

Effect of Temperature on the Evolution of Colour during the Maceration of Fruits in Liquor

ISABEL PAZ, ASCENSIÓN FERNÁNDEZ, CARMEN MATÍAS and GABRIEL PINTO

*Department of Industrial Chemical and Environmental Engineering,
School of Industrial Engineering, Technical University of Madrid, Madrid, Spain*

Abstract

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The effect of temperature on the kinetics of pigment extraction during the maceration of different fruits (raspberry, blackberry, and cranberry) into a commercially available hard spirit (orujo, with 42% v/v ethanol) was evaluated. The analytical method used was UV-Vis spectrophotometry. The initial extraction rate showed an Arrhenius-type dependence with apparent energy activation of 28.8, 69.8, and 55.6 kJ/mol, respectively. Furthermore, a study about the evolution of the colour (from colourless to reddish colour appearance) during the soaking process was done by calculating the CIE tristimulus values (X , Y , Z) for illuminant C, until reaching the apparent stabilisation of colour, which occurs after about two to four weeks for the studied temperatures (5, 23, and 40°C). Studies about the evolution of colour in the soaking process of this kind of fruit liquors can lead to a better understanding of this process, and thus to a better control over the mechanisms underlying it.

Keywords: ethanol; spectral method; spirit; anthocyanins; kinetics

A distilled beverage, liquor or spirit, is usually considered as an alcoholic beverage containing ethanol that is produced by distilling ethanol produced by means of fermenting grain, fruit, or vegetables. It contains no added sugar and has at least 20% ethanol by volume.

Liquors with macerated fruits are popular alcoholic beverages in several countries. Nowadays there is an increasing industrial production of these drinks made by soaking different fruits (raspberries, blackberries, cherries, mulberries, strawberries, dry figs, cranberries, and others) in several spirits, where the ethanol softens the fruits and promotes the extraction of several pigments and substances that give to the liquor a characteristic colour, flavour, and smell. Usually a certain amount of sugar and other flavourings such as cinnamon or grains of coffee are added (THÖNGES 1990). Sometimes there is also a distillation from the product of maceration. For example, Kirsh is a well-known clear, colourless brandy traditionally made by double distillation of morello cherries, a dark-coloured cultivar of the sour cherry (*Prunus cerasus*).

The colour evolution during the soaking process of fruits in liquors is of major interest for quality control, since it is related to developed organoleptic properties. The knowledge of changes that pigments of fruits undergo with processing is important with respect to their role in colour quality because the appearance of a food product can greatly influence a consumer's purchasing decision.

Recent papers published in this Journal pointed out the importance of colour analysis of different foods (HRUŠKOVÁ *et al.* 2011) and of the characterization of alcoholic beverages (SÍŘIŠTOVÁ *et al.* 2012; PANKIEWICZ & JAMROZ 2013).

The ways in which the colour changes occur in red wines have been investigated by a number of authors (SOMERS & EVANS 1979; RIBÉREAU-GAYON *et al.* 1983; BAKKER *et al.* 1986; MIRABEL *et al.* 1986;), because of the economic importance and magnitude of production of this product worldwide, and it is well known that the colour originally arises from anthocyanins, the pigments contained in the skin of black grapes.

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Studies about the evolution of colour in the soaking process of fruits into liquors can lead to a better understanding of this process, and thus a better control over the mechanisms underlying it. That question will be of interest for improving the industrial control of a process which, until today, has been characterised by skilled craftsmanship, since extracting the liquor involves a certain “art” (THÖNGES 1990), based on experience rather than on precisely measured amounts of component properties. NEGUERUELA and ECHÁVARRI (1992) reported a study on the evolution of colour during the soaking process of sloe berries in several liquors, with different amounts of fruits, in order to produce a liquor known as pacharán, which is very popular in Spain (it is also known as patxarana in Basque, one of the official languages in Spain).

Recently, LIU *et al.* (2007) reported an interesting experimental study about the feasibility of the use of visible spectroscopy to assess soluble solids content in other hard spirits (rice wines).

