EVALUATION OF GRAPE QUALITY PARAMETERS BY A SIMPLE VIS/NIR SYSTEM

R. Guidetti, R. Beghi, L. Bodria

ABSTRACT. *Visible/near-infrared (Vis/NIR) spectroscopy is a rapid and nondestructive technique requiring minimal sample processing before analysis, and coupled with chemometrics methods it appears to be one of the most convenient and straightforward analytical tools for studying fruit quality and ripeness. Chemometrics is applied to solve both descriptive and predictive problems in the chemical, pharmaceutical, and food sectors. With this aim, an optical, portable, experimental system (Vis/NIR spectrophotometer) for nondestructive and quick prediction of ripening parameters of fresh berries and homogenized samples of grapes in the wavelength range 450-980 nm was built and tested. A total of 156 grape samples, representing vintage years 2005 and 2006 and harvested in the Valtellina viticultural area of Italy, were evaluated by Vis/NIR spectroscopy for ripeness parameters (soluble solids content, titratable acidity, and pH value) and for phenol ripening parameters (anthocyanins and polyphenols content). Accurate and good calibrations to predict ripeness parameters were obtained for both the 2005 and 2006 vintage years. Calibrations for technological ripening and for anthocyanins had good correlation coefficients (r_{CV} >0.90). These models were extensively validated using independent sample sets. Good statistical parameters were obtained for soluble solids content (r > 0.8, SEP < 1.24 ˚Brix) and for titratable acidity (r > 0.8, SEP < 2.00 g tartaric acid L^{-1}), showing the validity of the Vis/NIR spectrometer. Similarly, anthocyanins could be predicted accurately compared with the reference determination. Finally, for qualitative analysis, spectral data on grapes were divided into two groups on the basis of grapes' soluble content and acidity in order to apply a classification analysis (PLS-DA). Good results were obtained with the Vis/NIR device, with 89% of samples correctly classified for soluble content and 83% of samples correctly classified for acidity. Results indicate that the Vis/NIR portable device could be an interesting and rapid tool for assessing grape ripeness directly in the field or upon receiving grapes in the wine industry.*

Keywords. *Grapes, Nondestructive, Ripening, Visible and near-infrared spectroscopy.*

The food sector could be greatly helped by new analytical methods that are accurate, rapid, and integrated into the production process to meet consumer demand and respect limits imposed by international standards (El-Masry et al., 2008; Jha and Matsuoka, 2004).

Grape composition at harvest is one of the most important factors determining the future quality of wine. Measurement of grape characteristics that impact product quality is a requirement for vineyard improvement and for optimum production of wines (Carrara et al., 2008). Inspection of grapes upon arrival at the winery is a critical point in the wine production chain (Elbatawi and Ebaid, 2006). This check determines both the quality of the wine and the viticulturers' fees. This control is usually performed only on small samples that are not always representative of the whole; thus, the importance of this operation is easy to understand, as it determines the economic value of the entire stock.

Traditionally, grape quality evaluation is achieved by a visual and taste assessment of the fruits and evaluation of the total soluble solids (TSS) and acidity (Krstic et al., 2003). According to Cozzolino et al. (2006), these parameters are insufficient as quality indicators, and it is not possible to adequately assess quality by taste alone. Phenolic compounds contribute to the sensory properties of red wine and, in particular, color and mouth-feel. Their concentration in grapes and wines depends on many factors, including grape variety, ripening conditions, viticultural techniques, and winemaking methods (Rodrigriguez-Delgado et al., 2002). Surely, development of an advanced enological analysis must necessarily include application of innovative methods that can become the technology of reference for DOC (controlled denomination of origin) and DOCG (controlled and guaranteed denomination of origin) production support and defense.

The conventional methods for determination of grape quality parameters (soluble solid content, acidity, and phenolic compounds) are time consuming, require preparation of samples, are often expensive, and generally highlight only one or a few aspects of grape quality. Established methods for grape quality assessment are based generally on either colorimetric or chromatography techniques such as HPLC. The Glories method is the one most widely used among viticulturers for analysis of phenolic compounds (Glories, 1979). However, the difficult preparation of samples for this analy-

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sis requires a well-equipped laboratory, as well as waiting 8 or 10 h for results. A limited number of laboratories and lack of quick information mean that wineries must begin the process of winemaking without having such data available, reducing their chances to diversify production and achieve high-quality products.

