

Measurement of Condensed Tannins and Dry Matter in Red Grape Homogenates Using Near Infrared Spectroscopy and Partial Least Squares

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Samples ($n = 620$) of homogenized red grape berries were analyzed using a visible and near-infrared (NIR) spectrophotometer (400–2500 nm) in reflectance. The spectra and the analytical data were used to develop partial least-squares calibrations to predict dry matter (DM) content and condensed tannins (CT) concentrations. The coefficient of determination in cross-validation and the standard error of cross-validation were 0.92 and 0.83% w/w for DM and 0.86 and 0.46 mg/g epicatechin equivalents for CT, respectively. The standard error in prediction was 1.34% w/w for DM and 0.89 mg/g epicatechin equivalents for CT, respectively. By implementing a NIR spectroscopy method to measure DM and CT in red grape homogenates, we have developed an approach that is suited to large-scale compositional analysis in commercial wine production facilities, as it enables the analysis of large numbers of samples needed to stream batches of fruit. From an economical point of view, the calibration models could be achieved with relatively small data sets. Thus, NIR offers a suitable and efficient tool for the simultaneous measurement of DM and CT in addition to other important parameters in red grape homogenates such as total anthocyanins, total soluble solids, and pH, with minimal sample preparation and low cost.

KEYWORDS: Near-infrared spectroscopy; red grapes; homogenized; condensed tannins; dry matter

INTRODUCTION

The analysis of food quality has been characterized in the past by univariate measurements of single parameters. The development of new multivariate techniques such as near-infrared (NIR) spectroscopy combined with chemometrics facilitates the estimation of many quality factors on the basis of simultaneous measurement of large amounts of composition-related data. Once the mathematical relationships between the instrumental parameters and the traditional quality assessment are established, it should be possible to develop rapid, low-cost, and reproducible methods for objective assessment and control of food quality (1).

The search for a simple technique to assess chemical and physical characteristics of grapes has been receiving increasing attention in recent years. Both viticulturists and winemakers have long sought objective measures of grape composition that closely relate to wine quality (2–4). However, the lack of simple, fast, and reliable methods for the determination of the chemical composition of grapes has been one of the main obstacles for the development of rapid quality control methods or techniques in both industry and commercial trade (2–4). The ability to objectively measure fruit quality is an important requirement

to further enhance the production of competitively priced high-quality wines by the Australian wine industry (2–4). Objective quality measures will allow vineyard managers to target required quality levels and will allow rewards for quality, in terms of quality-related grape payment systems (2–8). To assist in benchmarking of fruit quality, information sourced from surveys and historical data can be an alternative to reference chemical data to evaluate the potential quality of a given region (2, 8). Observations that can be made in the vineyard (e.g., crop load, fruit exposure, berry size, leaf area/fruit ratio, and cane development) may be useful for segregation of vineyards but are no guarantee of ultimate quality and are difficult to apply at point of delivery (2–4). Good color extraction is a quality that winemakers seek when making red wines, and there is objective evidence that wine quality does indeed correlate with grape color (2–8). Although fruit must achieve target ripeness to maximize quality, sugar maturity alone does not guarantee quality. This concept is supported by the empirical observation that for a given region and variety, fruit harvested early in the season can produce better quality wines than fruit achieving the same °Brix later in the season, therefore highlighting the need for additional quality measurements (2–4).

Phenolic compounds are chemical constituents of grapes and wine that contribute to sensorial properties such as color, flavor, astringency, and bitterness (8). Measuring tannins in a wine

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industry setting has been made far simpler and more widely accessible recently, by the development of a simple, robust method, the methylcellulose precipitable (MCP) tannin assay by the Australian Wine Research Institute (AWRI) Tannin Group (9, 10).

Moisture determination is one of the most important and widely used measurements in the processing and testing of agricultural products and foods. It is well-known that the amount of dry matter (DM) in a food is inversely related to the amount of moisture it contains and can influence the stability and quality of foods. Moisture determination is important in many industrial situations such as for the evaluation of raw materials or in determination of processing losses. The latter will be of importance in the wine industry, being related to optimizing harvest date (e.g., gross shivel) and processing of grapes (11). In the wine-processing situation, the maximum potential extraction of juice from grapes is related to the proportion of DM; hence, these measurements can indicate potential wine yield. The DM content may also give insights into new quality measures, but to expedite data gathering and benchmarking, a rapid method to determine DM in red grapes would be advantageous (11).