The main objectives of this work were (i) to study experimentally the influence of temperature on the kinetics of pigment extraction during the maceration of three kinds of fruits, i.e. raspberry (*Rubus idaeus*), blackberry (*Rubus caesius*), and cranberry (*Vaccinium corymbosum*), into liquor, and (ii) to gain insight into the colour evolution of the corresponding soaking processes.

As pointed out by CHALERMCHAT *et al.* (2004), the rate of mass transfer during extraction is of interest for the process design.

Experimental studies on the evolution of the visible absorption spectrum during the soaking processes with different temperatures (from 5°C to 40°C) were done. Thus the effect of temperature on the kinetics of pigment extraction during the maceration of these fruits into orujo can be studied. Orujo is a typical colourless Spanish pomace brandy. It is a liquor made from the distillation of marc (the solid remains left after pressing of the grapes). It is composed mainly of a hydroalcoholic solution with an ethanol content over 50% (v/v). In order to simplify the study, other ingredients such as sugar and occasionally tea, cinnamon or grains of coffee used in fruit liquors were not considered.

Dark red colour in these kinds of fruits arises from pigments called anthocyanins (KUHNAU 1976; MAZZA & MINIATI 1993). Anthocyanins (Greek: anthos, flower; kyanos, blue) is a family of phenolic phytochemicals that give many flowers, fruits and leaves colours from orange to blue (EIDONWE *et al.* 2011).

Anthocyanins consist of sugar molecules bound to a benzopyrylium salt (called anthocyanidin), and they are members of the flavonoid family of natural products (TANAKA *et al.* 2008). More details about anthocyanins were provided by CURTRIGHT *et al.* (1994, 1996).

This paper reports further developments in previously reported investigations of the feasibility of visible spectroscopy in the analysis of foods, for example the industrial control of the filtration in the beer manufacturing process (LARENA *et al.* 1989) and the influence of temperature on the kinetics of pigment extractions and on the evolution of colour during the maceration of cherries into a hard spirit (PAZ & PINTO 2002; PINTO & PAZ 2004).

MATERIAL AND METHODS

Apparatus. The analytical method used was UV-Vis absorption spectrophotometry. Visible absorption spectra (400–800 nm) of pigment solutions prepared from the maceration of fruits in the liquor were recorded on a UV-260 Shimadzu spectrophotometer (Shimadzu, Munich, Germany) with a 1-cm path length quartz cell.

Reagents and chemicals. Fruits (raspberries, blackberries and cranberries) were picked from Redipueñas (a village of León, Spain). A commercial Ponte Ulla hard spirit (orujo) produced by Ruavieja S.A. (Santiago de Compostela, Galicia, Spain), with 42% ethanol (v/v), was used for the maceration of fruits.

General extraction procedure. 25.0 g of fruits were analysed for each run. Samples for the experiment were carefully selected in terms of skin and colour homogeneity. Samples selected for each run were immersed in a beaker containing 50.0 ml of the colourless liquor, and preheated/cooled to the required temperature. The range of the temperatures tested was 5, 23, and 40°C. For the temperature higher than room temperature, the experiments were performed in a thermostatic bath and for the lowest temperature (5°C) the experiment was performed in a refrigerator. The solutions were kept in the dark for four months.

After selected times liquors were stirred to homogenise the solutions; a sample of 5 ml of each beaker was removed for measuring the visible spectrum and, after the measurement, returned to the recipient for avoiding a dilution effect. The reference cell used was the hard spirit without fruits. Before measuring the visible spectra, each sample was centrifuged in order to avoid the presence of particles suspended in the solution that cause scattering.

RESULTS AND DISCUSSION

The values of the optical absorption spectra of samples showed a clearly defined peak centred on ~525 nm for raspberry and blackberry liquors and on ~537 nm for cranberry liquors. This band was attributed to be due to the presence of anthocyanin pigments (CURTRIGHT *et al.* 1994; EDIONWE *et al.* 2011). As it is well known, these cases consist of more than one anthocyanin (GARBER *et al.* 2013).

