Geographic Classification of Spanish and Australian Tempranillo Red Wines by Visible and Near-Infrared Spectroscopy Combined with Multivariate Analysis

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Visible (vis) and near-infrared (NIR) spectroscopy combined with multivariate analysis was used to classify the geographical origin of commercial Tempranillo wines from Australia and Spain. Wines (*n* = 63) were scanned in the vis and NIR regions (400–2500 nm) in a monochromator instrument in transmission. Principal component analysis (PCA), discriminant partial least-squares discriminant analysis (PLS-DA) and linear discriminant analysis (LDA) based on PCA scores were used to classify Tempranillo wines according to their geographical origin. Full cross-validation (leave-one-out) was used as validation method when PCA and LDA classification models were developed. PLS-DA models correctly classified 100% and 84.7% of the Australian and Spanish Tempranillo wine samples, respectively. LDA calibration models correctly classified 72% of the Australian wines and 85% of the Spanish wines. These results demonstrate the potential use of vis and NIR spectroscopy, combined with chemometrics as a rapid method to classify Tempranillo wines accordingly to their geographical origin.

INTRODUCTION

Wine has become a commodity of significant commercial value, and consumers expectations depend on many factors, such as grape variety and maturity, geographic origin, and vinification techniques (*1*). In most wine producing countries in Europe, wine quality value is associated with both climate and soil characteristics, in particular defined by geographical classification or denomination of origin systems (*2–4*). Today, the determination of food authenticity and the detection of adulteration are major issues in the food industry and are attracting an increasing amount of attention for wine producers, researchers, and consumers (*3*). Wine quality is related to an obvious commercial value, determining that adulteration is possible to be practiced, which may bring an unfair competition in the wine industry and harm the rights of consumers (*2, 3*). Thus, there is significant interest in accurate methods for wine characterization that could be used to prevent adulteration.

Current research has primarily focused on wine classification according to geographical origin, using sophisticated and expensive analytical equipment such as high performance liquid chromatography, inductively coupled plasma spectrometry, gas chromatography, and atomic absorption spectroscopy (*2, 3*). Additionally, the use of multivariate statistical techniques (chemometrics) on chemical and sensory data has gained increasing attention as a tool to classify wines from different geographical regions and to describe similar sensory and chemical characteristics. A diverse range of physicochemical parameters have been measured in wines to classify samples according to geographic origin, such as phenolic compounds (*5, 12*), macro- and trace elements (*6, 7, 10, 11*), physical and chemical characteristics (*8–10*), amino acids and biogenic amines (*13*), and volatile compounds (*4, 14*). Although these methods provide valuable information, most of them involve time-consuming, laborious, and costly procedures.

Near-infrared (NIR) spectroscopy has been used to quantitatively predict the concentration of various constituents in food and agricultural products, including wine (*15–16*). NIR spectroscopy is commonly used by the wine industry to monitor fruit quality and to determine the concentration of several chemical parameters in wine using commercially available instruments (*17, 18*). One advantage of NIR spectroscopy is that it can record the response of the molecular bonds of its chemical constituents to the NIR spectrum (e.g., O−H, N−H, and C−H bonds) and thereby build a characteristic spectrum that behaves as a fingerprint of the sample (*15, 16*). It is well-

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Table 1. Number of Samples Used, Vintage, and Origin of Commercial Tempranillo Wine Samples Analyzed

	1999	2000	2001	2002	2003	2004	total
Australia			2	6	10	18	36
South Australia				2	2	13	
New South Wales			2				
Victoria				4	4	5	
Western Australia					4		
Spain (D.O.)	2	2	6	4	13		27
Rioja			4	2	5		
La Mancha			2				
Ribera del Duero	2	2		2	4		
Toro					4		

a D.O. = denomination of origin.

known that visual examination of the NIR spectra cannot discriminate between authentic and adulterated product (*3*, *16*, *19*, *20*). Therefore, the application of multivariate data analysis techniques like principal component analysis (PCA) or discriminant analysis (e.g., partial least-squares discriminant analysis, PLS-DA) opens the possibility to unravel and interpret the optical properties of the sample and allows a classification without the use of chemical information (*3*, *19*, *20*, *21*). Several reports have been found on the use of NIR spectroscopy to classify foods according to geographical origin such as classification of white grapes (*22*), herbal medicines (*23*), two rice varieties (*24*), soy sauce (*25*), and olive oil samples (*26*). To date, there do not appear to have been any attempts to apply the visible (vis) and NIR spectroscopy to differentiate wines according to geographical origin.

