

Discrimination between Shiraz Wines from Different Australian Regions: The Role of Spectroscopy and Chemometrics

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ABSTRACT: This study reports the use of UV–visible (UV–vis), near-infrared (NIR), and midinfrared (MIR) spectroscopy combined with chemometrics to discriminate among Shiraz wines produced in five Australian regions. In total, 98 commercial Shiraz samples (vintage 2006) were analyzed using UV–vis, NIR, and MIR wavelength regions. Spectral data were interpreted using principal component analysis (PCA), linear discriminant analysis (LDA), and soft independent model of class analogy (SIMCA) to classify the wine samples according to region. The results indicated that wine samples from Western Australia and Coonawarra can be separated from the other wines based on their MIR spectra. Classification results based on MIR spectra also indicated that LDA achieved 73% overall correct classification, while SIMCA 95.3%. This study demonstrated that IR spectroscopy combined with chemometric methods can be a useful tool for wine region discrimination.

KEYWORDS: NIR, MIR, regionality, classification, wine, Shiraz, Australia

INTRODUCTION

Producers, exporters, regulators, and consumers are all demanding analytical tools for cost-effective routine quality control of wine.^{1–3} The quality of wines primarily depends on the type of grape, climate, soil, and the different techniques used during the cultivation and production process.^{2,4}

In search of a clearer, simpler, and more transparent policy on wine quality, the EU has established two classes of wines, those which possess a geographical indication and those which do not.^{2,5} Wines produced in specified regions are clearly identified and controlled by different governing bodies at both the national and the regional level. Furthermore, a wine produced in a specific region with well-defined cultivation and elaboration practices verifiable by the competent bodies is awarded the Denomination of Origin (DO).^{2,5} This denomination guarantees the provenance indicated on the label as well as a superior quality.^{2,4,5} Additionally, geographical denominations bring many advantages to producers and consumers, such as protecting these products from possible frauds, guarantee high product quality standards, and defining strict production protocols, regulations, and policies for production.^{5,6} Geographical denominations are also useful to preserve the environment because the quality and composition of a given product are strictly linked with the production environment and traditions.

The Australian wine industry is one of the largest exporters in the world, where the South Australian wine industry produces more than 50% of the annual wine output (<http://www.wineaustralia.com/australia/>).^{7,8} Coonawarra, Barossa Valley, Clare Valley, and McLaren Vale are well-known wine geographical South Australian regions (<http://www.wineaustralia.com/australia/>).^{7,8} Although these regions, from a geographical point of view are quite close, their soil and climate characteristics present differences that could have some impacts on the wine quality.^{7–9} For example, these soil differences are often emphasized by wine makers as marketing strategies focused on associating the product image and the perception of quality with a specific region and/or variety.^{7–11}

Around the world, several laboratories study the DO or the authenticity of a wine using labor-intensive and costly analyses, which look for specific chemical features that can be identified with a given geographical origin.^{6,12–14} Parameters allowing the determination of the geographic origin of food are called indicators of origin, and examples of wine geographical origin indicators are mineral content, micro and trace elements,^{15–18} amino acids content,¹⁹ phenolic compounds,^{4,20,21} volatile compounds,^{22,23} and sensory characteristics.²⁴ However, this type of analysis is based on instrumental techniques that, being selective and reliable, require experienced operators and are difficult to automate and implement in routine and on-site applications.

Alternatively, nonsophisticated techniques and direct measurements, like visible (Vis) and infrared (IR) spectroscopy, combined with multivariate data analysis techniques, have demonstrated the ability to characterize wines through rather simple procedures.^{4,5,12,25} The main advantage of this approach is simplicity and robustness of the procedure that relies on the pattern recognition system [e.g., principal component analysis (PCA) or discriminant techniques].¹³ However, the complexity of these statistical tools negatively affects the slightly improved classification rate because their implementation makes routine analysis rather difficult.

The aim of this study was to investigate the use of UV–visible (UV–vis), near-infrared (NIR), and midinfrared (MIR) spectroscopy methods combined with chemometrics to discriminate Shiraz wines produced in five Australian regions, namely, Barossa Valley, Coonawarra, McLaren Vale, Clare Valley, and Western Australia.

