

FT-NIR Analysis and Temperature Dependence of Different Italian Wine Samples

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Abstract

Food classification represents an important task for quality control and identification of foodstuff product adulteration. At the present time, consumers are gradually looking for quality seals and trust marks on food products, and expected manufacturers and retailers to provide products of high quality. Wine is, from a chemical point of view, a complex mixture of water, alcohol, organic acids, phenolic compounds, sugars, amino acids and various minerals. The Italian wine is one of the most valued commodities from the international wine and food industry. The aim of this paper was to enhance any possible spectral difference, if present, between in box, commercial and homemade wines both red and white, related to sample temperature, by Fourier transform near infrared spectroscopy (FT-NIR). In particular the minimum located at 1660 nm was studied, because it shifted towards lower wavelengths when the sample temperature increases. In the next future it could be interesting to extend the analysis in order to determine whether and how the wine contamination can effectively affect the spectral behavior of food matrices.

Keywords: FT-NIR, wine NIR spectra, wine temperature dependence, Italian wine authentication

1. Introduction

Wine is, from a chemical point of view, a complex mixture of water, alcohol, organic acids, phenolic compounds, sugars, amino acids and various minerals. The Italian wine is one of the most valued commodities from the international wine and food industry. Features which ensure the high quality of this product depend on many factors, such as grape variety and maturity, geographic origin and wine making techniques (Cordella, Moussa, Martel, Sbirrazzuoli, and Lizzani-Cuvelier, 2002). Today, the wine and food industry is more and more interested in quality controls over the entire production chain to avoid any possible adulteration of products (Cordella et al., 2002). Thus, there is a significant attention to improve accurate methods that could be used to prevent adulteration (Reid, O' Donnell, and Downey, 2006) and to classify wine coming from different geographical areas (Fischer, Roth, and Christmann, 1999). Several studies were carried out about wine components and their properties. For example, Garofolo, Giannini, Favale, and Savino (2006) determined the phenolic content and free radical scavenging activity (using the DPPH method) from grapes and wines of seven different clones of the *Cesanese d'Affile* cultivar, an autochthonous high-quality vine. The specific antiradical activity, expressed as the molar ratio between antioxidant compounds and DPPH, was correlated to quality rather than amount of total polyphenols. In particular, it is interesting to notice how the major antiradical activity in *Cesanese* wines after short ageing enhances their natural aptitude to an early consumption, with a strict relationship between sensorial and healthy characteristics (Garofolo et al., 2006). Scientific research has demonstrated that the polyphenols present in grapes and in wines alter cellular metabolism and signaling, which is consistent mechanistically with reducing arterial disease (German and Walzem, 2000). One of the most powerful antioxidants among polyphenols is resveratrol. It has shown interesting properties related to biomedical limitation of oxidative stress, to inhibition of the cancer promotion and propagation.

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Moreover resveratrol has a cardioprotective action due to the inhibition of oxidation of low-density lipoprotein (LDL) and preventive effects of Alzheimer's disease and of senile dementia (Fabris, Momo, Ravagnan, and Stevanato, 2008). Among the most important analytical techniques used to verify the authenticity of high value wine and food products, Near Infrared (NIR) spectroscopy is emerging thanks to the excellent results achieved, in agreement with those obtained using primary techniques. The infrared spectrophotometry is used to determine the physico-chemical properties of agricultural and food matrixes. Specifically, NIR spectrophotometry, ranging from 780 nm to 2500 nm, has the considerable advantage of being a rapid, non-invasive and non-destructive technique, and also it requires no sample preparation. In fact the time of spectrum acquisition is of a few minutes; in addition the NIR radiation has a low energy content, therefore the sample can be reused after the analysis. Cozzolino et al. (2004) concluded that the NIR spectrophotometry could be used as rapid alternative method for the prediction of the concentration of phenolic compounds in red wine fermentations. NIR spectrophotometry was used to simultaneously predict the concentrations of malvidin-3-glucoside (M3G), pigmented polymers (PP) and tannins (T) in red wine. Fernández-Navales, López, Sánchez, Morales, and González-Caballero (2009) assessed the feasibility of the NIR spectroscopy for predicting reducing sugar content during grape ripening, winemaking, and aging. Caprara and Pezzi (2010) verified the potential use of NIR technique for the detection of some fungal diseases in grapes conferred in the cellar. The interaction of the NIR radiation with the substance analyzed generates the typical absorption spectrum, in which can be appreciate peaks related to the specific functional groups present in the sample. Appreciable absorption bands in the spectral range of the NIR radiation are due to overtones or vibrational transitions of molecular bonds (i.e. CH, OH) (Osborne, Fearn, and Hindle, 1993).