The Tempranillo variety of wine grape is one of the most important red grape cultivars grown in Spain (*27*). It is defined as a neutral cultivar with subtle aroma and flavor that produces wines with intense fruity, spicy, and woody aromas. In recent years, it has been planted in Australian vineyards, and its wines are becoming increasingly popular with consumers within this country.

The objective of this study was to investigate the potential use of vis and NIR spectroscopy combined with multivariate analysis to differentiate the geographical origin of Tempranillo wines from Australia and Spain.

MATERIALS AND METHODS

Wine Samples and Reference Analysis. A total of 63 samples (8 labels × 4 replicates; 14 labels × 2 replicates, and 3 bottles × 3 replicates) comprised of 25 commercially available Australian (*n* = 15) and Spanish (*n* = 10) Tempranillo wines were used. The wines showed a diversity of sensory and chemical characteristics and ranged in vintage from 1999 to 2004 for Spanish and 2001 to 2004 for Australian wines, respectively (**Tables 1** and **2**). Samples were analyzed for chemical characteristics such as alcohol by distillation followed by hydrometry and pH using a pH meter; and titratable acidity (TA) is measured on a degassed sample by reacting a known volume of wine with a strong base (e.g., 0.1 M NaOH) to a predetermined end point (8.2 for Australian requirements); glucose plus fructose (G+F) is measured using the Boehringer Mannheim enzymatic method and in the Roche Cobas FARA automated instrument; total phenolics (TP) are calculated by measuring the absorbance at 280 nm in a UV/vis spectrophotometer; wine color density is calculated by measuring the optical density (OD) of the wine sample at two wavelengths at the actual wine pH (OD520 nm plus OD420 nm); and wine color hue is calculated as the relationship OD420/OD520 at the wine pH (http://www.awri.com.au/analytical_service/analyses/).

Spectroscopic Measurements. Wine samples taken from freshly opened bottles were scanned in transmission mode (400−2500 nm) using a scanning monochromator FOSS NIRSystems 6500 (FOSS

NIRSystems, Silver Spring, MD). Spectral data were collected using Vision software (version 1.0, FOSS NIRSystems, Silver Spring, U.S.A.). Samples were scanned in a rectangular cuvette in a 1 mm path length and equilibrated at 33 °C for 3 min before scanning. Spectral data were stored as a logarithm of the reciprocal of transmittance [log(1/*T*)] at 2 nm intervals. The spectrum of each sample was obtained in triplicate, and the mean of the three measurements was used. Instrument performance was checked following the diagnostic protocols provided by the manufacturer.

Multivariate Data Analysis. Spectra were exported from the Vision software in NSAS format into *The Unscrambler* software (version 9.2, CAMO ASA, Norway) for chemometric analysis. PCA was used to reduce the dimensionality of the data to a small number of components, to examine any possible grouping of samples according to the geographical origins, and to visualize the presence of outliers (*28*). PCA models were developed after mean-centering (it is a default option in *The Unscrambler*) using both raw and pre-processed data [standard normal variate (SNV) and second derivative].

The spectra were pre-processed using the SNV (*29*) as scatter correction followed by the second derivative. The second derivative was performed using Savitzky−Golay derivation and smoothing (10 point and second-order filtering operation) to reduce baseline variation and enhance the spectral features (*28*, *31*).

Discrimination models were developed using the PLS-DA technique and linear discriminant analysis (LDA), respectively (*19*, *28*, *31*−*32*). PLS-DA is a variant of partial least-squares regression (PLS1). In this technique, each sample in the calibration set is assigned a dummy variable as a reference value (set as Australian wines = 1 and Spanish wines = 2). The classification of the wine samples according to geographic origins was on the basis of the 1.5 cutoff value. The PLS one (PLS1) regression method was used in this study. The coefficient of determination in calibration (*R*²) and the root-mean-square of the standard error of cross-validation (RMSECV) were used to evaluate the accuracy of the PLS-DA calibration models to predict new samples. Additionally, calibrations generated for classification were developed and evaluated on separate calibration and validation sets. Wine samples were split randomly into calibration (*n* = 32) and validation sets (*n* = 31). The validation set was used to evaluate the accuracy of the models to classify samples according to the geographical origin.

LDA is a supervised classification technique where the number of categories and the samples that belong to each category are previously defined (*28*, *32*). The criterion of LDA for selection of latent variables is the maximum differentiation between the categories and minimizes the variance within categories (*19*, *28*). The method produces a number of orthogonal linear discriminant functions, equal to the number of categories minus one, that allow the samples to be classified in one or another category (*28*, *32*). LDA was carried out using JMP software (version 5.01, SAS Institute, Inc., Cary, NC) on the PCA sample scores on principal components (PCs) 1−3 which gave the highest level of separation (high variance) in the PCA models developed.