The combination of novel instrumentation and chemometric techniques has allowed the development of rapid methods that utilize multivariate data from NIR spectra of samples and the measurement of the concentration of specific chemical constituents (12–14). NIR spectroscopy is a physical and nondestructive technique using the region of the electromagnetic spectrum that lies between the visible (400–750 nm) and infrared region (750–2500 nm) and contains information concerning relative proportions of C–H, N–H, and O–H bonds of the organic molecules (12–14). Previous research at the AWRI on the application of NIR spectroscopy and chemometrics, has demonstrated the ability of this technique to determine the concentration of anthocyanins, total soluble solids, and pH in red grape homogenates (2–4, 8, 15). This study was designed to investigate the use of NIR spectroscopy to measure DM contents and condensed tannin (CT) concentrations in red grape homogenates.

MATERIALS AND METHODS

Grape Samples. Samples ($n = 620$) of five *Vitis vinifera* red grape cultivars [Cabernet Sauvignon ($n = 230$), Shiraz ($n = 243$), Merlot ($n = 120$), Grenache ($n = 12$), and Pinot Noir ($n = 15$)] were collected from four vintages (2004–2007) and eight Australian growing regions, spanning a diversity of climates and soil types. The samples were collected as whole berries and stored frozen ($-18\text{ }^{\circ}\text{C}$) for up to 6 months before analysis.

Sample Preparation and Chemical Analysis. Samples were homogenized after thawing overnight at $4\text{ }^{\circ}\text{C}$, using approximately 200 g of sample at 8000 rpm for 20 s in a Retsch Grindomix GM200 (Retsch GmbH & Co, Haan, Germany). Samples were homogenized cold ($<10\text{ }^{\circ}\text{C}$) and analyzed on the day of homogenization for DM, CTs, and by NIR spectroscopy (15, 16). DM determination was performed using an AMB 50 moisture balance (AMB 50, Adam Equipment Co Ltd., Milton Keynes, United Kingdom) (17), and results are expressed as % w/w. The concentration of CTs was measured using the MCP tannin assay (9, 10). This assay permitted the quantification of CT in red grape extracts prepared with 50% aqueous ethanol as solvent. Details of the method are reported elsewhere (9, 10).

Spectral Data Collection. Thawed red grape homogenates were scanned without temperature equilibration, in a FOSS NIRSystems 6500 (FOSS NIRSystems, Silver Spring, MD), in reflectance mode at 2 nm intervals over the wavelength range of 400–2500 nm. Samples were placed in a 10 mm path length quartz cuvette (Part number NR-7063-10, FOSS NIRSystems). A reference scan (using the instrument internal

Table 1. ANOVA (ANOVA, F Ratio, and Probability Values) for DM and CT in Relation to Growing Region, Variety, and Vintage

variable	factor	F ratio	p
DM	variety	7.3	<0.001
	region	10.01	<0.001
	vintage	17.34	<0.001
CT	variety	46.6	<0.001
	region	2.18	<0.001
	vintage	43.6	<0.001

ceramic reference tile) was performed before each sample. Spectra were stored as the logarithm of the inverse of reflectance ($\text{Log } 1/R$) as the average of 32 scans. Instrument control and data collection were performed with Vision software (FOSS NIRSystems).

Data Analysis. Chemometric analyses were performed with The Unscrambler software (version 9.5, CAMO, Norway). The data pretreatment used was standard normal variate (18), and no derivatives were applied. Calibrations were developed using partial least-squares (PLS) regression with six cross-validation groups using the NIR region (1100–2500 nm) (19, 20). Principal component analysis (PCA) was performed before PLS regression models were developed (19, 20). PCA was used to derive the first 10 principal components from the spectral data (20). These were used in further analysis to examine the relevant and interpretable structure in the data as well as outlier detection. Of the overall set of samples, 50% of the samples ($n = 310$) were used for cross-validation as the training or calibration set, while the remaining 50% ($n = 310$) were used as the validation set for testing the calibration models. Selection of both training and validation sets was performed using the algorithms available in the WinISI (v. 1.50) software package (21). Samples used for the NIR analysis were selected to represent the whole spectral and chemical variability in the target population in the calibration and validation groups, respectively. The Mahalanobis distance (H) was used as a criterion for selecting those samples in the population that were more variable on the basis of spectra features (21). The ISI algorithm CENTER was used to establish population boundaries with a maximum standardized H distance of 3.0. Then, the ISI algorithm SELECT was used for efficient selection by choosing samples with a minimum standardized H distance of 0.6 from their nearest neighbors. The coefficient of determination in cross-validation ($R^2\text{CV}$), the standard error in cross-validation (SECV), the standard error of prediction (SEP), and the coefficient of correlation (R) were calculated. The residual predictive deviation ($\text{RPD} = \text{SD}/\text{SECV}$), defined as the ratio between the standard deviation of the population (SD) and the SECV for the NIR predictions, is a useful statistic that is often applied to evaluate how well a calibration model can predict chemical data (22, 23). If the SECV is large as compared with the range of compositions (as SD), a relatively small RPD value results, and the NIR calibration model is considered not robust (22, 23). The higher the value of the RPD is, the greater the probability of the model to predict the chemical composition accurately in samples outside the calibration set.