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MATERIALS AND METHODS

Wine Samples. In total, 98 available Shiraz (vintage 2006) wines sourced from four South Australian wine regions, namely, McLaren Vale ($n = 28 + 1$), Barossa Valley ($n = 18 + 1$), Clare Valley ($n = 16 + 1$), and Coonawarra ($n = 22 + 1$), and from one region of Western Australia ($n = 10$), representing 47 commercial brands, were used.

Spectroscopic Measurements. Samples taken from freshly opened bottles of wine were scanned in transmission mode (400–2500 nm) using a scanning monochromator FOSS NIRSystems6500 (FOSS NIRSystems, Silver Spring, MD). Spectral data were collected using Vision software (version 1.0, FOSS NIRSystems). Samples were scanned in a rectangular cuvette in a 1 mm path length (part no. 7063-1, FOSS NIRSystems) and pre-equilibrated at 33 °C for 1 min before scanning. Spectral data were stored as the logarithm of the reciprocal of transmittance [$\log(1/T)$] at 2 nm intervals. The spectrum of each sample was the average of 32 successive scans (1050 data points). Wine samples were also scanned in transmission mode in a Multispec system Bacchus/Multispec System (Thermo Nicolet, Avatar 380, Bacchus, 2007) where the UV–vis and MIR (400–4000 cm^{-1}) regions were collected. Bacchus acquisition software was used for spectra collection and instrument diagnostics (Quant, version 4, 2001). Typical MIR and NIR spectra are shown in Figure 1.

Chemical and Reference Data. The tannin concentration was determined using the method described elsewhere.²⁶ Samples were analyzed for chemical characteristics such as alcohol, pH, titratable acidity (TA), and volatile acidity (VA) using Bacchus/Multispec System. The wine color density was calculated by measuring the optical density (OD) of the wine sample at two wavelengths at the actual wine pH (OD 520 nm plus OD 420 nm), and wine color hue was calculated as the relationship OD420/OD520 at wine pH.²⁷

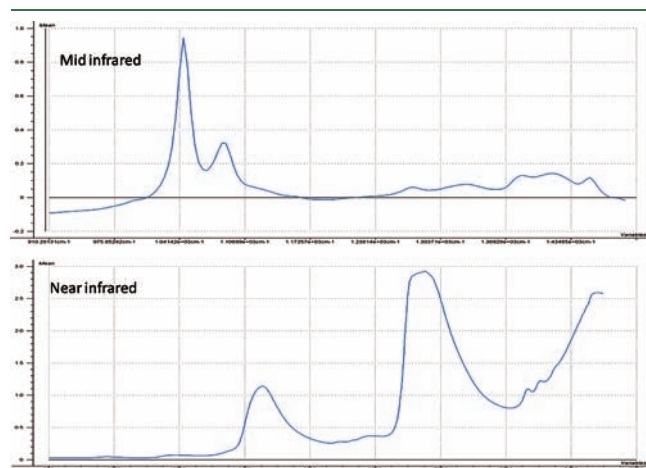


Figure 1. Typical MIR and NIR spectra of wine samples analyzed.

Data Analysis and Preprocessing. Analysis of variance (ANOVA) of chemical data was carried out using JMP software (v. 5.01, SAS Institute, Inc., Cary, NC), and mean comparisons were done by Tukey test ($p < 0.05$). Spectra collected from different instruments were exported in ASCII format to The Unscrambler software (v. 9.5, CAMO ASA, Oslo, Norway) for chemometric analysis. Spectral data were examined for unusual outlier samples using PCA before further analysis. The NIR spectra were preprocessed using the standard normal and variate transformation (SNV) as scatter correction followed by the second derivative.²⁸ 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.²⁹ Discrimination models were developed using linear discriminant analysis (LDA). LDA is a supervised classification technique where the number of categories and the samples that belong to each category are previously defined.²⁹ The criterion of LDA for selection of latent variables is the maximum differentiation between the categories and minimizes the variance within categories.^{29,30} This 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. LDA was carried out using the score values of the first three principal components (PCs) that gave the highest level of separation (high variance) in the PCA models developed (JMP, v. 5.01, SAS Institute, Inc.). Soft Independent Model of Class Analogy (SIMCA) provides a procedure for classification by means of PCA class modeling. The generated PCA class models were fully cross-validated by taking each sample, in turn, out of the calibration and using it for prediction. The SIMCA method is considered a procedure of “soft modeling” often used in chemical pattern recognition. Soft modeling means that two classes can overlap.^{29,30} Therefore, it is possible that wine samples have characteristics of both defined classes or of neither of the defined classes. SIMCA involves the application of PCA to each sample category studied. Boundaries of the SIMCA space around the model are determined by a critical distance obtained by means of Fisher statistics; there is no specific hypothesis other than that this distance should be normally distributed.^{29,30} This technique enables us to classify the samples into an already existing group, assigning new objects to the class to which they show the largest similarity.^{29,30} In this study, SIMCA is based on PCA, where each class is previously defined by an independent PCA, taking into account the optimal number of PCs for each class, which is endowed with a specific data structure (The Unscrambler, v. 9.5, CAMO, ASA). Both LDA and PCA models were developed using full cross-validation.^{29,30}