Wine spectra are comparable to that of aqueous solutions and as occurs in such solutions, there are spectral ranges more resolute alternating with areas difficult to investigate because of saturation signal or excessive noise due to water absorption. Recent studies (Rambla, Garrigues, and de la Guardia, 1997) have pointed out that the behavior of aqueous solutions spectra are dependent on the cuvette optical path length. In fact, the range of wavelengths studied increases if cuvettes with a small optical path length (1-2 mm) are used but, at the same time, the spectral resolution decreases (Yu et al., 2006). In addition, the vibrational intensities and frequency of molecular bonds of the organic molecules in the NIR region depend on temperature. An important study about this topic was carried out by Cozzolino et al. (2007) that investigated the effect of temperature on the visible and NIR wine spectra and on the predictive ability of calibration models for the measurement of wine chemical composition (alcohol, glucose, fructose and pH). The results showed that differences in the spectra around 970 nm and 1400 nm, related to O-H bonding were observed (Cozzolino et al., 2007). Yu et al. (2006) analyzed the behavior of absorption peaks: a) around 1185 nm, relative to O-H stretching second overtone; b) from 1690 to 1750 nm, related to C-H stretching first overtone and c) around 1810 nm, associated to sugar absorption. In this paper the behavior of the absorption spectra in wavelength range from 1600 nm to 1700 nm was investigated in order to enhance if spectral differences between Italian wines both red and white, coming from different geographical areas and characterized by different grape variety and maturity, and wine making techniques are present, when sample temperature increases.

2. Material and Methods

The instrument used in this study was a spectrophotometer FT-NIR Antaris II. The FT-NIR Antaris II analyzer includes an integrating sphere module, a transmission module, and a fiber optic module. This provides tools for analyzing most liquid and solid samples, ranging from films, powders, and tablets to free-flowing liquids, semi-solids, and pastes. In particular, wine is an aqueous solution. For this reason, only the transmission sampling module was considered useful to acquire sample spectra, because the transmission module was designed for quality control testing of solution, raw materials, chemicals, polymers, surfactants, and formulations, and provides quick transmission analysis of liquid samples in standard-size (0.5 mm to 1 cm thick) cuvettes, culture tubes, and card-mounted liquid cells, as well as transmission analysis of transparent solids and films. The 3-position sample holders allowed automatic sample, background, and liquid reference collections, ensuring consistent sampling and repeatable results. In addition, a software-controlled internal heater ensured accurate, repeatable analysis for temperature-sensitive measurements. Six red wines and three white wines, that differ for grape variety and maturity, geographical areas and wine making techniques, were analyzed.

The analyzed wine samples were also classified into:

- Bottled wine samples (2 red wine samples and 1 white wine sample),
- In box wine samples (1 red wine sample and 1 white wine sample)

- Homemade wine samples (3 red wine samples and 1 white wine sample).

