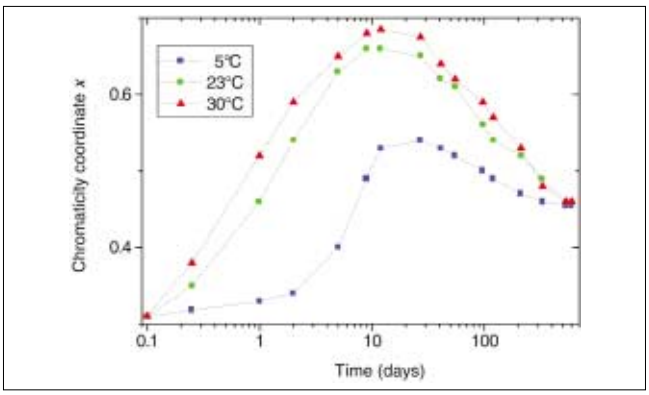

Figure 3. Evolution of the chromatic coordinate *x* with the time of maceration of cherries in the liquor.

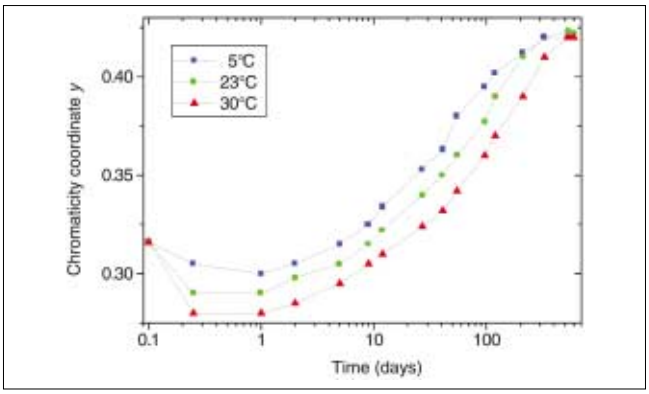

Figure 4. Evolution of the chromatic coordinate *y* with the time of maceration of cherries in the liquor.

examples, were the liquor prepared as described earlier, after 60, 200 and 600 days of maceration, respectively, at 25°C. It can be seen from Table 1 that there is a very good agreement between corresponding values obtained by both methods. Thus, the simplified method gives a good approximation to values determined by the more standard procedure, and was applied therefore to our set of samples.

Once the tristimulus values were obtained, we calculated *x* and *y* coordinates as discussed earlier.

Figures 3 and 4 show the variation of these coordinates versus the time at the temperatures studied. It can be observed that initially, there is a decrease in the value of *y*, at a rate that increases with temperature, whereas the value of *x* increases.

After a rapid variation of both chromaticity parameters (over one day for the values of *y* and over around ten days for the values of *x*), a slower variation was observed until the colour stabilised after 20 months. In an earlier study[2] we observed that the apparent stabilisation of colour took place in about 2–4 weeks, depending on the temperature, but the present study shows that there are molecular changes causing change of colour that take place over a period of almost two years.

Concluding remarks

We conclude that the experimental study described in this article shows that the simplified method, well established for wines, for calculating the *x* and *y* parameters of chromaticity is adequate for

the study of evolution of colour during the maceration of cherries in liquor. After a rapid change in the coordinates *x* and *y* during the first few days, a slow variation is observed until stabilisation occurs after around 20 months.

Acknowledgement

The authors are grateful to Professor John Chalmers for his valuable suggestions.

Table 1. *x* and *y* chromaticity values calculated by the simplified method (method A) and by a more rigorous method (method B), see text for details.

Sample	Method A		Method B	
	x	*y*	*x*	*y*
1	0.653	0.352	0.658	0.349
2	0.519	0.387	0.524	0.383
3	0.464	0.424	0.466	0.422

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