NIR Spectroscopy and Wine
Class-modeling for the characterization of Italian red wine

NIRS applied to differentiate wine samples according to the grape variety

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Abstract

Near-infrared spectroscopy (NIRS), combined with multivariate data analysis, was applied in order to distinguish wine samples according to the grape variety. Certified samples belonging to the 'Barbera d'Alba' and 'Dolcetto d'Alba' appellations were analyzed. The class-modeling method SIMCA was used on spectral responses. The results showed that NIR spectroscopy is a technique with significant potential in classifying red wine samples on the basis of the grape variety.

1. Introduction

The wine industry has a clear need for simple, rapid and cost-effective analytical methods for carrying out objective characterizations of oenological products. While the application of NIR spectroscopy to wine products is not new, [1-3], the scope has recently broadened to include qualitative analyses; e.g., to distinguish samples according to the grape variety or the geographical origin [4, 5]. In the present study, the capability of NIR spectroscopy to distinguish two Italian red wines from different grape varieties (Barbera d'Alba and Dolcetto d'Alba) is examined. Such an achievement may be of great interest to both wine protection consortia and consumer associations.

2. Materials and methods

Fifty-nine wine samples were analysed; the wines pertained to the commercial classes 'Barbera d'Alba' and 'Dolcetto d'Alba' and were from the same vintage and from the same production area, in order to limit grape variability due to vintage and geography. The authenticity of the 23 samples of Barbera and the 36 samples of Dolcetto was guaranteed by the DOC (i.e. controlled denomination of origin) status, which certifies their provenance from a defined region around Alba.

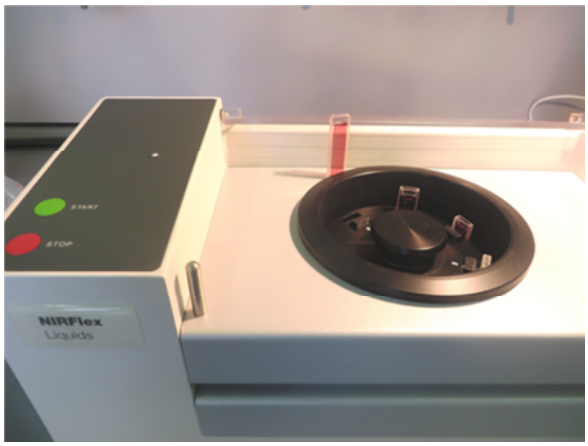

Figure 1: *Wine samples analysis in transmittance mode*

According to the respective DOC regulations, 'Barbera d'Alba' wine is produced entirely from Barbera cultivar, and 'Dolcetto d'Alba' wine is entirely produced from the homonymous grape variety.

NIR measurements were collected in transmittance geometry with an FT near-infrared spectrometer (BUCHI NIRFlex® N-500) over the range of 4000–10,000 cm^{-1} with 4 cm^{-1} resolution (figure 1). Samples were analysed in quartz cells (1-mm pathlength) in a temperature-controlled measurement cell held at 35.0 ± 0.5 °C.

Spectra were pretreated by various operations to optimize model performance. First derivative and standard normal variate (SNV) were applied to spectral data across a reduced wavenumber range of 4000 to 9000 cm^{-1}.

PCA (principal component analysis) was used to graphically visualize the data. SIMCA (soft independent modelling of class analogy) was applied as a class-modelling method [6]. The discriminant power of each variable, i.e., the measure of the contribution of the variable to the mathematical model, was evaluated in order to refine the SIMCA model; from the original 1251 variables, the 95 most discriminating ones were selected and used to build the class models. Approximately 25% of the original samples were used as an external test set, with each class frequency being balanced between the calibration and validation sets.

3. Results and discussion

The raw absorbance spectra for the 59 samples are shown in figure 2. The spectra show main maxima located at c. 6890 cm^{-1} and c. 5155 cm^{-1} related to the O-H second overtone and to the combination of the OH stretching first overtone and the O-H bending of water and ethanol, respectively. The absorption bands at c. 5910 cm^{-1} and c. 5586 cm^{-1} can be attributed to either the first overtone of the $C\text{-}H_3$ stretch, or compounds containing C-H aromatic groups in combation with the first overtone of a C-H stretch vibrational mode. The peaks at c. 4400 cm^{-1} and c.

4338 cm^{-1} are due to C-H combination and O-H stretching overtones [7].

