Port wine spectral monitoring

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Organoleptic properties

Port wine is a soft wine with varieties for different occasions ("soft wine" is a term used in Portugal to distinguish Port wine from table wine). Port's organoleptic properties are well appreciated throughout the world. There are categories of Port in both white and red wines.[1] Some varieties can be sweeter than others and the way that they are served is also important (chilled or at ambient temperature, depending on the occasion).

Quality evaluation is made in several ways: chemical analysis, human evaluation (by the "Câmara de Provadores", specialists who evaluate the wine's quality using human sensory organs like eyes, nose and tongue) and recently electronic methods have also been used (see Figure 1).

Spectral classification of the various types of wine has been used for about ten years, by measuring the transmission spectra of samples in the laboratory of the Port Wine Institute. Our Group also made a contribution in the past to create the Portuguese Standard[2] for Port Wine Classification in terms of colour.

The main problem is that the wine passes through a long production process, which is carried out by traditional methods that do not yield, during production and aging, any precise information to the producer.

Colour, aroma and taste properties (that are typical in a Port) are created by a certain combination of macromolecules diluted in the wine. These molecules can be in a too low or excess concentration, and the way to control them is to perform measurements during production. This allows the producer to make changes that improve quality.

At the beginning of the production, the grapes are crushed and fermentation is started. These actions can introduce some bacteria and yeast to the wine, and the wine can become turbid due to the presence of these substances. The way to overcome the problem is to filter the product with rare earths. Producers introduced the filtration process a long time ago, and they can visualise its effectiveness with the use of turbidimeters.

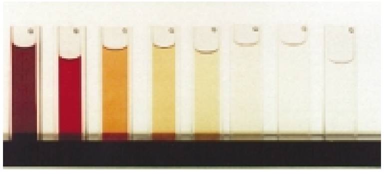


Figure 1. Human sensing and different colours of Port wine.

Turbidity is by convention measured at a single wavelength (with a narrow wavelength band), and the scattered light is only measured at 0º and 90º. This provides only limited information, but no other method is presently available or accepted.

From our knowledge of the state-of-the-art and international standards for measurements of colour and turbidity, we decided to try to push the methods to the limit, hoping to acquire more information than results by conventional methods can provide.

By making use of recent developments in optical technology, we can obviously bring the measurements to the industrial location. Also, using Arizona Test Dust (ISO 12103) it is possible to create a calibration procedure for turbidity measurements.

At the beginning of our research, we tested the scattering properties of Port wine samples with three lasers, at different wavelengths (Blue: λ = 441.6 nm, Green: λ = 514.5 nm and Red: λ = 632.8 nm). They scatter radiation (for the three wavelengths) in every direction but the preferred directions are 0º and 90º (as in conventional turbidimeters).

By using a white light source and a portable spectrometer, we measured spectra of angular scattered radiation for colour and turbidity evaluation. By the addition of some specially-designed mechanical support, we could integrate the measurements into the transfer lines of the wine producing process, to verify and control the effectiveness of the production process.

Colour evaluation

Because of the great variety of colour in Port wine, it was necessary to create a Portuguese Standard in order to classify the different Ports. This Standard[2] assumes the CIE 69 procedure for colour evaluation through spectral measurements. The Agricultural Ministry has also arranged Port wine in different colour classes.[3–5] It should be emphasised that the final wine colour has a close correlation with the region of origin and the production methods used to create it.

To measure colour coordinates according to the CIE method, we must measure the sample's transmittance spectrum:

$$Trans_{\lambda}(\%) = 100 \times \frac{I(0)_{\lambda}^{\text{sample}}}{I(0)_{\lambda}^{\text{distilled water}}} \qquad (1)$$

where distilled water is our reference and the resultant spectrum is represented in percentage.

Colour coordinates are evaluated from a transmittance spectrum.[6] Although there are a large variety of coordinate systems of colour, it is easy to convert from one to another. We used the CIE Lab system.[7]

Turbidity

Some more specialised consumers consider buying only the most limpid (clear) wines. If the wine shows some cloudiness, or contains some particle deposition at the bottom of the bottle, the consumer will lose interest in its purchase.

