

Vis-NIR, FT-NIR and FT-IR spectroscopy for quick selection and exploitation of grapes entering the winery

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Introduction

Conventional methods for determining grape quality parameters (soluble solid content, acidity and phenolic compounds) are time consuming, require sample preparation and are often expensive. Besides, each aspect of grape quality needs a specific method. In particular for the evaluation of phenolic compounds, the Glories method is widely used even if it requires up to 8 or 10 h for results.

Therefore, there is a strong need in the modern wine industry to have a simple, rapid and easy to use method to objectively evaluate grape quality. During recent years, developments in both chemometric methods and spectroscopic instrumentation have resulted in rapid methods for predicting the concentrations of chemical constituents. In particular, near infrared (NIR) spectroscopy is a rapid and non-destructive technique, requiring minimal sample processing before analysis; coupled with chemometric methods it appears to be one of the most convenient and straightforward analytical tools for studying food products. NIR spectroscopy has proven effective at measuring TSS in different fruits¹ and several authors have reported the use of NIR spectroscopy to measure total soluble solids (TSS) in grapes and must.²⁻⁴ Further, visible (Vis) and NIR spectroscopy have been used to predict TSS, pH and total anthocyanins in red grapes since 1999 in the Australian wine industry.⁵

Spectroscopic techniques (from Vis to IR range) were tested for a selection of grapes entering wineries. These methods could be a valid and simple tool to reduce analytical time and cost of ripeness assessment at grape receiving in wine industry.

Materials and Methods

Materials

A total of 180 grape samples harvested in the Valtellina viticultural area (Nebbiolo, ecotype Chiavennasca) during the 2008 and 2009 vintages were analysed. 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 in seventeen different zones, throughout the entire vine area of the valley, in order to represent environmental variability.

Methods

Laboratory reference tests on grapes

Samples were centrifuged and TSS was measured on the supernatant using a digital portable refractometer (Atago-PR-32). Grape titratable acidity (g tartaric acid.l⁻¹) was measured using an automatic sample titrator (Crison, Titromatic 2S-3B).

The Glories method⁶ was used to estimate the phenolic content of the grapes. According to this method, potential anthocyanins (PA; mg anthocyanins.l⁻¹) extracted at pH 1, extractable anthocyanins (EA; mg anthocyanins.l⁻¹) extracted at pH 3.2, and total polyphenols (TP) were evaluated. Quantification of phenolic compounds was based on optical density measurements at 540 nm and at 280 nm for anthocyanins and for polyphenols respectively, using a UV/Vis spectrophotometer (Jasco V530).

Vis/NIR spectroscopy

Homogenised samples in glass Petri capsules were scanned in reflectance mode using an automated Vis/NIR system (QS_200®, Unitec spa), in the wavelength range 600–1200 nm. Three spectral acquisitions for each sample were performed. The QS_200 Vis/NIR system includes a halogen light source, a fiber optic probe, a Vis/NIR (600–1200 nm) detector and a personal computer with a software for automated data acquisition.

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FT-NIR spectroscopy

Measurements were made with a FT-NIR spectrometer (MPA, Bruker Optics, Ettlingen Germany) equipped with an integrating sphere. Data were collected over the range 12000–4000 cm^{-1} with OPUS version 6.0 (Bruker Optics, Germany). Homogenised samples were scanned in a quartz cuvette with a 10 mm path length. Spectral data were stored as the logarithm of the reciprocal of reflectance [$\log(1/R)$] at 8 cm^{-1} . The spectrum of each sample was collected at room temperature and it was the average of 32 scans.

FT-IR spectroscopy

FT-IR spectra (4000 to 700 cm^{-1} ; resolution 16 cm^{-1}) were collected by using a VERTEX 70 spectrometer (Bruker Optics, Ettlingen, Germany) equipped with a multiple reflection germanium crystal for attenuated total reflectance (ATR).