For improving the quantification of the absorbance band, the three-point correction was carried out: two reference wavelengths were chosen on either side of the analytical wavelength and the background absorbance at the analytical wavelength was estimated by linear interpolation, as pointed out in a previous work (PAZ & PINTO 2002).

It was observed that for all temperatures there is initially an increase of absorbance in the band with the maceration time until reaching a maximum that increases with temperature, followed by a slow decrease. SKREDE *et al.* (2000) reported recently that anthocyanins as well as other polyphenolics are readily oxidised because of their antioxidant properties and, thus, susceptible to degradative reactions during various processing unit operations. The increase of maximum reached absorbance value with the increase of the maceration temperature could be due to an increase in the solubility of anthocyanins, given the fact that in such mass transfer the flux is strongly dependent on the driving force, i.e. on the difference between the maximum possible concentration in the phase (solubility) and the concentration (McCABE *et al.* 1985) at that moment. Figure 1 shows the variation of the absorption band for the temperature of 23°C taken as an example for the three kinds of liquors.

As it is well known, the absorbance of an absorbing dye solution is governed by the Beer-Lambert law (JOSHI 2000), which establishes the proportionality between absorbance and concentration for a given optical path length.

The first derivative of the values of absorbance vs. time for different temperatures gives the values

Table 1. Initial rate of pigment extractions at different temperatures

Temperature (°C)	Rate (absorbance units/h)		
	raspberry	blackberry	cranberry
5	0.0086	0.0006	0.0004
23	0.0171	0.0027	0.0014
40	0.0345	0.0147	0.0059

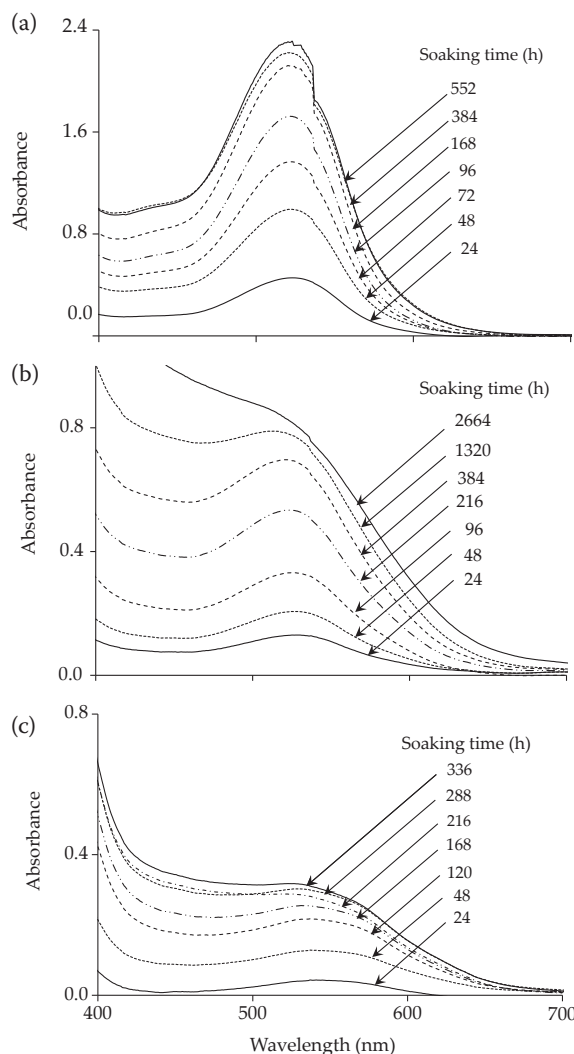


Figure 1. Visible absorption spectra of liquors at 23°C for different times of maceration: (a) raspberry liquor, (b) blackberry liquor, and (c) cranberry liquor

of the initial rate of extraction shown in Table 1. As expected, the extraction rate increased with temperature due to the fact that, generally, the mass transfer coefficient increases with temperature.