Technically speaking we use the term turbidity to qualify any liquid sample in terms of clarity. Some people consider turbidity a science, and some companies have developed instrumentation to evaluate this parameter in fluid samples.

Recently a new concept was introduced to distinguish monochromatic turbidity data from spectral data—spectronephelometry,[8] and its full potential is still under examination.

Turbidity is usually defined by τ:

$$\tau = N_s \langle I_{scat} \rangle / (I_0 - N_e \times \langle I_{ext} \rangle) \qquad (2)$$

where I_0 is the intensity of the incident beam, $<I_{scat}>$ the mean intensity of scattering, $<I_{ext}>$ the intensity of extinction, N_s the number of particles contributing to scattering, and N_e the number of particles contributing to extinction.

For practical purpose, an operational turbidity parameter is considered as the ratio:

$$Turb(\theta)_\lambda = \tau_{\theta,\lambda} = \frac{I(\theta)_\lambda}{I(0)_\lambda} \qquad (3)$$

where $I(\theta)_\lambda$ is the wavelength λ radiation flux collected at angle θ relative to the illumination direction (after sample scattering and attenuation by absorption), and $I(0)_\lambda$ is the wavelength λ of the radiation flux collected at an angle $\theta = 0$ (illumination line of sight). With our equipment and measurement settings we used a spectral bandwidth of the order of 5 nm and a collecting aperture smaller than 5°. For turbidity evaluation, we performed measurements at 0°, 30°, 60° and 90° to get an equal-spaced range within the forward scattered radiation. This multi-angle and multi-wavelength measurements are considered as spectronephelometric measurements.

For Port wine, turbidity covers a broad band of values: *Retinto* (the darkest type) 11.3 NTU (Normalised Turbidity Units) and 0.45 mm filtered *Retinto* 2.5 NTU; *Branco Palha* (the clearest one) 6.4 NTU and 0.45 mm filtered *Branco Palha* 2.5 NTU. Turbidity is combined with a strong absorption that is responsible for low signal levels. Although particle sizes, due to Port wine filtration, are of the order of 0.6 mm or less, it is still possible to detect particle signatures in the turbidity spectra.

From a series of studies of Port wine samples, the angles of measurement were selected by dividing the forward scattering quadrant into equal parts (since scattering behaviour was homogeneous), so that we could access a great deal of information.

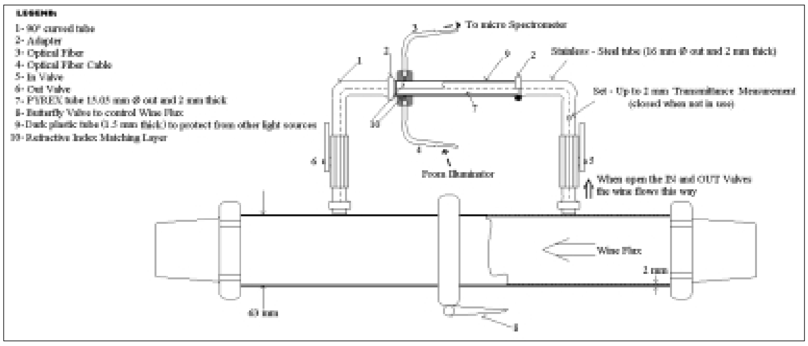


Figure 2. Field sensor device (not to scale).

Figure 3. Turbidity and transmittance measurement support.

Sensor design

We have designed and developed a sensing device capable of performing spectronephelometric measurements with the objective of determining colour and turbidity. It was our intention to implement the measurements in the wine transfer process as well. We have developed a mechanical bypass (to introduce into the transfer line), which is capable of both conducting the wine flow and at the same time support the measurements. This has resulted in the field sensor that is represented schematically in Figure 2.

This mechanical support allows the wine to pass through with a part of its flux passing in the upper bypass. In the central part of the bypass a Pyrex tube is placed to serve as a sensing window. This tube is completely covered with a black rubber tube to ensure that no external light enters the sensing area, see Figure 3. A plastic support with some angular holes was placed around the Pyrex tube to permit the optical fibre cables to illuminate the wine sample and to detect the scattered radiation. The larger tube has a diameter similar to that used by producers to guarantee the flux stability and pressure maintenance.