Data processing

Chemometric analysis was performed using The Unscrambler version 9.6 (CAMO ASA, Oslo, Norway). A principal component analysis (PCA) was performed on Vis/NIR, FT-NIR and FT-IR spectra to examine sample groupings and to identify outliers. Different treatments were applied to the spectra, namely scatter correction (standard normal variate and multiplicative scatter correction) and derivatives, before building the calibration models. The first and second derivatives were performed using Savitzky-Golay transformation and smoothing (15 point and 2nd order filtering).

VIS/NIR, FT-NIR and FT-IR spectra were correlated with technological ripening parameters (TSS and titratable acidity) and with phenolic ripening indexes (EA, PA and TP content) using the partial least squares (PLS) regression algorithm. Calibration models were developed using cross validation, while the number of significant terms in PLS calibration models were determined by the prediction residual error sum squares (PRESS) function in order to avoid over fitting the models. Cross validation estimates the prediction error by splitting all the samples into groups: one group was used for calibration, and the other for validation. The process was repeated until all samples had been used for validation once. To evaluate the calibration performance the statistics used were the correlation coefficient in calibration (r_{cal}), the root mean standard error of calibration (RMSEC), the coefficient of correlation in cross validation (r_{cv}) and the root mean standard error in cross validation (RMSECV). The optimum calibrations were selected based on minimising the RMSECV.

Results and Discussion

Descriptive statistics for ripeness parameters (TSS, titratable acidity, pH) and for phenol ripening parameters (anthocyanins and polyphenols content) show wide variability in composition as a result of different sampling times before harvest.

Prediction of technological and phenol ripening parameters of grapes

The optimised PLS regression models for pretreated Vis/NIR spectra are shown in Table 1. These models were obtained by correlating the Vis/NIR spectra with chemical properties of grapes (TSS, titratable acidity, pH, PA and EA). For example, TSS content proved to be well correlated to spectral data (Figure 1). In fact, a good model was obtained with a correlation coefficient in calibration equal to 0.91; the validation samples were predicted with a RMSECV and r of 0.7 and 0.89, respectively. Good models were also elaborated for the other parameters with correlation coefficients in cross validation of about 0.9.

Table 2 shows results for PLS regression models for pretreated FT-NIR spectra. Here, spectral data were correlated with the same parameters as for Vis/NIR data, with the addition of TP. The best result was obtained for TSS with a correlation coefficient in calibration of 0.97 and in cross validation equal to 0.96, with a RMSECV less than 0.5. For the phenol ripening parameters, good results were obtained for anthocyanin content (Figure 2), with correlation coefficients in cross validation of 0.93 and 0.91 for PA and EA respectively.

Finally, PLS regression models for pretreated FT-IR spectra are shown in Table 3. Very good results were obtained for ripeness parameters (TSS, titratable acidity, pH), with correlation coefficients in cross validation > 0.95 for all indices. Regarding phenol ripening parameters, good models were elaborated for EA ($r = 0.92$ and RMSECV = 37.9) and PA ($r = 0.94$ and RMSECV = 57.1; Figure 3).

These good statistical parameters suggest that spectroscopic techniques (from Vis to IR range) can be used to predict the most important ripeness parameters of grapes directly from the homogenised grape spectra.

Table 1. Evaluation of the Vis/NIR ability to predict technological and phenol ripening parameters of grapes.
(r = coefficient of correlation; RMSEC = root mean square of standard error of calibration; RMSECV = root mean square of standard error of cross validation; LV = latent variable)

Dependent variables	Data processing	Wavelengths range (nm)	LV	Calibration			Cross validation		
				Range	r _{cal}	RMSEC	Range	r _{cval}	RMSECV
TSS (°Brix)	SNV	600–1200	9	17.1–25.8	0.91	0.6	17.1–25.8	0.89	0.7
Titrateable acidity (g tart. acid.l ⁻¹)	SNV	600–1200	11	4.94–15.50	0.92	0.97	4.94–15.50	0.90	1.09
pH	SNV	600–1200	11	2.83–3.60	0.89	0.07	2.83–3.60	0.86	0.08
PA (mg.l ⁻¹)	SNV	600–1200	10	159.1–1620.0	0.94	71.6	159.1–1620.0	0.92	78.8
EA (mg.l ⁻¹)	SNV	600–1200	10	109.4–713.3	0.88	45.9	109.4–713.3	0.86	50.8