The wine spectra are comparable to that of aqueous solutions and presented spectral ranges more resolute alternating with areas difficult to investigate because of saturation signal or excessive noise due to water absorption. However, because the analysis conducted by using high optical path length cuvettes increased the spectral resolution and allowed to achieve a more detailed information in the bands of interest (1185 nm, 1650-1735 nm, 1790 nm), it was considered appropriate to use 8 mm path length cuvettes. All the samples were analyzed only with the transmission module. Each acquisition was carried out with the following set of parameters: 64 scan and 4 cm⁻¹ resolution. In addition, in order to evaluate how temperature influences the sample behavior, the acquisition temperature was also considered. For this reason, in this study all the spectra were collected at different temperatures ranging from 35 °C to 85 °C, at interval of 5 °C. Moreover, before all the measurements, a spectrum of an empty cuvette was acquired and the so obtained spectrum was subtracted from sample spectra in order to remove the background noise. After then, all the raw spectra, were analyzed using data analysis and graphics processing software, i.e. Peakfit and Origin. Peakfit software allowed the deconvolution of each acquired spectrum in Gaussian curves; this process allows us to identify absorbance peaks. Instead Origin was used to plot and compare spectra relative to the different variety of samples.

3. Results

The spectra of commercial, in box and homemade red wine spectra, acquired at T=35°C, are reported in Fig. 1, whereas, in Fig. 2 the absorption spectra of white wine samples, at the same temperature, are shown.

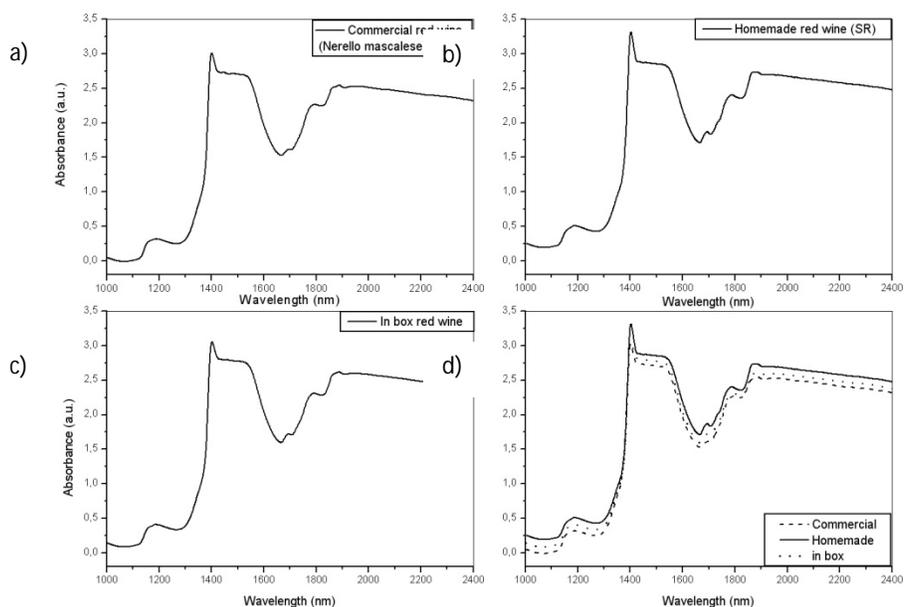


Figure 1: NIR spectra of different red wine samples. a) NIR spectrum of a commercial red wine; b) NIR spectrum of a homemade red wine; c) NIR spectrum of an in box red wine; d) comparison between the three different red wines NIR spectra