Calibration of the equipment

After the integration of the equipment and software we performed a calibration on the device in terms of colour and turbidity evaluation. For standard transmittance (and colour coordinate) evaluation, we used a spectrophotometer (Cary 5E from Varian). The spectra had the same form in both cases, but it was observed that there was a y-axis displacement. To correct for this offset we developed a software routine to convert the sample's optical path of 15.05 mm (on the field sensor) to 2 mm (as in Cary 5E cells). This compensation considers the difference of absorption. After this correction was made, spectra from both methods are coincident and the CIE method for colour coordinate evaluation can be performed without significant error.

In terms of turbidity we performed a calibration using Arizona Test Dust in a measurement cycle. This cycle consisted of measuring different wine samples that had been filtered previously with a 0.45 µm membrane, followed by an addition of a known concentration of the dust and finally after a sec-

Figure 4. Closed circuit for calibration of sensor.

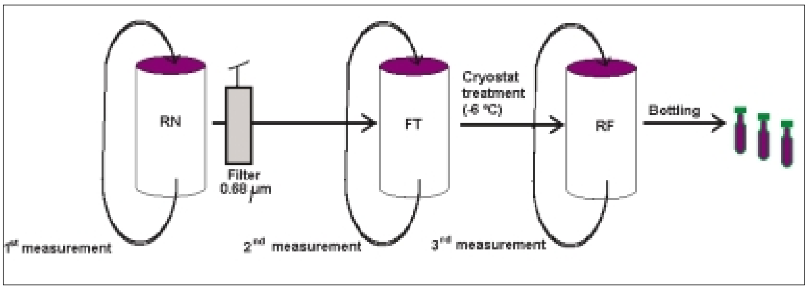


Figure 5. Schematic representation of the measurements at Sandeman.

ond filtration and measurement. We also made a simulation with a wine sample flowing in a closed circuit, see Figure 4, to verify the differences between static and dynamic measurements. They were minimal.

Field results and conclusions

Making use of the opportunity created by Sandeman (a well-known Port wine producer) to measure, and by adjusting our measurement timing to their production process, we could control the most important steps of a Ruby wine creation.

The first stage is after the blending and creation of a "*Lote*". This is called "Reunido" (RN), and is stored in larger containers (1.5×10^6 L).

The wine is then filtered with fossilised earths (perliters), and a "Filtrado" (FT) is generated. A further step in treatment follows with cryogenic filtering (–6°C), to generate wine at the "Refrigerado" (RF) stage. After this last stage, the wine is bottled for selling.

The wine was measured in each of the stages, by siphoning it from the large containers (0.5 to 1.5×10^6 L) and pumping it back again to the container after it has passed through the sensor head. A schematic of the measurement process is shown in Figure 5.

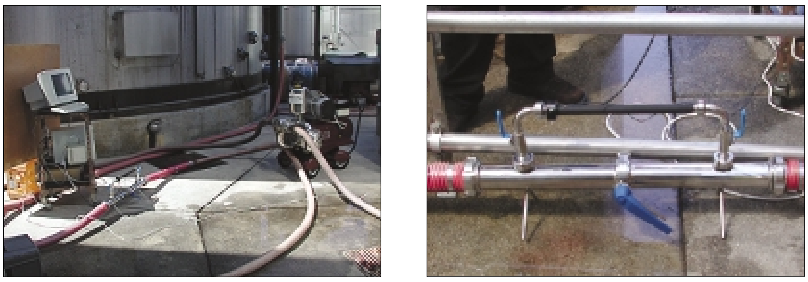


Figure 6. *In situ* measurements at Sandeman cellars.