Figure 2 documents Arrhenius plots of the initial pigment extraction rates. As shown in this figure, the \ln (initial extraction rate) vs. the inverse of absolute temperature data can be represented by straight lines, with correlation coefficients R higher than -0.996 for all cases, and the values of R^2 0.997, 0.997 and 0.992, respectively, according to Eq. (1) for raspberry, Eq. (2) for blackberry, and Eq. (3) for cranberry, as follows:

$$y = 7.62 - 3.45 \times 10^3 x \quad (1)$$

$$y = 22.50 - 8.38 \times 10^3 x \quad (2)$$

$$y = 16.06 - 6.66 \times 10^3 x \quad (3)$$

where: $y = \ln v_0$; x – proportional to the reciprocal value of the absolute temperature

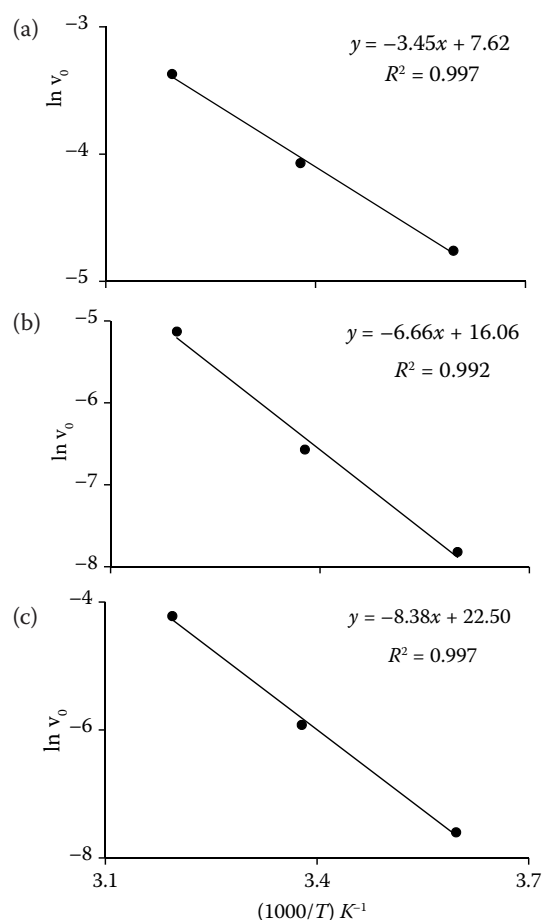


Figure 2. Arrhenius plot of the initial pigment extraction rate ($\ln v_0$) measured by the variation of absorbance of the absorption maximum: (a) raspberry liquor, (b) blackberry liquor, and (c) cranberry liquor

From the slope of this plot the apparent energies of activation (E_a) were calculated, and the obtained values (in kJ/mol) were 28.8, 69.8 and 55.6 for raspberry, blackberry, and cranberry, respectively. In our previous work (PAZ & PINTO 2002) for cherries macerated in similar liquor, the obtained value for the activation energy of the process was 78.2 kJ/mol. Thus, in all cases the values for activation energy are of the same order of magnitude. As it is well known, when the rate is controlled by a chemical reaction, the activation energy is generally higher than that expected for a diffusion-controlled process, which generally exhibits activation energies of only a few kilocalories per mole (YILDIRIM *et al.* 2011). Thus, as expected, the extraction of pigments in the liquor of fruits is a diffusion-controlled process.

The colour of fruit liquors originally arises from the anthocyanins contained in fruits. As observed in Figure 1 for 23°C, the different temperatures allow these molecules to be extracted within the first