Therefore, there is a strong need in the modern wine industry for a simple, rapid, and easy-to-use method for objectively evaluating the quality of grapes. Such a tool would enable real-time analysis at the receiving station and allow preliminary decision-making about grapes during consignment by the rapid analysis of various parameters simultaneously.

Chemometrics is applied to solve both descriptive and predictive problems in the chemical, pharmaceutical, and food sectors (Beebe et al., 1998). In descriptive applications, properties of chemical systems are modeled with the intent of learning the underlying relationships and structures of the systems. In predictive applications, properties of chemical systems are modeled in order to predict new samples of interest. The datasets are often very large and highly complex, often involving thousands of variables. In recent years, developments in both chemometrics and instrumentation have resulted in rapid methods for predicting the concentration of specific chemical constituents. In particular, near-infrared (NIR) spectroscopy is a rapid and nondestructive technique requiring minimal sample processing before analysis; coupled with chemometric methods, it appears to be one of the most powerful analytical tools for studying food products. The NIR region of the electromagnetic spectrum lies between the visible and infrared regions and spans the wavelength range between 750 and 2500 nm. This region contains information concerning the relative proportions of C-H, N-H, and O-H bonds, which are the primary structural components of organic molecules (Williams and Norris, 2002). Quantitative NIR measurements are usually based on the correlation between sample compositions, as determined by defined reference methods, and the absorption of light at different wavelengths in the NIR region, measured either by reflectance or by transmission spectroscopy (Cen and He, 2007).

Several authors have reported the use of NIR spectroscopy to measure total soluble solids (TSS) in grapes (e.g., Osborne et al., 1993; Gishen et al., 2000; Gishen and Dambergs, 1998; Dambergs et al., 2003a; Arana et al., 2005; Shenk et al., 1992). Some authors have studied and developed Vis/NIR or NIR nondestructive systems in order to determine technological parameters useful for classifying grapes (Dambergs, et al., 2006; Dambergs et al., 2003b; Gishen and Dambergs, 1998; Herrera et al., 2003; Cabassi et al., 2006; Casiraghi et al., 2006). In particular, Vis/NIR spectroscopy has been used to predict TSS, pH, and total anthocyanins in red grapes since 1999 in the Australian wine industry (Cozzolino et al., 2004; Dambergs et al., 2003a).

The aim of this study is to design, develop, and test a portable optical system (Vis/NIR spectrophotometer) for single sample, nondestructive (when used on fresh berries), and quick prediction of quality parameters of grapes. This system was tested on Nebbiolo grapes, ecotype Chiavennasca, harvested in the Valtellina viticultural area of Italy. For this grape variety, dedicated chemometric models were created.

Materials and Methods

Portable Vis/NIR System

The grape samples were analyzed in the Vis/NIR range (400-1000 nm) using a portable system. In this system, samples were hit by radiation produced by a lighting system, and the reflected component was measured by a spectrophotometer and registered through dedicated software. The system was composed of five elements: a lighting system, a fiber optic probe, a portable spectrophotometer, a PC for data acquisition control, and a battery.

Lighting System

The light source was a 50 W halogen lamp (Decostar Coolblue, Osram, Munich, Germany) with a color temperature of 4500 K and maximum emission at 500 nm. The color temperature of a light source is determined by comparing its chromaticity with that of an ideal black-body radiator. The temperature at which the heated black-body radiator matches the color of the light source is that source's color temperature. The light source was embedded in a metal holder that enabled the lamp to face the optical fiber in a steady way (the fiber is described in the following paragraph). This lamp was chosen because of its maximum emission peak at about 500 nm, useful for maximizing the intensity of radiation in the anthocyanins range of light absorption. A metal holder (fig. 1), which allowed positioning the halogen spotlight at one end and the optical fiber transmitting radiation to the samples at the other end, was specially created. In this way, the lamp was bound up with the optical fiber, thereby avoiding fluctuations in the radiation intensity striking the samples.

Fiber Optic Probe

Light radiation was shone on the fruit sample through a bidirectional fiber optic probe ("step index" type, model FCR-19IR200-2-ME-S1, Avantes, Eerbeek, The Netherlands) (fig. 2). The choice of this optical fiber was based on the need to acquire spectra in diffuse reflectance. Among the fibers available on the market, a model with a large diameter to carry as much light as possible was chosen. It allowed the light radiation produced by the halogen lamp to shine on the sample while simultaneously collecting the radiation coming from the sample and transferring it to the spectrophotometer. The cable was covered entirely with a metal sheath to avoid excessive twisting. A supplementary plastic cap could be placed on the fiber optic probe to touch the sample perfectly while avoiding environmental light interference.