Table 2. Evaluation of the FT-NIR ability to predict technological and phenol ripening parameters of grapes.
(r = coefficient of correlation; RMSEC = root mean square of standard error of calibration; RMSECV = root mean square of standard error of cross validation; LV = latent variable)

Dependent variables	Data processing	Wavenumbers range (cm ⁻¹)	LV	Calibration			Cross validation		
				Range	r _{cal}	RMSEC	Range	r _{cval}	RMSECV
TSS (°Brix)	SNV-d ¹	10900–3810	6	17.1–25.8	0.97	0.33	17.1–25.8	0.96	0.41
Titrateable acidity (g tart. acid.l ⁻¹)	d ¹	10900–3810	3	4.94–15.50	0.93	0.77	4.94–15.50	0.92	0.82
pH	SNV-d ¹	10900–3810	4	2.83–3.60	0.92	0.05	2.83–3.60	0.91	0.06
PA (mg.l ⁻¹)	SNV	10900–3810	10	159.1–1620.0	0.95	60.69	159.1–1620.0	0.93	71.36
EA (mg.l ⁻¹)	SNV	10900–3810	8	109.4–713.3	0.94	32.79	109.4–713.3	0.91	38.87
TP (mg.l ⁻¹)	d ¹	10900–3810	3	20.5–41.8	0.88	1.85	20.5–41.8	0.86	1.95

Table 3. Evaluation of the FT-IR ability to predict technological and phenol ripening parameters of grapes.
(r = coefficient of correlation; RMSEC = root mean square of standard error of calibration; RMSECV = root mean square of standard error of cross validation; LV = latent variable)

Dependent variables	Data processing	Wavenumbers range (cm ⁻¹)	LV	Calibration			Cross validation		
				Range	r _{cal}	RMSEC	Range	r _{cval}	RMSECV
TSS (°Brix)	SNV	4000–2840	5	17.1–25.8	0.96	0.40	17.1–25.8	0.95	0.44
Titrateable acidity (g tart. acid.l ⁻¹)	SNV-d ¹	4000–2840	4	4.94–15.50	0.97	0.51	4.94–15.50	0.97	0.56
pH	SNV-d ¹	4000–2840	7	2.83–3.60	0.97	0.04	2.83–3.60	0.96	0.05
PA (mg.l ⁻¹)	SNV-d ¹	4000–2840	10	159.1–1620.0	0.97	42.56	159.1–1620.0	0.94	57.11
EA (mg.l ⁻¹)	SNV-d ¹	4000–2840	8	109.4–713.3	0.95	29.38	109.4–713.3	0.92	37.88
TP (mg.l ⁻¹)	d ¹	4000–2840	3	20.5–41.8	0.74	1.65	20.5–41.8	0.70	1.82

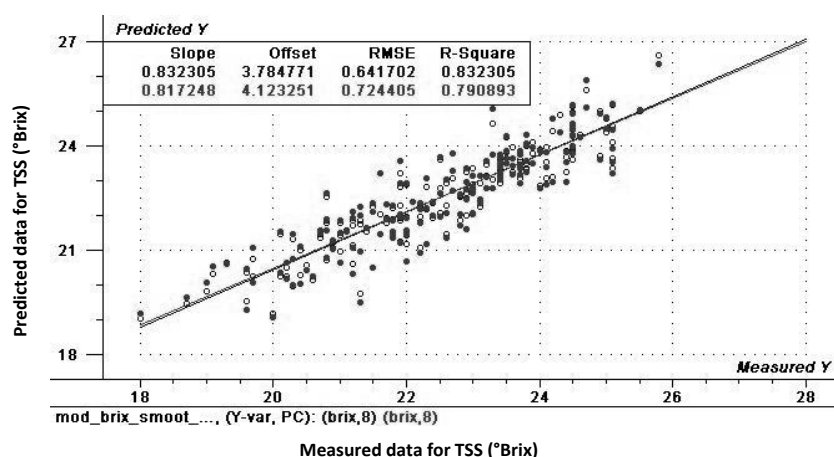


Figure 1. Correlation between TSS content evaluated on grape samples and predicted data by Vis/NIR spectra.