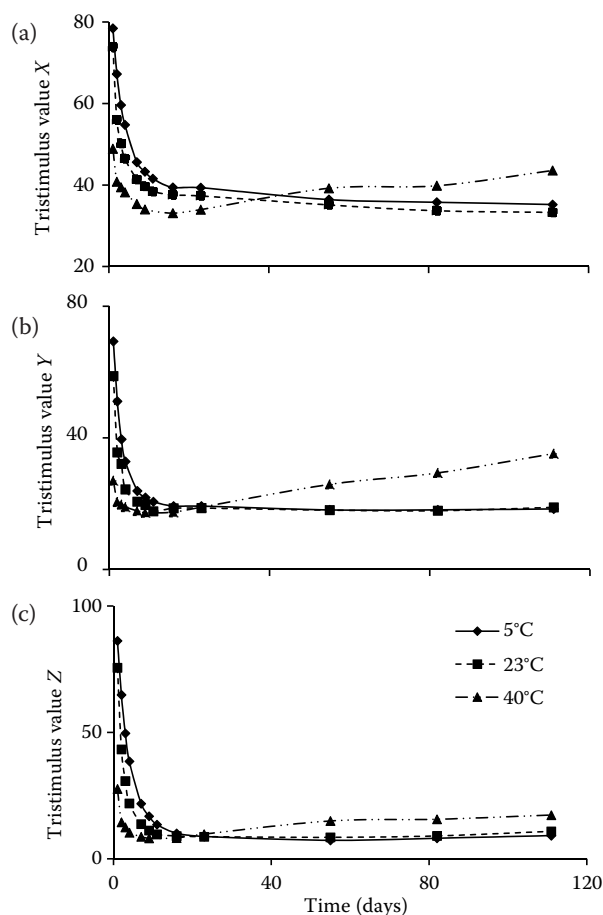


Figure 3. Evolution of the tristimulus coordinates with the time of maceration of raspberry in the liquor: (a) coordinate X, (b) coordinate Y, and (c) coordinate Z

two to four weeks of maceration and, after this time, anthocyanin content decreases due to chemical and biochemical reactions in the complex medium, as pointed out by MIRABEL *et al.* (1999) for wine solutions with wine aging. We consider as a preliminary hypothesis that the compounds obtained by these reactions cause the increase of the absorbance observed at the shoulder at the violet zone of spectra. Nevertheless, a discussion about this phenomenon is beyond the scope of this article.

The ways in which the colour changes occur and copigmentation phenomena have been studied by a number of authors for wine aging (TIMBERLAKE & BRIDLE 1976, 1977; MINIATI *et al.* 1992).

In order to quantify the evolution of colour with the time, for each studied temperature, the tristimulus coordinates for illuminant C were calculated, following the method proposed for wines and explained in previous works (PAZ & PINTO 2002; PINTO & PAZ 2004), according to the equations:

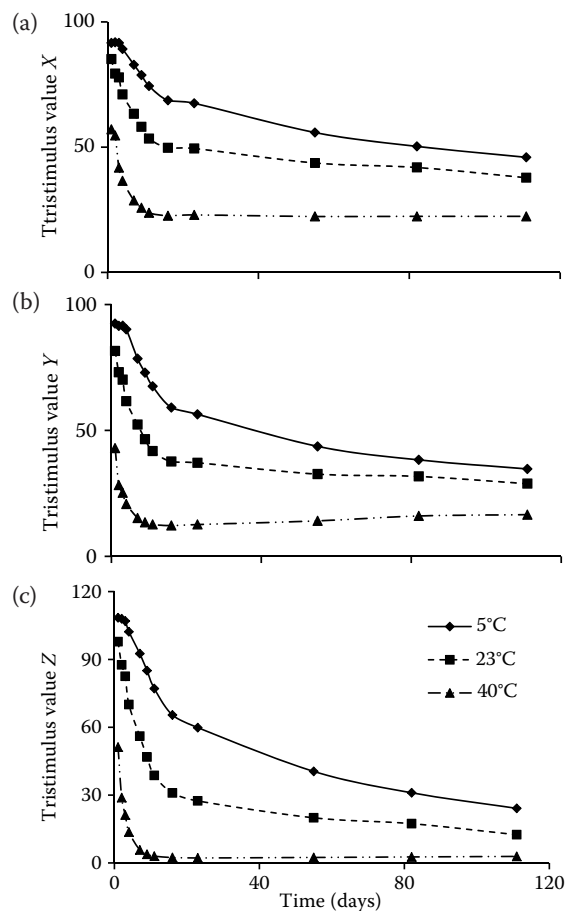


Figure 4. Evolution of the tristimulus coordinates with the time of maceration of blackberry in the liquor: (a) coordinate X, (b) coordinate Y, and (c) coordinate Z