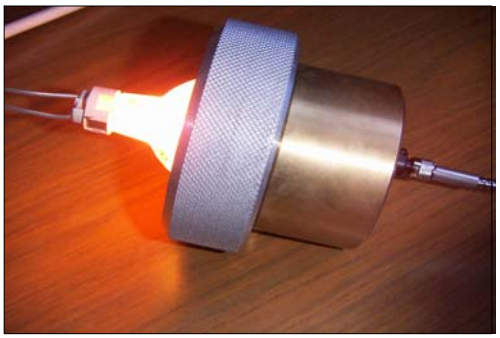

Figure 1. Metal holder for the lamp and the fiber optic probe.

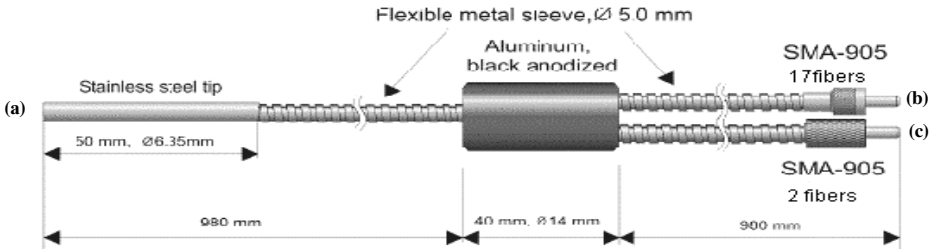

Figure 2. Fiber optic probe: (a) the probe consists of 19 fibers of 200 µm diameter, (b) 17 fibers carry light to the samples, and (c) and two fibers carry radiation back from the sample to the spectrophotometer.

Portable Spectrophotometer, PC, and Battery

The fiber optic probe was connected to a portable spectrophotometer (AvaSpec-2048, Avantes, Eerbeek, The Netherlands). The spectrophotometer was equipped with a diffractive grating for acquisition in the spectral range 450-980 nm and a CCD sensor with a 2048 pixel matrix to record each wavelength signal intensity with a wavelength resolution of 0.3 nm.

The system was controlled by a portable PC with dedicated software for data processing and DAQ for automatic control of the halogen lamp. In this way, samples were illuminated only for the time necessary for acquisition of the spectrum, thereby avoiding wasting energy, for greater autonomy of the system. Thus, it was possible to acquire spectra from more than 300 samples without decreasing the intensity of the radiation produced by the lamp.

The device was powered by a 12 V battery that provided energy for the lamp during acquisitions of Vis/NIR spectra. All components were housed in a backpack to allow transport in the field. The optical cable and PC remained outside the backpack.

Grape Samples

Nebbiolo is one of the most important red grape varieties in Italy. The Valtellina viticultural area, an important wine region of northern Italy, has 1200 ha planted with Nebbiolo, ecotype Chiavennasca. A total of 71 fresh berry samples and 156 homogenized grape samples, of vintage years 2005 and 2006 and harvested in Valtellina, were analyzed. For fresh berries, each sample was obtained by averaging the spectral acquisitions of 20 individual berries. Samples were collected during the last period of ripening just before harvest. Each year, five samplings were carried out from the end of August to the beginning of October. Samples were drawn from 17 different zones, throughout the entire vine area of the valley, in order to represent environmental variability. The samples were analyzed before wineries in the valley received the grapes. Every sample was drawn from different production areas in order to monitor the entire production region of DOC and DOCG wines. Both fresh berries and homogenized samples were analyzed with the portable Vis/NIR system (fig. 3). Every day, one spectrum was recorded without lighting the lamp. The registered signal, obtained only with environmental light, was used as a baseline and subtracted from the spectra of samples. For homogenized material analysis, fresh berries were homogenized for 2 min using a commercial blender (Waring model LB10S) before chemical and spectroscopic analysis.

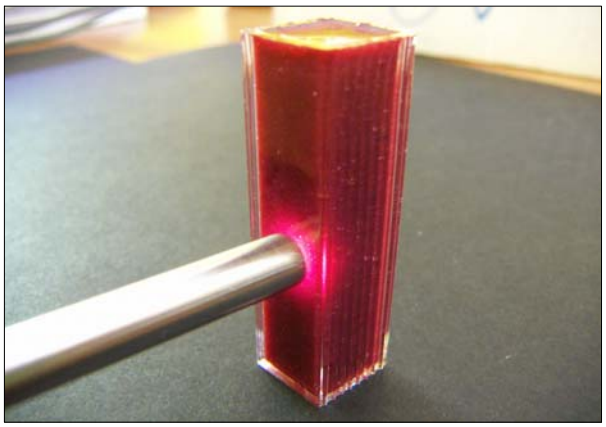

Figure 3. Images of spectral acquisition phases (top) on fresh berries and (bottom) on homogenized samples.