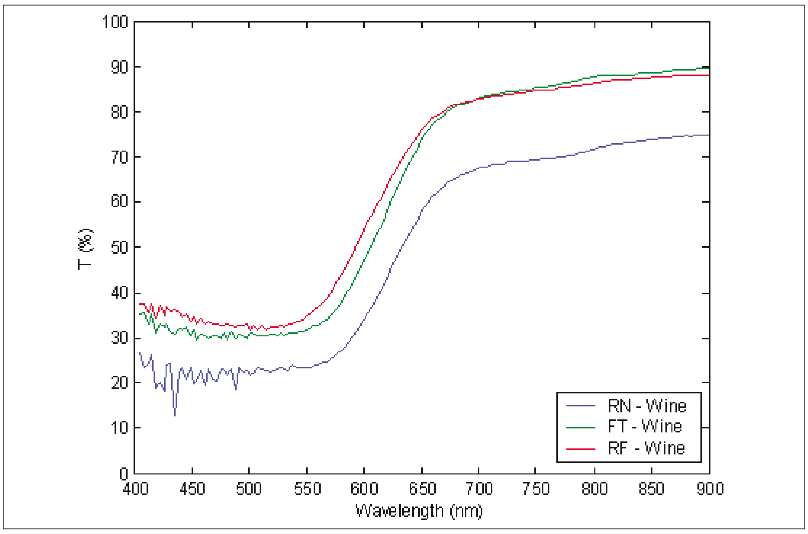


Figure 7. Transmittance evolution of the wine sample through the three stages of production.

Some special points relating to the measurements conditions were:

- In-line pressure 1–2 atm
- Refractive index matching at the sensor head optical fibre tips
- Data clipping
- Data from averaging of ten measurements
- Colour determination by the CIE Lab model
- Turbidity parameter = $[I_\theta / I_{\theta=0}]$.

We can see in Figure 6 a general view and a detail of the sensor head during the course of colour and turbidity *in situ*, in-line and real-time measurements.

As described above, for each stage of the wine, 10 measurements were acquired to perform a statistical analysis. The evolution of the mean results is presented next.

Transmittance and colour evolution

It is obvious from Figure 7 that the wine becomes more transparent as it passes from RN through FT and RF. The RF case is a little more transparent then the FT case (for wavelengths below 700 nm), although the difference is small, showing that the final stage of the wine is the better one.

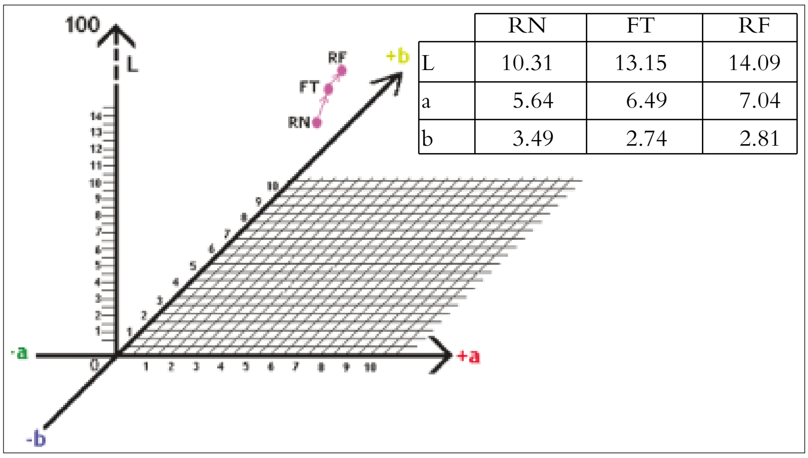
We can see in Figure 8, that from the first to the second stage, the wine has a significant variation in the colour coordinates **a** and **b**. As the coordinate **a** rises, the wine becomes redder, and as **b** diminishes, the wine loses the yellow tone. The significant rise in **L** makes the wine become clear. This means that the turbidity has diminished, as we shall see from the evolution in turbidity spectra below.

The variation between Filtrado and Refrigerado is small compared with the difference between Reunido and Filtrado. Although it is important to notice that the wine becomes clearer (**L** rises), and redder (**a** increases also). The rise in **b** is insignificant, so the variation in the yellow/blue line is small.

Turbidity evolution

In considering turbidity, we can see an evolution from the first stage to the last (the wine becomes clear—the level of the turbidity signal diminishes) (Figure 9). As in the case of colour variation, the greater difference in turbidity occurs from the first to the second stage. The last stage is very similar to the second in terms of colour and turbidity.

Although it is not presented here, the system can perform measurements



	RN	FT	RF
L	10.31	13.15	14.09
a	5.64	6.49	7.04
b	3.49	2.74	2.81

Figure 8. Colour coordinates evolution through the production process.

on-line, via an Internet server. Other aspects to improve Port wine quality remain in our interest. One of these is organoleptic particle concentration control.