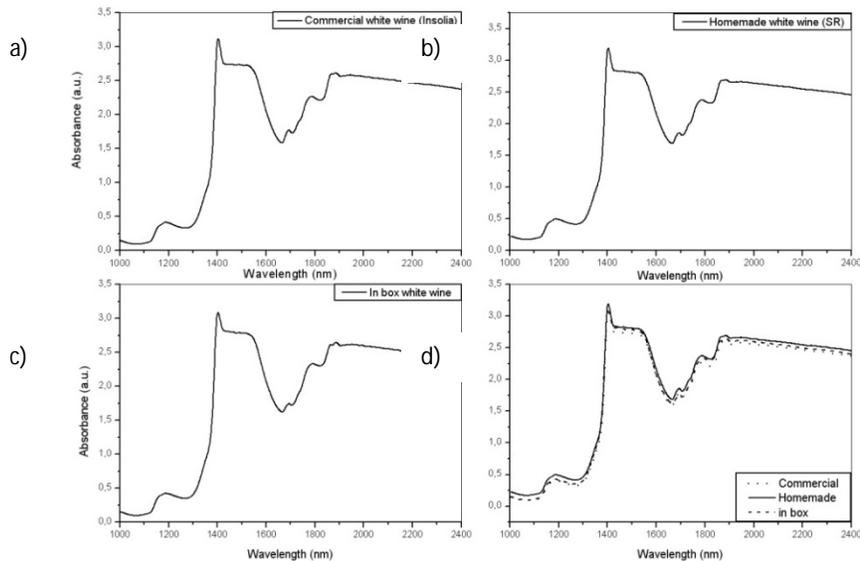


Figure 2: NIR spectra of different white wine samples. a) NIR spectrum of a commercial white wine; b) NIR spectrum of a homemade white wine; c) NIR spectrum of an in box white wine; d) comparison between the three different white wine NIR spectra

In order to study in detail absorption bands, each spectrum has been analyzed by using peakfit software to perform the deconvolution process, to enhance the absorption peaks in the wavelength range 1000 – 2500 nm. In Fig. 3 an example of a homemade red wine spectrum before and after the deconvolution process, is reported.

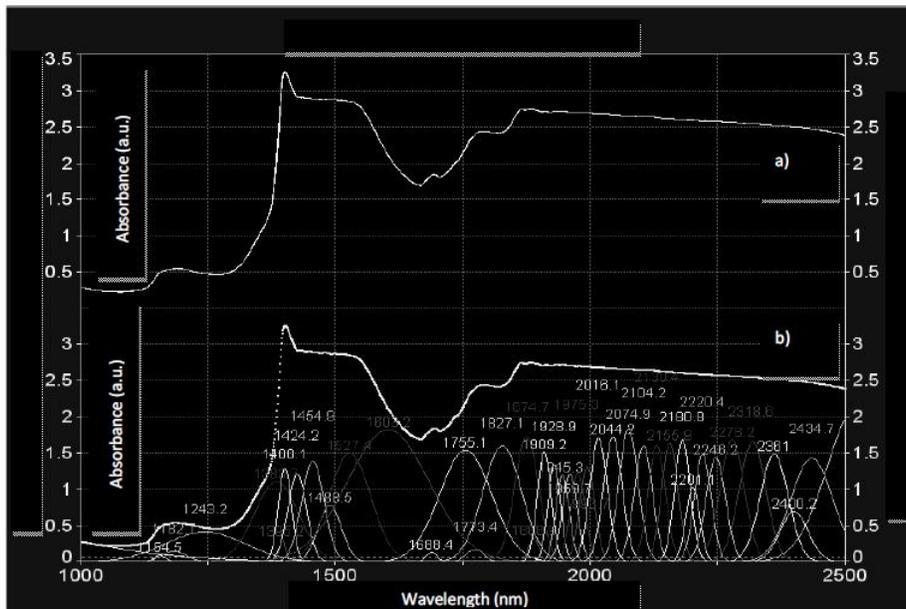


Figure 3: NIR spectrum of a homemade red wine before (A) and after (B) the Deconvolution Process

The wine spectral behavior at different temperatures was also analyzed in order to verify if the sample temperature could modify the spectral trend: in Fig. 4, spectra of a homemade red wine at three different temperatures ($T=40^{\circ}\text{C}$, 60°C , 80°C) are shown, whereas in Fig. 5 the spectra of a homemade white wine acquired at the same temperature values are reported.