Chemical Analysis

Samples were centrifuged and total soluble solids (TSS) were measured on the supernatant using a digital portable refractometer (model PR-32, Atago, Tokyo, Japan). Grape titratable acidity (g tartaric acid L^{-1}) was measured using an automatic sample titrator (Titromatic 2S-3B, Crison, Barcelona, Spain).

The Glories method (Glories, 1979) was used to estimate the phenolic content of the grapes. According to the method, potential anthocyanins (PA) extracted at pH 1 and extractable anthocyanins (EA) extracted at pH 3.2, both expressed as mg anthocyanins L^{-1}, and total polyphenols (TP) were evaluated. The phenolic compounds quantification was based on the OD measurement at 540 nm and 280 nm for anthocyanins and polyphenols, respectively, using a UV/VIS spectrophotometer (model V530, Jasco Corp., Tokyo, Japan).

DATA PROCESSING

Chemometric analysis was performed using the Unscrambler software package (version 9.6, CAMO ASA, Oslo, Norway). Principal component analysis (PCA) was performed on Vis/NIR spectra to examine sample groupings and identify outliers (Naes et al., 2000).

Different treatments were applied to the Vis/NIR spectra, namely multiplicative scatter correction (MSC) and derivatives, before building the calibration models. The first and second derivatives were performed using Savitzky-Golay transformation and smoothing (15-point and second-order filtering).

All samples available were used for the creation of a chemometric regression model for each parameter considered. The Vis/NIR spectra were correlated with ripeness parameters (TSS and titratable acidity) and with phenolic ripening parameters (anthocyanins and polyphenols content) using the partial least square (PLS) regression algorithm. In PLS regression, an orthogonal basis of latent variables is constructed one by one in such a way that they are oriented along directions of maximal covariance between spectral matrix *X* and response vector *Y*. This method ensures that the latent variables are ordered according to their relevance for predicting the *Y* variable. Interpretation of the relationship between the *X* data and the *Y* data (the regression model) is then simplified, as this relationship is concentrated on the smallest possible number of latent variables. The PLS method performs particularly well when the various *X* variables express common information, i.e., when there is a large amount of correlation, or even colinearity, which is the case for spectral data of intact biological material (Nicolai et al., 2007).

The developed models were tested using both independent fresh and homogenized samples as validation sets. Both validation sets comprised 25% of the total samples.

To evaluate model accuracy, the statistics used were the coefficient of correlation in calibration (r_{cal}), coefficient of correlation in prediction (r_{pred}), root mean square error of calibration (RMSEC), and root mean square error of prediction (RMSEP).

Correlation coefficients (r_{cal} and r_{pred}):

$$r_{cal} \text{ or } r_{pred} = \sqrt{1 - \frac{\sum_{i=1}^{n} (y_i - \hat{y}_i)^2}{\sum_{i=1}^{n} (y_i - \bar{y})^2}} \quad (1)$$

where y_i are the reference values, $\hat{y}_i$ are the values predicted by the PLS model, and $\bar{y}$ is the averaged reference value.

Standard errors of calibration and prediction (RMSEC and RMSEP):

$$\text{RMSEC or RMSEP} = \sqrt{\frac{\sum_{i=1}^{n} (y_i - \hat{y}_i)^2}{n}} \quad (2)$$

where *n* is the number of validated objects, and $\hat{y}_i$ and y_i are the predicted and measured values of the *i*th observation in the calibration or validation set, respectively. This value gives the average uncertainty that can be expected for predictions of future samples. The optimum calibrations were selected based on minimizing the RMSEP. Percent errors (RMSEC% and RMSEP%) were also calculated as: RMSEC (%) = RMSEC / averaged reference values of each parameter.

Qualitative Analysis

Finally, a qualitative analysis was performed. Grape spectral data were divided into two groups on the basis of soluble content and acidity in order to apply a classification analysis using the PLS discriminant analysis (PLS-DA) method. The objective of PLS-DA is to find models that allow the maximum separation among classes of objects (Wold et al., 1998). In this context, PLS-DA accomplishes a rotation of the projection to latent variables focusing on class separation. A matrix of artificial (dummy) variables, assuming a discrete numerical value (zero or one), was used as *Y* data. The *Y* dummy matrix was constructed so that the value of the objects belonging to the class was one, and the value of all other objects was zero (Musumarra et al., 2005; Liu et al., 2007).