RESULTS AND DISCUSSION

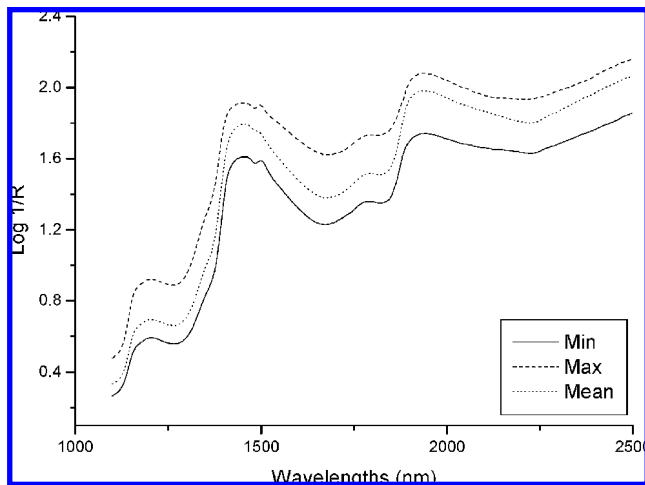
Analysis of variance (ANOVA) showed that DM and CT varied significantly ($p < 0.001$) in relation to the classifying variables, growing region, grape variety, and vintage of production. It was observed that CT was most affected by variety and vintage classifying variables (Table 1).

Table 2 shows the mean, range, and SD of DM and CT for the red grape homogenates as determined by the reference methods for both calibration and validation sets. Grape DM ranged from approximately 23 to 39% w/w, as an indication of the maturity of the samples, while grape CT ranged from 2.8 to 10.7 mg/g epicatechin equivalents. Levels of ripeness were representative of commercial maturity (range from 22.3 to 25.5 °Brix). The variability in the concentration of parameters in the samples analyzed was considered suitable for developing a NIR calibration.

It is well-known that collinearity in the spectral data is handled by the PLS algorithm (19, 24), but an important

Table 2. Summary Statistics of DM (% w/w) and CT (mg/g Epicatechin Equivalents) Measured in Red Grape Homogenates in Both Calibration and Validation Sets^a

	mean	SD	range
calibration set			
DM (<i>n</i> = 310)	30.3	2.9	23.7–38.6
CT (<i>n</i> = 140)	5.9	1.53	2.8–9.72
validation set			
DM (<i>n</i> = 310)	30.6	3.0	22.6–39.2
CT (<i>n</i> = 140)	5.8	1.58	2.1–10.7

^a *n*, number of samples.**Figure 1.** Mean and range of NIR reflectance spectra of red grape homogenates.

consideration with chemometric calibrations is collinearity in the analytical data (reference method), as this may result in surrogate calibrations that are actually based on the most dominant collinear analyte (3, 19, 24). With this sample set, both DM and CT showed some increase with grape maturity. Although within a given patch of grapes there is a strong relationship of CT with maturity, previous surveys in Australia have shown that with grapes from different vineyards CT and maturity (expressed as TSS) are not necessarily coupled (25). In this study, only weak collinearity between the two parameters was observed, as a positive and low Pearson correlation ($P < 0.05$) between DM and CT ($r = 0.26$). The complete sample set was large enough ($n = 620$) that the calibration and validation sets had similar means and SDs to the full data set.