The PCA, LDA, and PLS-DA calibration models were developed using full cross-validation (CV; leave *one* out method). Full internal CV was used to validate the calibration models developed. The number of latent variables used in the calibration models was selected by the PRESS function (predicted residual error sum-of-squares) (*28*).

Statistical analysis of the chemical composition was performed by *JMP* statistical software (version 5.01, SAS Institute, Inc., Cary, NC) with GLM procedure.

RESULTS AND DISCUSSION

Chemical Analysis. **Table 2** shows the alcohol content, pH, TA, G+F, TP, wine color density, and wine color (hue) of the wine samples analyzed. It was noticed that the chemical composition of Australian wines varied more widely than that of the Spanish wines. No statistically significant differences were observed between the Australian and Spanish wines in alcohol content, G+F, TP, color density, and hue values. However, statistically significant differences were observed for pH and

Table 2. Range of Chemical Composition for the Australian and Spanish Wines Analyzed

|		alcohol (%)	pH	TA pH 8.2 (g L^{-1})	G+F (g L^{-1})	TP (A.U.)	color density (A.U.)	hue
Australia ($n = 36$)	mean	13.8[a]	3.6[a]	6.2[a]	1.2[a]	53.2[a]	7.6[a]	8.8[a]
	S.D.	0.8	0.1	0.5	1.6	7.2	1.1	0.6
	min	12.6	3.4	5.4	0.0	40.5	5.8	7.9
	max	15.2	3.8	7.1	5.7	63.2	9.7	10.3
Spain ($n = 27$)	mean	14.0[a]	3.7	5.2	0.3[a]	57.2[a]	7.1[a]	8.6[a]
	S.D.	0.2	0.1	0.6	0.2	4.7	1.1	0.5
	min	13.6	3.5	4.4	0.2	50.1	5.2	7.9
	max	14.2	3.9	5.9	0.9	62.8	9.2	9.7
significance of difference[b]		NS	*	*	NS	NS	NS	NS

[a] TA, titratable acidity; G+F, glucose + fructose; S.D., standard deviation; min, the minimum value; max, the maximum value; A.U., absorbance unit. [b] NS, not significant; *, significant difference ($p < 0.05$).
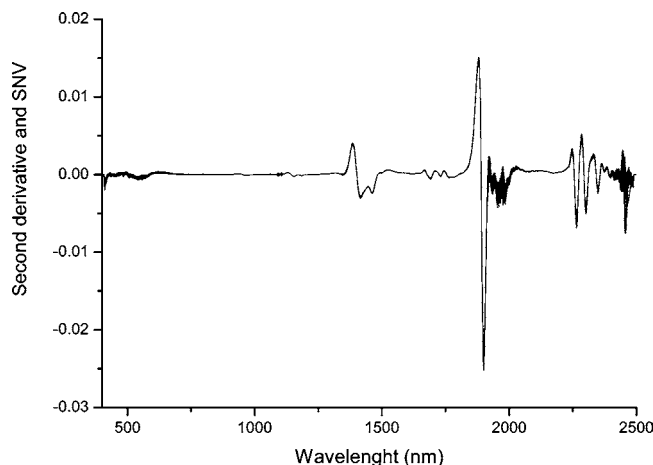
Figure 1. Vis and NIR spectra of Australian and Spanish Tempranillo wines after second derivative and SNV transformation.

TA. These data suggest that the Australian wines contain more acidity than the Spanish wines.

Spectra Interpretation. Figure 1 shows the vis and NIR spectra of wines after SNV and second derivative transformations. The second derivative inverts the spectra, so the bands of the original spectra become troughs (*30, 31*). Two wavelength regions were not used, between 1000–1100 nm (changes of detector in the instrument) and between 1880–2000 nm (off-scale, absorbance higher than 2 absorbance units). Absorptions at 1450 nm and 1950 nm (not included for chemometric analysis) were related to O–H second and first overtones of both water and ethanol (*31, 33*). Additionally, absorptions were observed around 976 nm related to the O–H stretch third overtone associated with water and ethanol, at 1690 nm related to the C–H stretch first overtones associated with sugars (*33, 34*), and at 2268 nm and 2306 nm related to C–H combination and overtones associated with ethanol, sugars, and phenolic compounds (*33, 36*). Absorption in the vis region was observed around 540 nm related to wine pigments (total anthocyanins) (*35*). No obvious differences in the vis and NIR spectra between wine samples from different geographical origins were observed. Therefore, the spectra were processed by means of multivariate analysis, to reveal any differences between them.