RESULTS AND DISCUSSION

Chemical Analysis. Table 1 shows the descriptive statistics for the chemical constituents in the set of wines analyzed. No statistically significant differences (Tukey mean comparison,

Table 1. Descriptive Statistics for the Chemical Composition in the Set of Wine Samples Analyzed^a

	Barossa Valley ($n = 19$)	Clare Valley ($n = 17$)	Coonawarra ($n = 23$)	McLaren Vale ($n = 29$)	Western Australia ($n = 10$)
alcohol (%)	12.8 (0.35) A	12.9 (0.63) A	12.3 (0.61) B	12.8 (0.29) A	12.1 (0.4) B
density	0.995 (0.001) A	0.994 (0.001) A	0.994 (0.001) A	0.995 (0.001) A	0.995 (0.001) A
pH	3.44 (0.04) A	3.45 (0.01) A	3.55 (0.6) A	3.46 (0.04) A	3.45 (0.05) A
TA (g/L)	6.74 A	6.49 A	6.66 A	6.50 A	6.90 A
VA (g/L)	0.60 A	0.60 A	0.60 A	0.60 A	0.60 A
tannins (epicatechin meq/L)	1.91 A	2.02 A	1.91 A	1.77 A	1.63 A
color density	1.13 A	1.17 A	1.01 A	1.13 A	0.97 A
hue	0.80 A	0.75 AB	0.81 A	0.81 A	0.76 AB

^a n , number of samples.

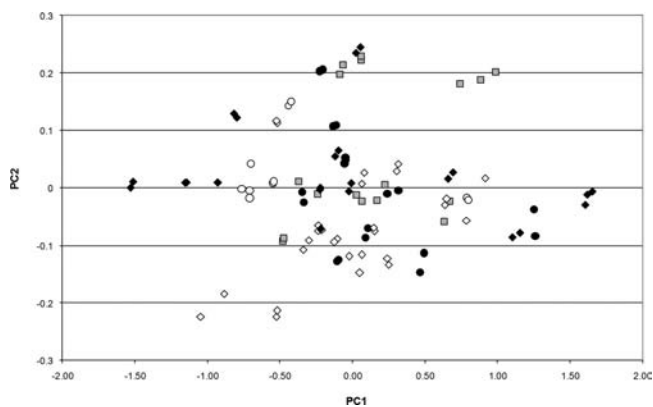


Figure 2. Score plot of the first two PCs derived from the UV spectra of Shiraz wines samples sourced from five Australian regions (MacLaren Vale, white diamond; Clare Valley, gray square; Barossa Valley, black circle; Coonawarra, black diamond; and Western Australia, white circle).

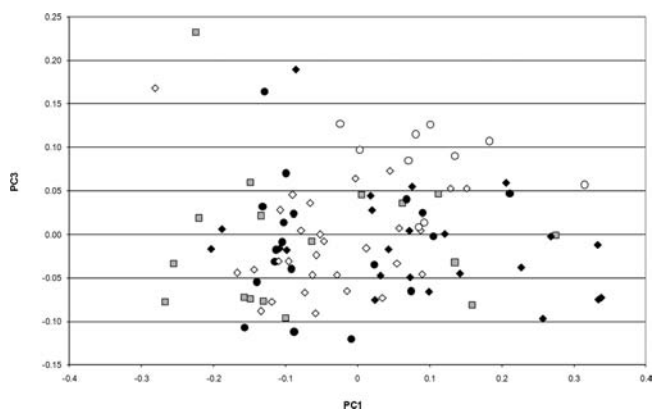


Figure 3. Score plot of the first two PCs derived from the NIR raw spectra of Shiraz wines samples sourced from five Australian regions (MacLaren Vale, white diamond; Clare Valley, gray square; Barossa Valley, black circle; Coonawarra, black diamond; and Western Australia, white circle).