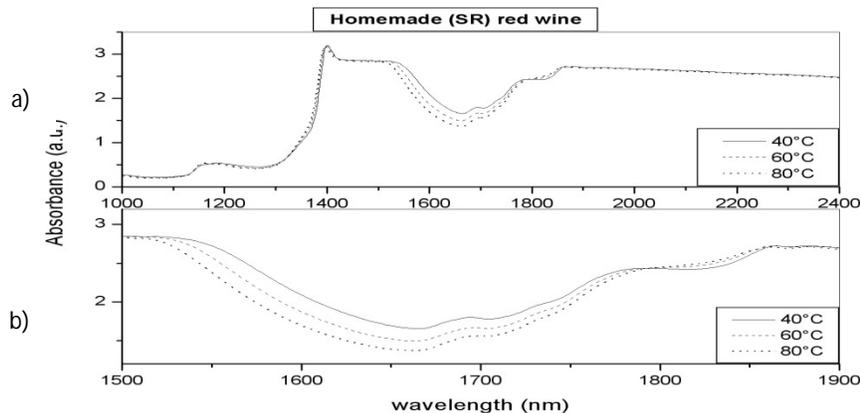


Figure 4: NIR spectra of a homemade red wine sample acquired at three different temperatures ($T=40^{\circ}\text{C}$, 60°C , 80°C). In b) the shift of the 1660 nm minimum towards lower wavelengths when the sample temperature increases was evident

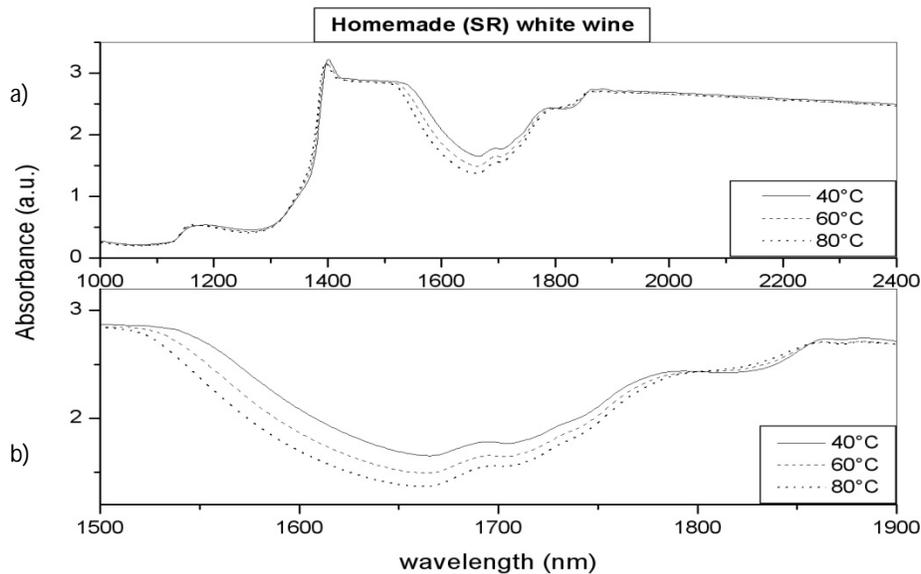


Figure 5: NIR spectra of a homemade white wine sample acquired at three different temperatures ($T=40^{\circ}\text{C}$, 60°C , 80°C). In b) the shift of the 1660 nm minimum towards lower wavelengths when the sample temperature increases was evident

In all the examined wine samples, the minimum placed at 1660 nm shifted towards lower wavelength values, when the acquisition temperature increased. The 1660 nm minimum arises from the intersection between the water and ethanol absorption bands; because the water has a boiling point higher than the ethanol one ($T=100^{\circ}\text{C}$ for water and $T=78,37^{\circ}\text{C}$ for ethanol at atmospheric pressure), the contribution of the ethanol will decrease faster with increasing temperature, causing a shift of the minimum under investigation. In order to investigate the trend of the 1660 nm minimum shift, the wavelength value related to the minimum of absorbance was reported as a function of the acquisition temperature, ranging from 35°C to 85°C . The trends of a homemade, a commercial and an in box red and white wines are showed in Fig. 6 and 7 respectively.