RESULTS AND DISCUSSION

Descriptive statistics for ripeness parameters (TSS, titratable acidity, pH) and for phenol ripening parameters (anthocyanins and polyphenols content) are shown in table 1. Wide variability in composition was observed as a result of different sampling times before harvest.

Figure 4 shows Vis/NIR spectra and the effect of preprocessing treatments, necessary for maximizing useful information and reducing spectral noise. Observed changes in the visible region spectra between 500 and 700 nm are due to changes in the amount of pigment during the ripening period. PCA was performed to provide partial visualization of the dataset in a reduced dimension, and three principal components with eigenvalues greater than one, accounting for 99.1% of the total variance, were obtained. The PCA results show no relevant samples grouping (fig. 5).

Table 2 shows the results obtained with fresh berries. Good results were obtained for TSS, not so much in calibration, where the r_{cal} value of 0.72 was low and the RMSEC% value was 5.89%, but rather in prediction, where r_{pred} improved (0.82) and RMSEP% increased slightly (7.31%). The pH regression model was very good, with r_{cal} = 0.84 and a very low RMSEC% (3.05%). In prediction, correlation fell slightly (r_{pred} = 0.81) and RMSEP% increased, reaching 5%.

Table 1. Descriptive statistics for ripeness parameters (TSS, titratable acidity, pH) and for phenol ripening parameters: potential (PA) and extractable (EA) anthocyanins and polyphenols content (TP).[a]

Parameter	No. of Samples	Mean	SD	Min.	Max.
TSS (°Brix)	134	20.1	2.4	11.7	24.0
Titratable acidity (g tart. acid dm^{-3})	134	11.3	3.7	5.8	28.8
pH	136	3.0	0.2	2.6	3.4
PA (mg dm^{-3})	137	709.1	271.7	148.1	1350.0
EA (mg dm^{-3})	135	407.1	154.6	94.5	823.7
TP (OD 280 nm)	127	36.5	6.8	18.1	57.4

[a] SD = standard deviation, Min. = minimum, and Max. = maximum.