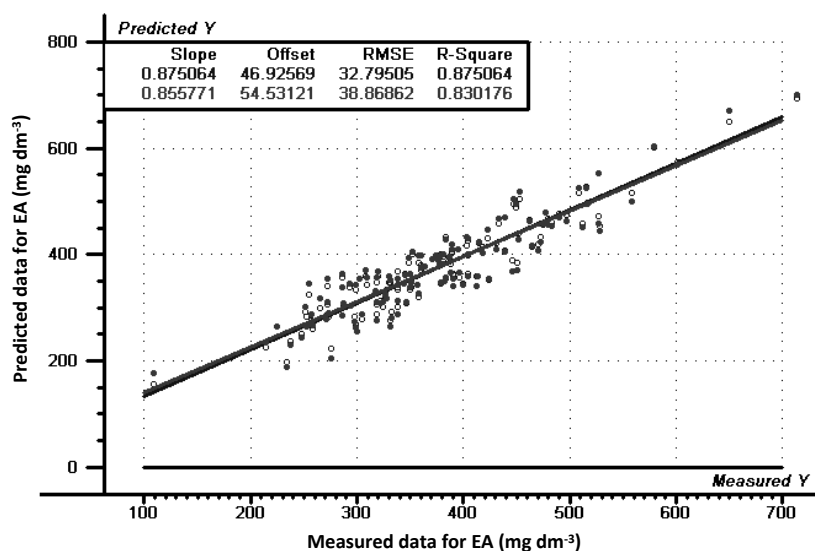


Figure 2. Correlation between EA content evaluated on grape samples and predicted data by FT-NIR spectra.

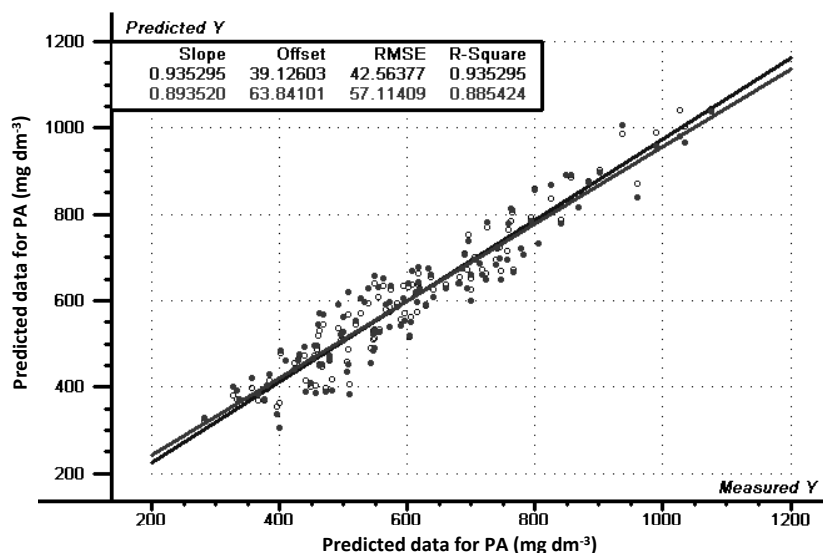


Figure 3. Correlation between PA content evaluated on grape samples and predicted data by FT-IR spectra.

Conclusion

Spectroscopic applications were shown to be rapid and non-destructive methods for evaluating grape quality. In particular, all the devices tested (Vis/NIR, FT-NIR and FT-IR spectrometers) were able to provide good predictions of technological ripeness indices (TSS, acidity and pH) and phenolic ripeness parameters of grapes (potential and extractable anthocyanins and polyphenols). Vibrational spectroscopy could be a valid and simple tool for reducing the analytical time and cost of monitoring these compounds in the assessment of ripeness at grape receiving in wine industry. However, for some specific parameters, a higher number of samples might be necessary to develop a more robust method to be used for industrial application. More samples are also needed to improve the specificity, accuracy and robustness of the calibration.

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