The PCA score plot (PC1 vs PC2) of the grape homogenate samples analyzed using NIR showed no major clusters or groups related either to vintage or to variety in the four vintages analyzed (data not presented). The first PC explains 76% of the variation in the spectra of red grape homogenates, while the second explains PC 15%. Hence, the PCA analysis of the NIR spectra of red grape homogenates indicates that vintage and/or variety had no clustering effect on the data set. This is of importance during the development of global models for compositional parameters for routine and industrial applications. These results agreed with those previously reported when a large data set was used (3, 15, 26, 30). The absence of vintage and variety effects demonstrated the suitability of the NIR calibrations for the measurement of chemical compositional parameters in a wide range of red grape homogenates. The mean spectrum, and range, of the red grape homogenates analyzed are shown in **Figure 1**. The NIR spectra are dominated by water with the main peaks being the OH stretch first overtone at 1450 nm and

Table 3. PLS Calibration Statistics for DM (% w/w) and CT (mg/g Epicatechin Equivalents) in the Set of Red Grape Homogenates^a

	DM	CT
<i>n</i>	287	140
R^2 CV	0.92	0.86
SECV	0.83	0.46
RPD	3.5	3.3
PLS factors	11	13

^a *n*, number of samples; and RPD, SD/SECV.**Table 4.** Validation Statistics for Prediction of DM (% w/w) and CT (mg/g Epicatechin Equivalents) in Red Grape Homogenates^a

	DM	CT
<i>n</i>	309	137
<i>R</i>	0.90	0.82
SEP	1.34	0.89
bias	0.48	0.02
RPD	2.2	1.8

^a *n*, number of samples; RPD, residual predictive value (SD/SECV).

the OH asymmetric stretch and bending combination at 1940 nm (3, 4, 26, 30).

Statistics for the PLS calibrations developed for homogenized grape samples using the NIR region (1100–2500 nm) are shown in **Table 3**. The R^2 CV and the SECV were 0.92 and 0.83% w/w for DM and 0.86 and 0.46 mg/g (epicatechin equivalents) for CT, respectively. This study demonstrates that the NIR calibrations accounted for a high proportion of the variation in the analytes measured, 92% for DM and 86% for CT, respectively. The suitability of a given calibration to predict the chemical composition of a new sample is often interpreted based on the R^2 ; however, this statistic is dependent on the range and distribution of analytical values. Clark and collaborators (19, 27, 28) proposed the use of the coefficient of variation ($CV = SEP/\text{mean}$) as a tool to evaluate NIR calibration equations for minerals in forages; however, the size and interpretation of the CV depend partly on the source of data used. For example, CV values higher than 5% may accrue from the determination of the reproducibility of functionality parameters, but in general, CV values lower than 20% are considered acceptable for most analytical purposes (19, 27, 28). In this study, the CV of the NIR calibrations obtained was 4.5 and 15% for DM and CT, respectively (27), indicating the suitability of these calibrations to predict both chemical parameters in a new set of samples.

The RPD values obtained were 3.5 and 3.3 for DM and CT, respectively, which is considered good for the prediction of new samples. The RPD values should be larger than 2.5, and lower RPD values can result from a narrow range of the reference values (small SD) or to a large error in the prediction (SECV) as compared with the variability of the reference values (22, 23). **Table 4** shows the validation statistics for DM and CT of red grape homogenates. The SEP obtained were 1.34% w/w and 0.89 mg/g epicatechin equivalents for DM and CT, respectively. The RPD values obtained in the prediction set were 2.2 and 1.8 for DM and CT, respectively. To validate the suitability of the NIR models to predict new samples, calibration models were developed on samples from 2006 and further used to predict samples from 2007 (**Table 5**). The same predictive ability of the NIR models was observed, indicating that the models are holding the variability between vintages, as shown in the PCA score plot.

Natural plant tissues contain concentrations of water around 70% of their fresh mass (ripe grape berries typically contain

Table 5. Calibration and Validation Statistics for DM (% w/w) and CTs (mg/g Epicatechin Equivalents) in the Set of Red Grape Homogenates^a

	R ² CV	SECV	RPD	R	SEP
CAL 2006					
DM (n = 189)	0.88	1.07	2.2		
CT (n = 130)	0.81	0.77	1.7		
VAL 2007					
DM (n = 130)			2.1	0.88	1.38
CT (n = 108)			1.7	0.80	0.99

^a n, number of samples; RPD, residual predictive value (SD/SECV).