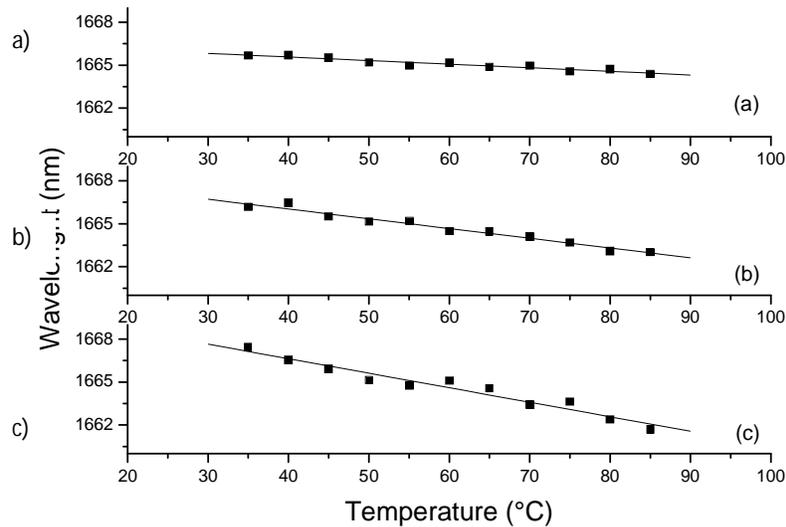


Figure 6: Trend of the minimum at 1660 nm as a function of temperature of an In box (A), a Homemade (B) and a Commercial (C) Red Wine

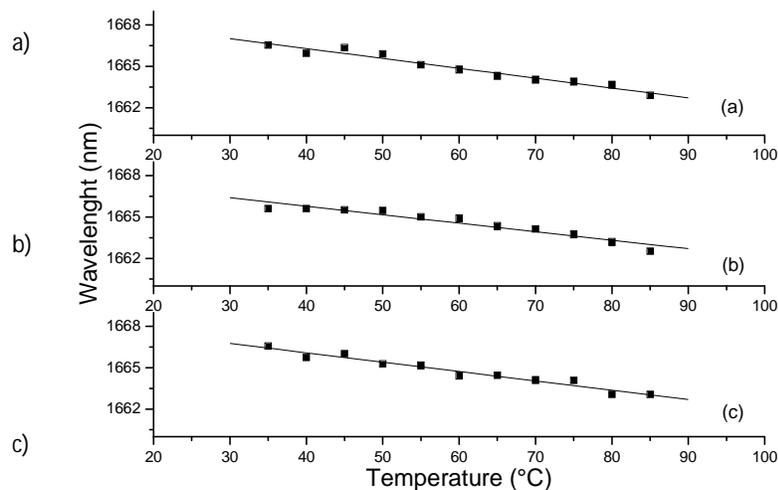


Figure 7: Trends of the minimum at 1660 nm as a function of temperature of an in box (a), a Homemade (b) and a Commercial (c) White wine

In all cases the linear trend of the shift of the 1660 nm minimum was verified and all wine samples were characterized by a correlation coefficient R ranging from 0.9753 to 0.9830.

4. Conclusions

Food classification is an important task for quality control and identification of foodstuff product adulteration. At the present time, consumers are gradually looking for quality seals and trust marks on food products, and expected manufacturers and retailers to provide products of high quality. All these factors have underlined the need for reliable techniques to evaluate the food quality. NIR spectroscopy has proven to be a successful analytical method that does not require pre-treatment of samples and is used for analysis of a variety of food products and beverages. Among the most important analytical techniques used to verify the authenticity of high value products, NIR spectrophotometry is emerging thanks to the excellent results achieved, in agreement with those obtained from primary techniques. The aim of this paper was to enhance any possible spectral difference, if present, between in box, commercial and homemade wines both red and white, when the sample temperature increases.

Moreover the temperature effect on NIR wine spectra was verified and extended to a higher range. The temperature dependence was particularly evident in the range from 1600 nm to 1700 nm: for this reason the minimum located at 1660 nm (at room temperature) has been studied; in fact, it presents a shift towards lower wavelengths when the sample temperature increases, as highlighted in Fig.4 and Fig.5, representing the behavior of a red wine and a white wine NIR spectrum respectively at different temperatures. This minimum is related to the intersection between the water and ethanol absorption bands; it is evident how the different boiling points, at atmospheric pressure, of water and ethanol, caused the shift towards lower wavelengths. All the examined samples presented the same behavior. In particular, in any case, a linear trend was observed characterized by a correlation coefficient R ranging from 0.9753 to 0.9830.

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