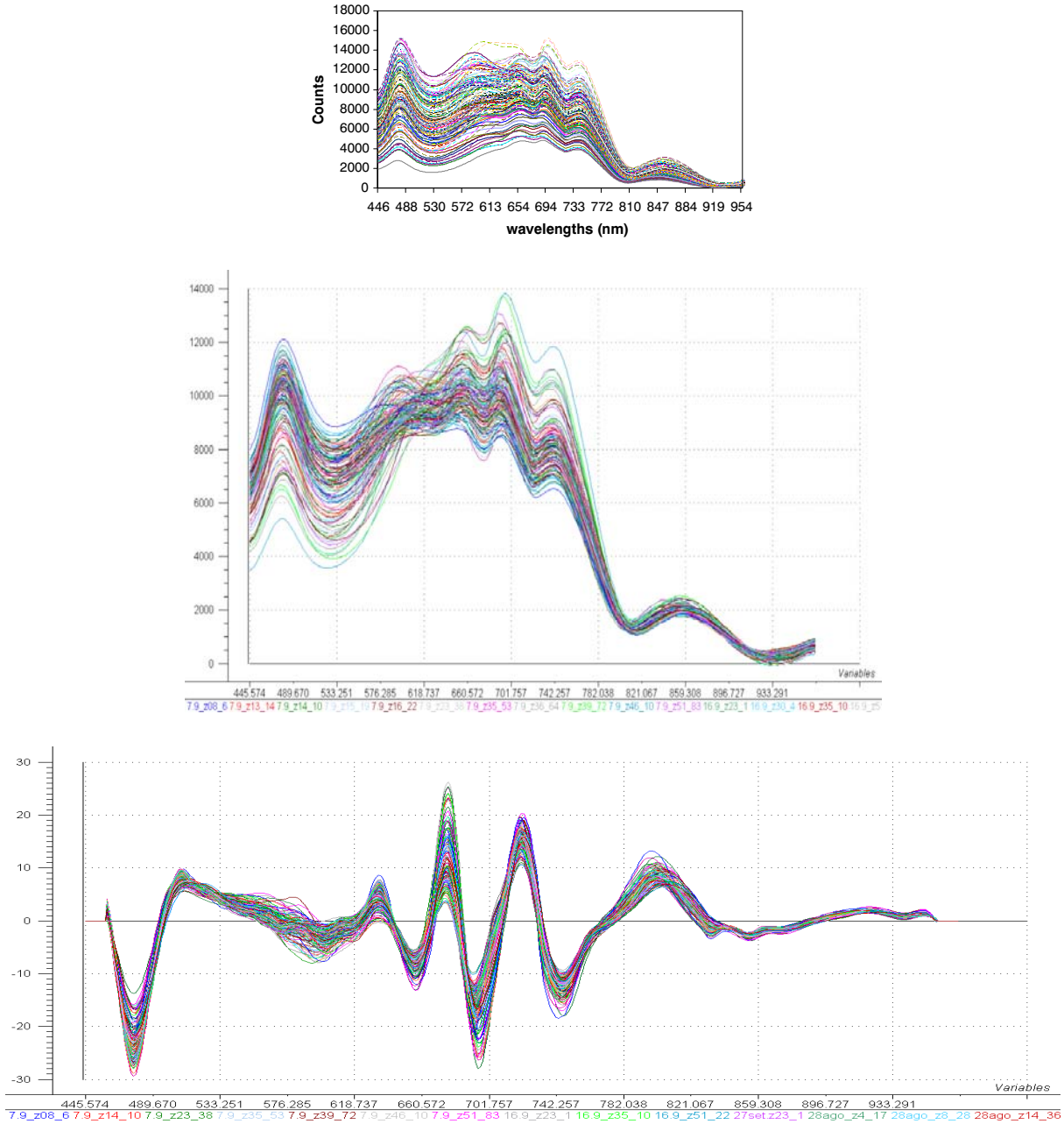

Figure 4. (top) Spectra of homogenized samples and effects of preprocessing treatments: (middle) multiplicative scatter correction and (bottom) second derivative.

In regard to acidity, the regression line had a correlation of 0.81 and RMSEC% of 11.86%. In prediction, the same correlation coefficient (r_{pred} = 0.81) was obtained, but RMSEP% was slightly higher (14.56%).

Regarding phenolic parameters, acceptable results for potential anthocyanins (PA) were obtained, with r_{cal} = 0.88 and RMSEC% of 9.75%. In prediction, correlation fell, reaching r_{pred} = 0.71, while RMSEP% became 16.7%. However, regression lines of the other two phenolic ripeness parameters, extractable anthocyanins (EA) and polyphenols, were insufficient. In fact, polyphenols presented r_{cal} = 0.73 and RMSEC% = 11.44%. In prediction, r_{pred} fell to 0.68. Similar results were obtained for extractable anthocyanins, with r_{cal} < 0.7 and high RMSEC% (13.74%). In prediction, the RMSEP% value increased by two percentage points (15.37%).

For some parameters, the errors obtained were rather high, especially for the estimation of phenolic compounds; however, the results are regarded as a promising starting point for the development of simplified tools for rapid assessment of grape ripeness.

Table 3 shows the results of PLS models developed for the homogenized samples. The model developed for TSS presents an excellent value for correlation (r_{cal} = 0.93) and a low value of RMSEC% (4.75%). In prediction, the correlation coefficient value was lower (r_{pred} = 0.75), but this value was covered by a further lowering of RMSEP% (4.57%).

Good results were also obtained for acidity. In calibration, a high correlation (r_{cal} = 0.95) with a fairly low RMSEC% (10.1%) was found. In prediction, the correlation dropped (r_{pred} = 0.85); however, RMSEP% (11.59%) remained stable. Good results were also obtained from the model developed

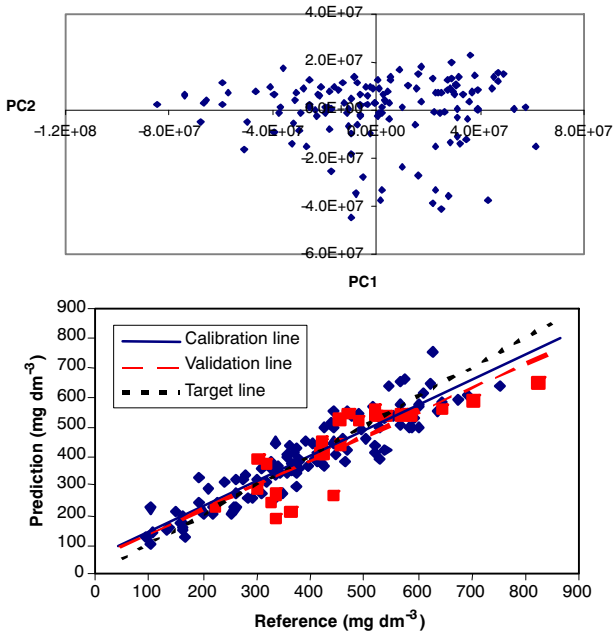

Figure 5. (top) PCA results and (bottom) PLS model for extractable anthocyanins on homogenized samples.