75–80% water by weight) (15, 26, 29). Pore space filled with water rather than air leads to less refraction at boundaries and deeper light penetration (29). This can lead to sample presentation problems at wavelengths longer than 1400 nm when wet materials such as grape berry homogenates are analyzed using NIR spectroscopy (15, 29). Either wet samples must be presented as thin films at those wavelengths, which is impractical for industry applications (time need for sample preparation), or alternatively longer wavelengths must be abandoned in favor of the Herschel infrared region (780–1100 nm) (29). Beyond 1400 nm, water in wet tissue will be the largest absorber as compared with other constituents in the grape matrix (29). In this study, additional NIR calibrations were developed using shorter NIR wavelengths (780–1400 nm). Improved prediction for CT was obtained using the Herschel infrared region (calibration R²CV = 0.90, SECV = 0.53 epicatechin equivalents mg/L, and SEP = 0.69).

Figure 2A shows the PLS regression coefficients for the NIR calibration models developed for DM (PLS terms = 11). The highest regression coefficients for DM were observed at 1200 nm (C–H stretch second overtone), at 1437 and 1498 nm (OH stretch first overtone, free and hydrogen bonded), and at 1930 nm (OH asymmetric stretch and bending combination) associated with the water content of the grape berries (3, 15, 26, 30). However, there may be some overlap with absorption bands related to the C–H stretch third overtone associated with carbohydrates (31–33). **Figure 2B** shows the PLS regression coefficients for the NIR calibration models developed for CT (PLS terms = 13). The highest regression coefficients were observed around 1512 nm associated with either N–H stretch first overtone or O–H stretch first overtone bands, at 1628 nm (C–H stretch first overtone associated with aromatic compounds), at 1726 nm (C–H stretch first overtones), at 1924 nm (O–H stretch plus deform combination, water), and between 2100 and 2300 nm related to C–H and C=C tones (30–33).

Additionally, absorption features of lignin range from 1400 to 2300 nm and are reported to be centered at 1688, 1870, 2008, and 2143 nm (31, 35). These spectral regions were reported by other authors to be related with CTs in legumes, Eucalyptus leaves, and Mediterranean shrubs (31–35). It has also been reported by other authors that similarities between lignin and tannin reflectance signatures might be due to their relatively similar chemical composition (31). Both contain aromatic rings as well as hydroxyl groups, which have very distinctive features in the NIR spectral region (31). **Figures 3** and **4** show the relationships between the reference method values and the predicted values for DM and CT using the NIR wavelength region.

By using NIR spectroscopy to measure DM and CT, we have developed a method that is suited to large-scale compositional analysis of red grape homogenates that will enable the wine industry to analyze the large number of samples needed to stream batches of fruit in a timely and cost-efficient manner. It

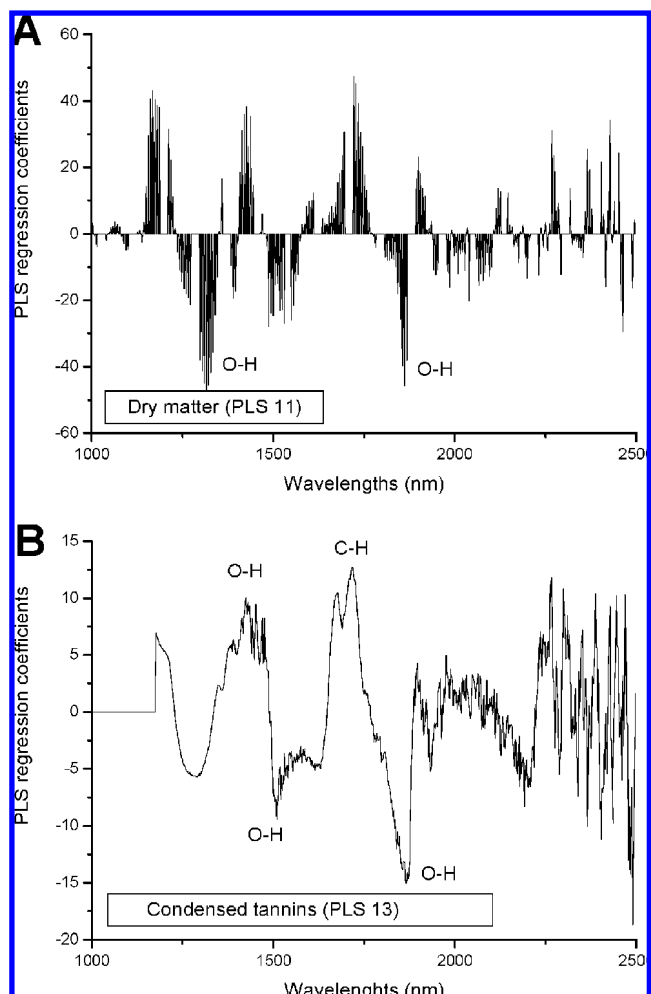


Figure 2. (A) PLS regression coefficients used to develop the calibration for DM in red grape homogenates. (B) PLS regression coefficients used to develop the calibration for CTs in red grape homogenates.