PCA. The PCA was applied to both the raw and the pre-processed spectra (SNV and second derivative). **Figure 2** shows the score plot of the first two PCs from the vis and NIR pre-processed spectra. The first three PCs explained 77% of the total variance of the spectra in the set of wines analyzed. It was observed that a separation existed between wines according to the geographical origin. However, two samples from two
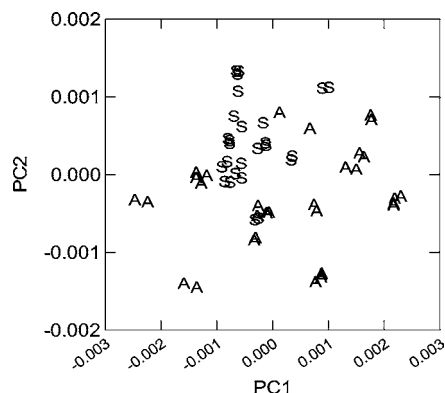
Figure 2. Score plot of the first two PCs of Australian (A) and Spanish (S) Tempranillo wines using vis and NIR spectra after SNV and second derivative transformation.
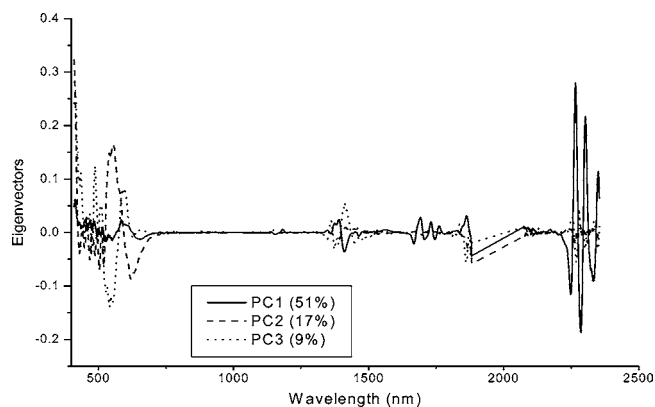
Figure 3. Eigenvectors of the three first PCs (PC1 51%, PC2 17%, and PC3 9%) of Australian and Spanish Tempranillo wines using vis and NIR spectra after SNV and second derivative transformation.

labels of Australian wines overlapped with the Spanish wine samples. The Australian wines have indicated on their back label that the vines that produce those wines were grown in a climate and in soil conditions similar to those present in Spain. Additionally, replicate samples of the same label were grouped in the same cluster, although they were not overlapped, as an indication of bottle to bottle variation. Similar results were reported in white wines (*21*). No obvious separation between samples related to vintage was observed.

Figure 3 shows the eigenvectors corresponding to PC1 (51%), PC2 (17%), and PC3 (9%). The highest eigenvectors in PC1 were observed in the NIR region around 2180–2300 nm wavelengths. Absorbances in this wavelength region are related to C–H combination and O–H stretch overtones (*31, 33, 36*), which indicated that the difference caused by organic compo-

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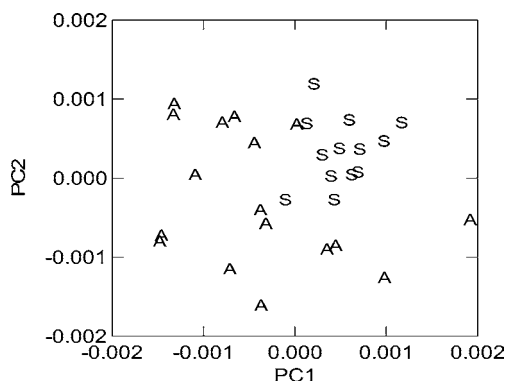*J. Agric. Food Chem.,* Vol. 54, No. 18, 2006   **6757**

Figure 4. PLS score plot of the first two PCs of Australian (A) and Spanish (S) Tempranillo wines using vis and NIR spectra (second derivative and SNV) for the calibration set.

Table 3. PLS-DA Classification Results of Australian and Spanish Tempranillo Wines Using Vis and NIR Spectra[a] Validation Set

	validation		
	Australia	Spain	total
Australia ($n = 18$)	18 (**100%**)	0	93.5%
Spain ($n = 13$)	2 (**14%**)	11 (**86%**)	

[a]Second derivative and SNV. The percent correct classification achieved is in brackets and in bold. n = number of samples.

nents such as alcohol content, sugars, phenolic compounds, and organic acids might contribute to explain the variations among the wines according to the different origins (*31, 33−36*). The highest eigenvectors in PC2 were observed in the vis region around 400−700 nm, related to wine pigments (color) (*35*). The highest eigenvectors in PC3 were observed around the vis region between 450 and 700 nm and in the NIR between 2200 and 2300 nm, related to wine pigments, ethanol, and phenolic compounds, respectively (*21, 31, 33, 36*).