to estimate pH. In calibration, a high correlation (r_{cal} = 0.85) with an excellent low value for RMSEC% (2.66) was found. These results were confirmed in prediction.

Regarding phenolic ripeness parameters, the PLS regression models obtained were rather good for two out of three parameters. In particular, good results were obtained for potential and extractable anthocyanins in calibration (r_{cal} = 0.95 and 0.93, respectively), whereas values of RMSEC% (12.25% and 14.77%, respectively) were slightly high. The model's predictive power is acceptable, with r_{pred} = 0.78 for potential anthocyanins and r_{pred} = 0.84 for extractable anthocyanins. Regarding the RMSEP% values, a slight increase for both parameters was seen. Finally, polyphenols are the parameter with the worst results. In calibration, a correlation value of r_{cal} = 0.80 was obtained, but with a quite good RMSEC% (10.48%), similar to that obtained for anthocyanins. In prediction, the correlation coefficient declined (r_{pred} = 0.7), and the RMSEP% value increased to 14.91%.

Finally, classification analyses were performed for fresh berries and homogenized samples using PLS-DA. These analyses were conducted for only the most important ripening parameters (TSS and titratable acidity). The samples were divided into two classes (not-ripe and ripe) for each parameter and separated by threshold limiting values: 21 °Brix for TSS, and 11 g tartaric acid dm^{-3} for titratable acidity. Table 4 shows the results of the classification of fresh berries with regard to TSS content and acidity.

Table 2. Results of PLS models for fresh berries.

Parameter	Pretreatment[a]	LV	Calibration r	Calibration RMSEC	Validation r	Validation RMSEP
TSS (°Brix)	MSC+d2	2	0.72	0.88	0.82	1.48
Titratable acidity (g tart. acid dm^{-3})	MSC+d2	3	0.81	1.24	0.81	1.48
pH	MSC+d2	2	0.84	0.09	0,81	0.15
PA (mg dm^{-3})	MSC+d2	7	0.88	80.25	0.71	133.90
EA (mg dm^{-3})	MSC+d2	4	0.67	68.97	0.67	81.87
TP (OD 280 nm)	MSC+d2	5	0.73	4.45	0.68	4.74

[a] MSC = multiplicative scatter correction, and d2 = second derivative.

Table 3. Results of PLS models for homogenized samples.

Parameter	Pretreatment[a]	LV	Calibration r	Calibration RMSEC	Validation r	Validation RMSEP
TSS (°Brix)	MSC+d2	5	0.93	0.95	0.75	0.95
Titratable acidity (g tart. acid dm^{-3})	MSC+d2	6	0.95	1.16	0.85	1.12
pH	MSC+d2	5	0.85	0.08	0.80	0.13
PA (mg dm^{-3})	MSC+d2	5	0.95	80.90	0.78	129.00
EA (mg dm^{-3})	MSC+d2	3	0.93	57.70	0.84	77.70
TP (OD 280 nm)	MSC+d2	4	0.80	3.74	0.70	5.81

[a] MSC = multiplicative scatter correction, and d2 = second derivative.

The PLS-DA model of soluble solids content presented strong classification calibrations for both not-ripe berries (two false negatives) and for ripe berries (only one false negative), and a good percentage of samples were correctly classified (91.7% total). In prediction, there was an increase in false negatives in the class of not-ripe berries as well as in ripe berries, and consequently a decline in the percentage of total samples correctly classified in the two classes.

A similar situation occurred in the classification of sample acidity contained in the berries. In calibration, only three samples were wrongly classified in the totality of the two classes; therefore, as with soluble solids content, the percentage of total samples correctly classified was 91.7%. In prediction, regarding the class of not-ripe berries, there were four false negatives, while for ripe berries 68.6% of samples were correctly classified. Table 5 presents the results of models of classification for homogenized samples.

Table 4. Results of PLS-DA classification models for fresh berries.