$p < 0.05$) were observed in TA, pH, VA, density contents, tannin concentration, and color density values between wines. Statistically significant differences ($p < 0.05$) were observed in alcohol content between wines sourced from Coonawarra and Western Australia as compared with wines sourced from the other three regions. Statistically significant differences ($p < 0.05$) were also observed in hue values between wines sourced from Clare Valley and Western Australia as compared with wines sourced from the other three regions. Additionally, a PCA analysis using the chemical data was carried out. No separation between wines sourced from the different regions was observed (data not shown). Overall, the chemical composition of the wine samples was considered to be typical for Australian table wines.³¹

PCA. PCA was performed on the UV–vis, NIR, and MIR spectra of the wine samples to examine the possible grouping of samples related to region of origin. Figures 2–4 show the score plots of the UV–vis, NIR, and MIR, respectively. The first PCs of each plot explain 97.8, 98.7, and 83.5% of the total variance of the MIR, UV–vis, and NIR spectra of the wine samples analyzed, respectively. No clear separation between wines according to their geographical region was shown by the PCA score plots

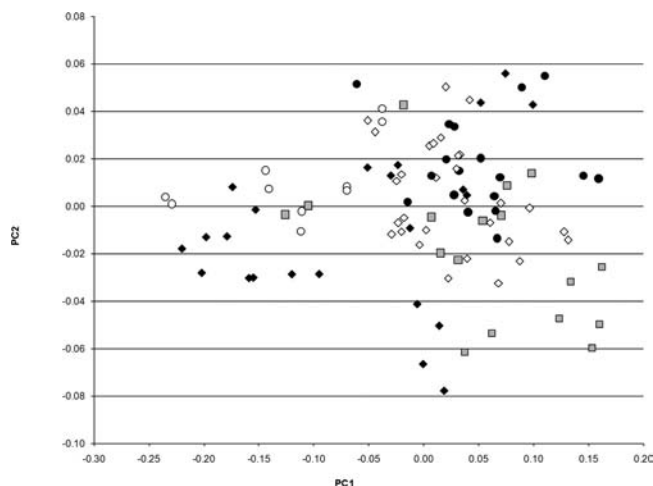


Figure 4. Score plot of the first two PCs derived from the MIR spectra of Shiraz wines samples sourced from five Australian regions (MacLaren Vale, white diamond; Clare Valley, gray square; Barossa Valley, black circle; Coonawarra, black diamond; and Western Australia, white circle).

Table 2. Percentage of Correct Classification of Wines According to Geographical Origin Obtained Using LDA and UV–Vis, NIR, and MIR Spectra

	Vis	UV	MIR	NIR
Barossa Valley	47.37	15.79	63.16	68.42
Clare Valley	41.18	58.82	64.71	41.18
Coonawarra	65.22	39.13	89.96	69.57
McLaren Vale	79.31	58.62	51.72	27.59
Western Australia	80	50	100	90
overall	62	46	73	60

using either UV–vis or NIR data. However, wines sourced from both Western Australia and Coonawarra were better separated from the other wine samples using the MIR region. It was observed that wines sourced from Barossa Valley, McLaren Vale, and Clare Valley overlapped in all plots, where no clear separation according to region was observed. Overall, the best separation among wines was achieved using the MIR region ($910\text{--}1488\text{ cm}^{-1}$). The eigenvectors of the first two PCs derived from the MIR were investigated to interpret the basis of the separation among wines according to the region. The highest eigenvectors were observed around $1045\text{--}1080\text{ cm}^{-1}$ related to the C–OH of ethanol, glycerol, and sugars (glucose and fructose), at 1268 cm^{-1} related with aromatic groups associated with phenolic compounds, and between 1419 and 1454 cm^{-1} related with CO=O and C=C, C–H₂, and C–H₃ associated with organic acids and aldehydes.^{10,32,33}