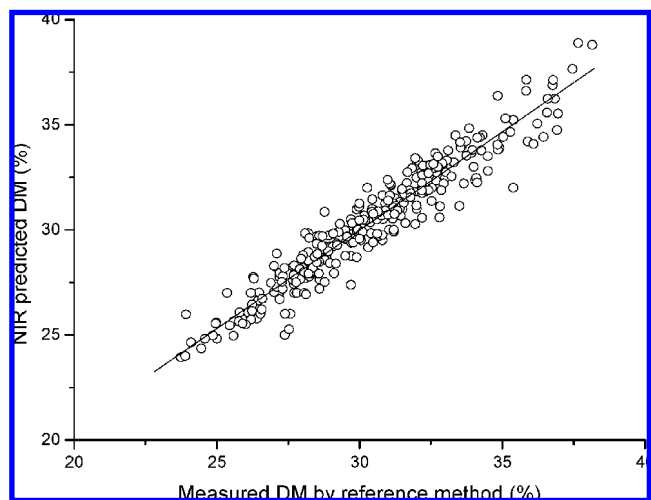


Figure 3. NIR predicted DM vs reference value for red grape homogenates using the validation set.

has been reported that the application of NIR models can reduce the time requirements by 80% as compared to standard analysis when applied to a single component (34, 35).

The power of the NIR spectra-based predictive models indicates that this approach can be recommended for industry use. Although UV/vis spectrophotometers may be less expensive than vis/NIR spectrophotometers, the advantage of the latter is

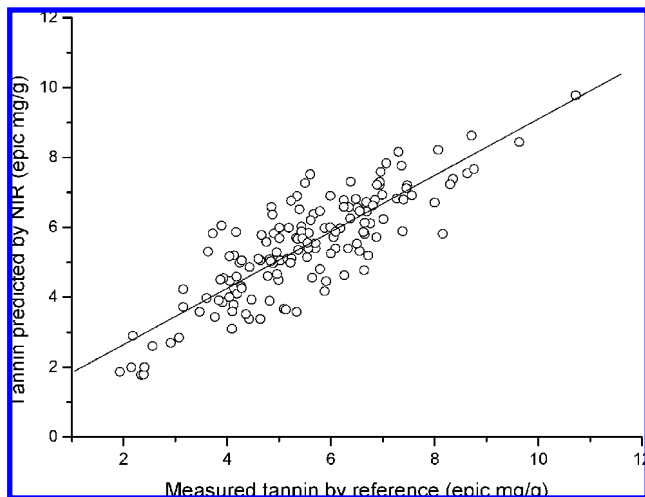


Figure 4. NIR predicted CT vs reference value for red grape homogenates using the validation set.

their ability to perform multiparameter testing of grapes (time for scanning 30 s) for compounds that do not necessarily have a UV fingerprint. The ability of NIR spectroscopy to capture compositional features of red grape homogenates in a more holistic way than targeted chemical analysis is, in our view, a major advantage of the method.

We suggest that NIR spectroscopy may confer other valuable benefits for the wine industry, first because examination of the NIR calibration loadings may provide insights into aspects of grape chemistry and composition that are related to characteristics of interest sought after by winemakers, and second because of the possibility to develop relationships between spectra and reference methods to measure several parameters simultaneously and rapidly, with minimal sample preparation.

This study has shown that NIR is able to predict DM and CT on homogenized grape berry samples. Thus, NIR offers a suitable and efficient tool for the simultaneous measurement of DM and CT in addition to other important parameters in red grape homogenates such as total anthocyanins, total soluble solids, and pH, with minimal sample preparation and low cost. These developments will give the wine industry tools to enable rapid, strategic, and economic decisions, including the analysis of grapes for streaming and payment purposes.

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