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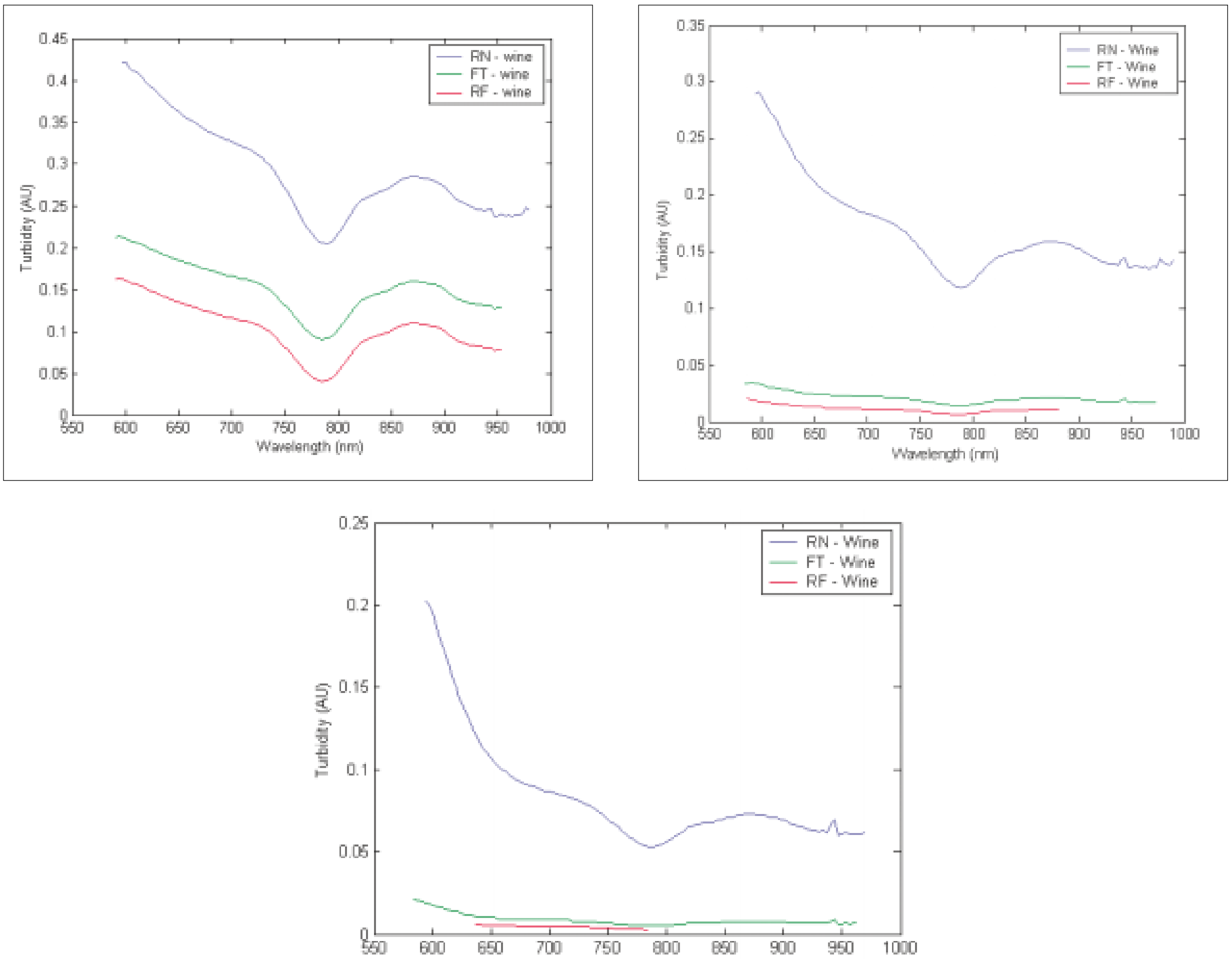

Figure 9. Turbidity evolution through the production process. Measurements made at 30° (top left), 60° (top right) and 90° (bottom).