$$X = 0.42T_{625} + 0.35T_{550} + 0.21T_{445} \quad (4)$$

$$Y = 0.20T_{625} + 0.63T_{550} + 0.17T_{495} \quad (5)$$

$$Z = 0.24T_{495} + 0.94T_{445} \quad (6)$$

where: T_{625} , T_{550} , T_{495} , T_{445} – transmittances of samples at 625, 550, 495 and 445 nm, respectively, through a sample of 1.0 cm path length

Figures 3–5 show the variation of the tristimulus coordinates with the maceration time for the different temperatures. It can be observed that initially there is a decrease in all tristimulus coordinates at a velocity that increases with temperature. After these coordinates have reached a minimum that decreases with the increasing temperature, there is a slow increase for all cases, until the apparent stabilization of colour has been reached. All this, obviously, is related to changes in the spectra analysed before.

CONCLUSIONS

We conclude that UV-Vis spectrophotometry is a good method for studying the kinetics of antho-

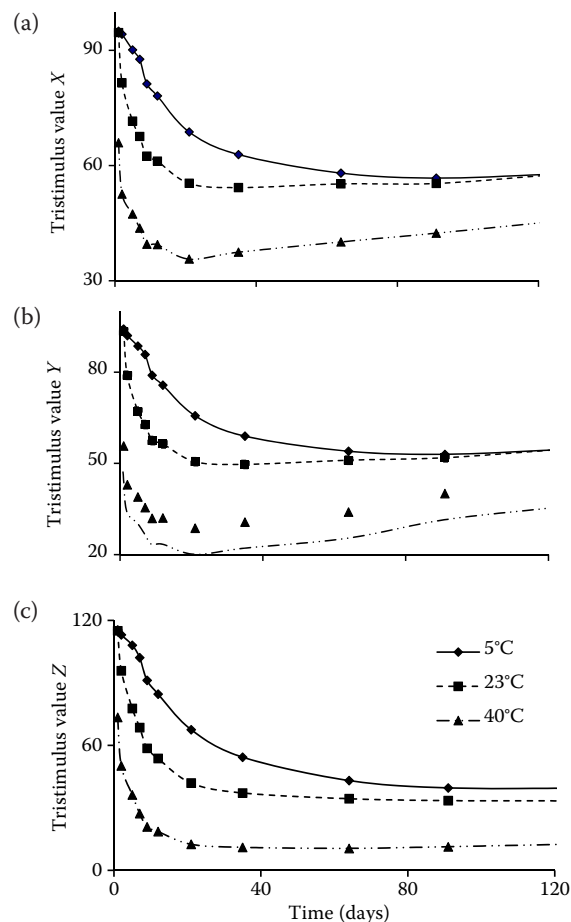


Figure 5. Evolution of the tristimulus coordinates with the time of maceration of cranberry in the liquor: (a) coordinate X, (b) coordinate Y, and (c) coordinate Z

cyanin pigment extraction during the maceration of different fruits in liquor. For the range of the studied temperatures (from 5°C to 40°C) this process has an apparent energy activation of 28.8 kJ/mol for raspberry, 69.8 kJ/mol for blackberry, and 55.6 kJ/mol for cranberry. All these values of activation energy were calculated through the Arrhenius equation with an excellent precision. The apparent stabilisation of colour for the liquor takes place in practice in a few weeks, as it was assessed by means of the determination of the tristimulus values X, Y, and Z.

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Corresponding author:

Prof Dr GABRIEL PINTO, Universidad Politécnica de Madrid, Departamento de Ingeniería Química Industrial y del Medio Ambiente, E.T.S.I. Industriales, José Gutiérrez Abascal 2, 28006 Madrid, Spain; E-mail: gabriel.pinto@upm.es