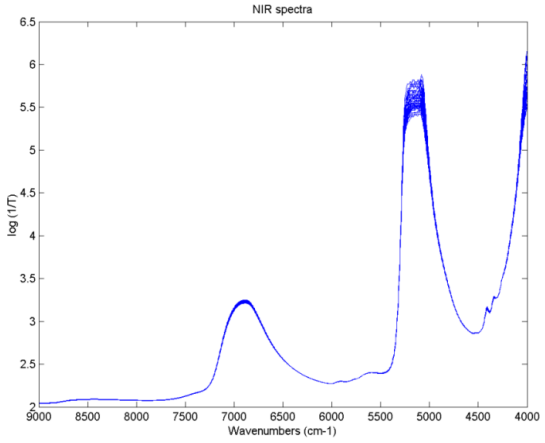

Figure 2: *raw NIR spectra of red wine samples analysed*

In Figure 3, the average spectra of Barbera and Dolcetto wines, pre-treated with SNV and first derivative®, are shown. No significant differences in spectral absorbance values were observed.

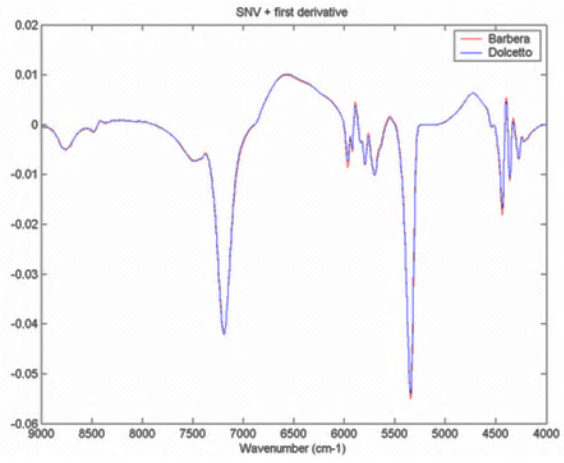

Figure 3: *NIR spectra pretreated with SNV and 1st derivative.*

The samples appeared really similar at first glance; nonetheless the NIR spectra in the 4000–9000 cm^{-1} range contained significant information to differentiate them according to the grape variety. In Figure 4, wine samples belonging to the 'Barbera d'Alba' and 'Dolcetto d'Alba' appellations are clearly clustered and distinguishable in the space defined by the first two PCs.

The following table shows the SIMCA results.

	Training set	Test set
Classification rate (%)	98	96
[1]Mean Sensitivity (%)	100	77
[1]Mean Specificity (%)	93	100
Efficiency (%)	97	88

[1]The Sensitivity of a class model is the proportion of samples belonging to the class accepted by the model. The Specificity of a model is the proportion of samples belonging to other classes rejected by the model of the studied class. The Efficiency of a model is the geometric mean of Sensitivity and Specificity values.

Since the authenticity of the 59 wine samples was certified by the DOC status, all samples were retained in the SIMCA models (i.e., to have 100% sensitivity in the training set).

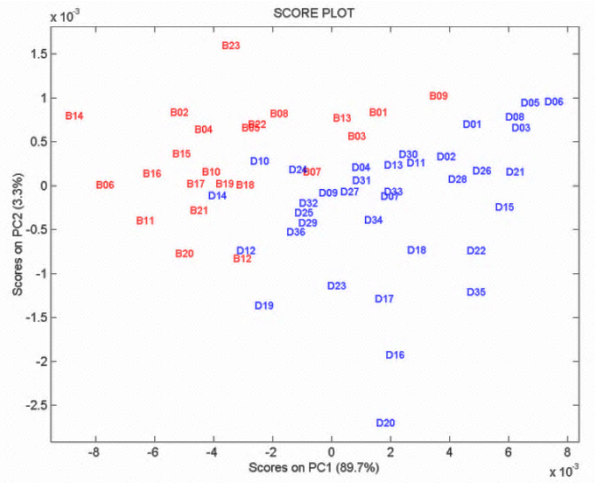

Figure 4: *Score plot on PC1-PC2 obtained by the NIR data. Samples are represented by their class symbol: Bxx (Barbera) and Dxx (Dolcetto).*

4. Conclusions

The SIMCA models exhibited excellent specificity (100%) and good sensitivity (77%) on the external test set, reflecting reliable models for the characterisation of Italian red wine belonging to the 'Barbera d'Alba' and 'Dolcetto d'Alba' appellations. Furthermore, the results confirmed the potential to use NIRS as a rapid and effective alternative to the classical methods used to distinguish red wine samples on the basis of the grape variety.

The composition of wine is influenced by many factors, such as grape varieties, soil composition and climate, harvesting period, technology of production, etc. Some of these factors are correlated to the specific

production area, while others cause variability between wines of the same location. The positive results of the current study should provide a basis by which to expand the sample set to include these additional variables and develop a practical and robust solution.

6. References

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7. Additional resources

Application Note No. 72/2012 Interlaboratory Test for the Determination of Total SO2 in Wine by Distillation and Titration

http://www.BUCHI.com/en/content/sulfur-dioxide-determination-wine