Discrimination. The PLS-DA model was developed using the vis and NIR pre-processed spectra. **Figure 4** shows the score plot of the first two PCs of the PLS-DA model. It is similar to the PCA score plot; however, separation of wines according to geographical origin appears more obvious. This might be explained from the fact that the PLS-DA algorithm maximizes the variance between groups rather than within the group (*28, 32, 37*). The PLS-DA loadings for the calibration models were similar to those observed in the PCA analysis (eigenvectors).

The R^2 and RMSECV for the PLS-DA calibration models were 0.95 and 0.16 (six PLS latent variables), respectively. The calibration statistics indicated that the model developed could be acceptable to classify new samples. **Table 3** shows the PLS-DA classification rates (percent of classification) for the validation set according to geographical origin. The PLS-DA models produce an overall rate of correct classification of 93.5%. Wine samples belonging to Australia were 100% correctly classified, while Spanish wines were 86% correctly classified.

Table 4 shows the LDA classification according to geographical origin based on the first three and eight PC scores from PCA, which account for more than 70% and 90% of the variance, respectively. An overall rate of 76.6% of correct classification was achieved using LDA. Australian wines were 72% correctly classified while 85% of the Spanish wines were correctly classified. Taken into account that the LDA models were developed using the scores from the PCA, it was not surprising to obtain lower rates of classification for the Australian wines. The inclusion of more PCs (from three up to

Table 4. LDA Classification Results of Australian and Spanish Tempranillo Wines Using Vis and NIR Spectra[a]

	correct classification (%)			
	number of PC used	Australia	Spain	total (%)
Australia ($n = 34$)	3	26 (**72%**)	12 (**28%**)	81.6
Spain ($n = 26$)	3	4 (**15%**)	23 (**85%**)	
Australia ($n = 34$)	8	31 (**91%**)	3 (**9%**)	
Spain ($n = 26$)	8	2 (**8%**)	24 (**92%**)	91.6

[a] Second derivative and SNV. The percent of correct classification achieved is in brackets and in bold. n = number of samples; PC, principal components.

eight) when LDA models were developed improved the classification results in both groups. It was noticed that some Australian wines from the 2004 vintage having higher alcohol content (>15%) were misclassified. This trend for high ethanol content in Australian red wine varieties was observed for Cabernet Sauvignon, Shiraz, and Merlot wines and reported elsewhere (*38*).

Classification methods, PLS-DA and LDA, achieved correct classification rates over 80%. PLS-DA and LDA using eight PCs achieved the highest rate of classification. These results verified that differences exist between the wines from different geographical origins and confirmed that vis and NIR spectra contain information able to discriminate among samples, verified in the eigenvectors/loadings for the PCA and PLS-DA models. However, related with the nature of the method used, it was not possible to define a single compound or group of compounds that explain the differences observed between the two geographical origins studied. Rather, the assumption has to be made that the spectrum of the wine (fingerprint) has information to predict the origin of wine samples.

The results of this study suggested that vis and NIR spectroscopy coupled with multivariate methods hold the necessary information for a successful classification of wine samples of different geographical origins. When using PLS-DA calibration models to predict wine samples, high classification rates were achieved. Additionally, the inclusion of more PCs when LDA models were developed yield classification rates similar to those obtained with PLS-DA. However, taking into account the relatively low number of samples used (25 wines) and the structure of the data set we need to be cautious of the ability to extrapolate the classification model to predict new samples in routine analysis. It was observed that some of the wines used in this study were produced from an Australian vineyard claimed to be located in a region with similar climate and soil characteristics to those present in Spain. Therefore, it will be necessary to incorporate more samples to develop a more robust method to be used commercially by the industry as an application.

In conclusion, vis and NIR spectroscopy combined with chemometrics achieved high correct classification rates (>80%) between the Tempranillo wine samples analyzed from two different geographical origins. Spectroscopic techniques could provide a similar degree of reliability on wine classification comparable to those obtained using chemical composition as the results of the traditional high-cost and time-consuming analysis. Although the NIR method presented here is qualitative in nature, it avoids the need of a further quantitative method that would require the use of standards and calibration. However, some factors limit the precision of the classification models, such as the number of samples used to build the calibration models and the similarities between some wines due to climate

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and soil characteristics. Therefore, before these methods can be used by the wine industry with confidence, more samples are needed to improve the precision of the classification models developed.

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