LDA. Table 2 shows the LDA classification rates obtained for the classification of wines according to their geographical origin using UV–vis, NIR, and MIR spectra. The best LDA classification rates were obtained using the MIR spectra (overall correct classification of 73%), while individual correct classification rates were obtained for wines sourced from Western Australia (100%) and Coonawarra (86.96%). The poorest classification rates (lower than 50%) were obtained using the UV wavelength region, indicating that neither color nor phenolic compounds alone explained the separation among wines related to their

Table 3. Classification Results Obtained by SIMCA Using MIR Region

	correct classification (%)	misclassification (%)
Barossa Valley	89.5 (17/19)	24.7
Clare Valley	88.7 (87/98)	100
McLaren Vale	100 (29/29)	23.2
Coonawarra	86.9 (20/23)	32
Western Australia	100 (10/10)	0

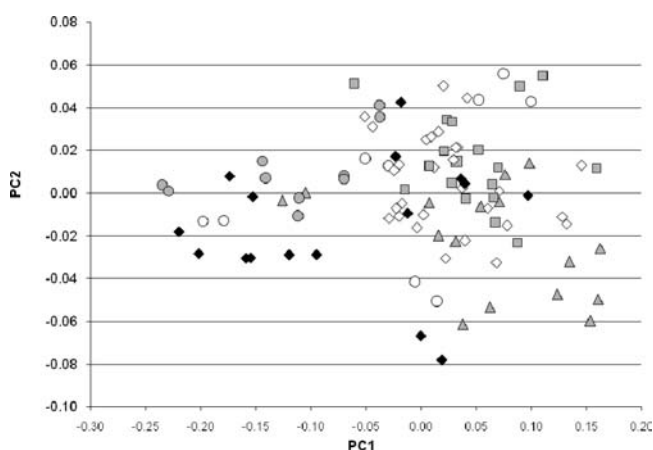


Figure 5. Score plot of the first two PCs derived from the MIR spectra of Shiraz wines samples sourced from five Australian regions labeled with the name of the region and type of soil according to the soil classification (hard apedal, white diamond; calcareous, gray square; sandy soil, black diamond; cracking soil, white circle; hard pedal, gray triangle; and calcareous sand, gray circle).

geographical origin. Intermediate correct classification rates (60%) were obtained using either Vis or NIR wavelength regions.

SIMCA. Table 3 shows the SIMCA classification results obtained using the MIR spectra. SIMCA classification was carried out using the information embedded in each PCA model developed for each wine geographical region. The objective of SIMCA modeling is to develop local PCA models, one for each wine region or class to be used later for interpretation and classification of new observations.¹³ The best classification rates were obtained for wines sourced from Western Australia and McLaren Vale (100% of correct classification). The highest misclassification percentage was observed for wines sourced from Clare Valley (>80%). One possible explanation for this misclassification might be related to the widespread of soils in Clare Valley. It is well-known that the Clare Valley wine region has soil types matching those observed in other wine regions. To verify this, the scores shown in Figure 3 were labeled again using the name of the main soil or soil group for the wine region analyzed (see Figure 5). Replacing the wine region labels on the PCA plot (Figure 4) with the soil name (Figure 5) revealed some grouping. This suggested that the characteristics of the soil from which the wine came from might have an influence on the spectral characteristics of the wines (e.g., wines produced in different regions but with similar soil characteristics presented similar spectra characteristics). Similar relationships between soil type and wine characteristics were reported by Liu and collaborators,²⁵ where Tempranillo wines sourced from Australia and Spain cultivated in similar climate and soil conditions

overlapped on the same PCA space, even if the country of origin was different. However, it has to be noted that both soil type and chemical characteristics sourced in this study were obtained from the information provided by the wine label and from available data in wine books⁹ and not from direct sampling of the soils from each of the wine regions analyzed. Although not many reports can be found in the literature that relates soil characteristics with grape and wine composition,¹¹ there is some evidence that soil characteristics can influence wine sensory properties.³⁴

This study proved that the combination of IR methods with multivariate statistical techniques (chemometrics) can be applied as a tool to classify Shiraz wines sourced from different Australian geographical regions. It was also observed that the classification rates using either NIR or MIR spectroscopy varies according to the classification technique applied. Overall, LDA did not achieve high classification rates (73% of correct classification) as compared with SIMCA. The best classification results were obtained using SIMCA and MIR spectra. It was also observed that wine samples from similar soil types were clustered together, indicating some influence of both soil chemical and physical characteristics on the fingerprint of the wine.

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