Ripeness Parameter	Class (and threshold)	Calibration Samples: Correctly Classified No.	Calibration Samples: Correctly Classified %	Calibration Samples: False Negatives	Validation Samples: Correctly Classified No.	Validation Samples: Correctly Classified %	Validation Samples: False Negatives
TSS (°Brix)	Not-ripe (<21 °Brix)	14/16	91.7	2	10/15	77.1	5
	Ripe (≥21°Brix)	19/20		1	17/20		3
Titratable acidity (g tart. acid dm^{-3})	Not-ripe (>11 g tart. acid dm^{-3})	13/14	91.7	1	10/14	68.6	4
	Ripe (≤11 g tart. acid dm^{-3})	20/22		2	14/21		7

Table 5. Results of PLS-DA classification models for homogenized samples.

Ripeness Parameter	Class (and threshold)	Calibration Samples			Validation Samples		
		Correctly Classified		False Negatives	Correctly Classified		False Negatives
		No.	%		No.	%	
TSS (°Brix)	Not-ripe (<21 °Brix)	32/34	95.8	2	27/33	88.7	6
	Ripe (≥21°Brix)	37/38		1	36/38		2
Titratable acidity (g tart. acid dm^{-3})	Not-ripe (>11 g tart. acid dm^{-3})	26/30	93.0	4	24/30	83.1	6
	Ripe (≤11 g tart. acid dm^{-3})	41/42		1	35/41		6

The PLS-DA model has an excellent ability to classify, in calibration, for TSS, with two false negatives in the class of not-ripe fruits and only one for ripe fruits. On the whole, in calibration, 95.8% of samples were correctly classified. In prediction, there was an increase in false negatives for the class of not-ripe fruits, while for the class of ripe fruits, only one false negative more than the calibration phase was predicted.

Regarding the acidity classification of homogenates, in the class of not-ripe fruits there was a total of four false negatives in calibration, while for the class of ripe fruits there was only one false negative sample. The number of correctly classified samples was high (93%). In prediction, there was an increase in false negatives, with the percentage of correctly classified samples decreasing to 83.1%. The classification analysis thus provided satisfactory results. Again, the best results were obtained for prediction of the class of ripeness of homogenized samples.

The results obtained with this system are overall encouraging, although better evaluation parameters for chemometric models can be found in the literature (Cozzolino et al., 2004; Dambergs et al., 2003a). On the other hand, it is important to emphasize that those results were obtained by sophisticated instruments not suitable for field applications.

Qualitative applications like this would give operators a simple tool for quick selection of grapes directly in the field or upon entering the winery. This would allow for better management of the early stages of the winemaking process.

Conclusion

Visible/near-infrared spectroscopy shows promise as a rapid, nondestructive method for evaluating grape quality parameters. A portable optical system (Vis/NIR spectrophotometer in the wavelength range 450-980 nm) for single sample, nondestructive, and quick prediction of grape quality parameters was built and tested.

For fresh berry analysis, PLS regression models show good results for ripeness parameters, especially for TSS and pH value, with a root mean square error of prediction (RMSEP%) for both of <8%. For phenolic ripening parameters, fairly good results were obtained, with correlation coefficient (r) values about 0.7 and RMSEP% between 10% and 15% for all parameters.

Better results were obtained with homogenized samples. Very good results were obtained for all parameters, with a correlation coefficient in calibration of about 0.9 and a correlation coefficient of cross-validation of about 0.8. RMSEP% values were less than 5% for TSS and pH, and between 10% and 15% for the remaining parameters.

Finally, a classification analysis was performed with both fresh berries and homogenized samples using the PLS discriminant analysis (PLS-DA) technique. This analysis was done only for the most important ripening parameters (TSS and titratable acidity). Samples were divided into two classes for each parameter and separated by a threshold limiting value. For fresh berries, the analysis showed good results in calibration, with 92% of samples correctly classified for both parameters. In the validation, the percentage of correct classified samples decreased to 70%. For homogenized samples, 95% of the samples were correctly classified in calibration and about 85% in validation for both parameters; however, a greater number of samples might be necessary to develop a more robust method for use in industrial applications. More samples are also needed to improve the specificity, accuracy, and robustness of the calibration.

Based on the results obtained, a simple, inexpensive, and quick experimental system has been tested, providing important solutions for the eventual realization of a portable Vis/NIR device. The most interesting qualitative parameters for Valtellina's wine production were analyzed; therefore, instruments of this kind can be an effective solution for agriculturists and wineries seeking to improve the commercial quality of their products.

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