

Investigating the Use of Element Analysis for Differentiation between the Geographic Origins of Western Cape Wines

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The aim of this study was to differentiate between the geographic origins of wines produced in the Western Cape on the basis of their element composition. A total of 96 market-ready red and white wines (Pinotage, Shiraz, Merlot, Cabernet Sauvignon, Sauvignon blanc, Chardonnay and Chenin blanc) were analysed by means of inductively coupled plasma atomic emission spectrometry (ICP-AES). The discriminant methods: stepwise discriminant analysis, canonical discriminant analysis and linear discriminant analysis were applied to the data sets. A classification accuracy of 38% for Pinotage, 55% for Shiraz, 68% for Merlot, 75% for Cabernet Sauvignon, 93% for Sauvignon blanc, 68% for Chardonnay and 100% for Chenin blanc was achieved. Subject to the conditions of this study, it was concluded that differentiation between wines according to geographical origin was possible using the elemental composition.

The chemical composition of wine depends on a number of factors, such as production area, viticultural practice, grape variety, type of soil, climate, yeasts and winemaking techniques. These factors all play an important role in the characterisation and differentiation of wines. Wine labelled as having the same variety, region and geographic origin should have a similar or typical composition that affords them distinctive characteristics, which allows the wine to be differentiated from other wines of known origin (Danzer *et al.*, 1999; Sivertsen *et al.*, 1999). Differentiation of wines according to grape variety can be effectively performed by determining parameters such as protein content (by electrophoresis), amino acids (by fast protein liquid chromatography; FPLC), polyphenols (by high-performance liquid chromatography; HPLC), elemental composition (by inductively coupled plasma; ICP), isotope ratios (by nuclear magnetic resonance; NMR) and aromatic compounds (by gas chromatography mass spectrometry; GC-MS) (Aleixandre *et al.*, 2002).

Several Spanish wines produced from different varieties were differentiated on the basis of polyphenols and aromatic compounds (Cabezudo *et al.*, 1992) and protein fraction (Pueyo *et al.*, 1993). Similarly, polyphenols, glycerine and sugar composition were employed to differentiate varietal wines from Majorca (Forcén *et al.*, 1992). Forina *et al.* (1986) based their studies on phenolic composition to differentiate varietal wines from the Piemonte region in Italy. Ortega-Meder *et al.* (1994), Almela *et al.* (1996), Arozarena *et al.* (2000) and Rossouw & Marais (2004) based their studies on the anthocyanin composition to differentiate varietal wines. Latorre *et al.* (1994) used the metallic compo-

sition for varietal and geographic differentiation of white wines from Galicia.

Pueyo *et al.* (1993) and González-Lara & González (1994) used protein profiles, which is one of the more widely used techniques, for differentiating between varietal wines. Its popularity can be attributed to the fact that the protein content is genetically established and not influenced by edaphic or climatic characteristics. Likewise, the amino acid content of wine (Etiévant *et al.*, 1988; Dizy *et al.*, 1992) and organic acid content (Etiévant *et al.*, 1989) can be used as differentiating parameters for varietal wines.

Symonds & Cantagrel (1982) and Maarse *et al.* (1987) established that aromatic compounds could be used to differentiate German varietal wines. Discriminant analysis has also been applied to volatile compounds of French and Spanish varietal red wines to differentiate between them (Noble *et al.*, 1984; Reboló *et al.*, 2000; Aleixandre *et al.*, 2002). Albariño and Nebbiolo wines were differentiated on the basis of volatile compounds (García-Jares *et al.*, 1995; Marengo *et al.*, 2001). Rapp *et al.* (1993) and Presa-Owens *et al.* (1995) obtained varietal differentiation of white wines on the basis of their aromatic composition. Minnaar & Booyse (2004) applied discriminant analysis to classic enological parameters of South African varietal young red wines.

The hydrogen isotope ratios of the methyl (D/H)₁ and methylene (D/H)₂ sites of ethanol determined by means of site-specific natural isotope fractionation-NMR (SNIF-NMR), and trace elements determined by ICP-mass spectrometry (ICP-MS), were measured in wine that originated from Bordeaux, to characterise the geographic origin (Martin *et al.*, 1999). Day *et al.* (1995)

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determined (D/H) $_{\text{w}}$ (average deuterium/hydrogen content of water in wine), (D/H) $_1$, (D/H) $_2$, $\delta^{18}\text{O}_{\text{w}}$ (average oxygen -18 content of the water in wine) and, $\delta^{13}\text{C}_{\text{a}}$ (carbon -13 of the wine distillate) ratios, including the elemental composition of wine from Burgundy, using ^2H -NMR and atomic absorption spectrometry (AAS) to determine geographical origin. Authenticity and geographical origin of wines from Slovenia were investigated. This was done by measuring $^{13}\text{C}/^{12}\text{C}$ and (D/H) $_1$ ratios by means of isotope ratio mass spectrometry (IRMS) and SNIF-NMR (Ogrinc *et al.*, 2001).

Since the work of Kwan & Kowalski (1978), trace and ultra trace elements have been studied for their capacity to characterise the geographic origin of wine (Latorre *et al.*, 1994; Martin *et al.*, 1999). Some authors have succeeded in identifying wine origin solely by analysis of the elemental content. The potential of multiple element analysis to determine the region of wine origin was shown by McCurdy *et al.* (1992). Using trace and ultra trace elements, Baxter *et al.* (1997) unequivocally identified the origin of Spanish and English wines originating from three different regions. The elemental content of wines could be an effective means by which to differentiate varietal wines. Various analytical techniques have been used to measure trace and ultra trace elements of wine, including: electrochemical techniques, X-ray fluorescence, atomic absorption spectrometry, neutron activation analysis, mass spectrometry and inductively coupled plasma spectrometry (ICP). Inductively coupled plasma spectrometry has been the most widely applied of all the mentioned techniques (Eschner *et al.*, 1989; Ströh *et al.*, 1994; Day *et al.*, 1995; Baxter *et al.*, 1997; Greenough *et al.*, 1997; Thiel & Danzer, 1997; Martin *et al.*, 1999; Castiñeira-Gomez *et al.*, 2001; Perez-Trujillo *et al.*, 2002; Taylor *et al.*, 2003). The analysis of elements by ICP, in particular Na, K, Ca, Mg, Mn, Li, Fe, Cu and Pb, has been extensively employed as one of the most promising methods, used either on its own, or in combination with other methods, for classification of wine and wine authenticity (variety, geographical origin) (Moret *et al.*, 1994; Baxter *et al.*, 1997; Galani-Nikolakaki *et al.*, 2002; Kallithraka *et al.*, 2001; Frias *et al.*, 2003).

The Spanish wines, Rías-Baixas and non Rías-Baixas, have been successfully classified according to geographical origin and wine type, using pattern recognition techniques and Li and Rb as key elements (Latorre *et al.*, 1994). The effectiveness of lanthanides in this regard has been clearly demonstrated, with La, Ce, Pr, Nd, Eu, Gd, Tb, Ho, Er, Tm, Yb and Lu being successfully employed for differentiation between French wines (Ströh *et al.*, 1994).

Peña *et al.* (1999) studied 39 red wines from Galicia (NW Spain) in terms of their trace elements. Differentiation was successfully made between Ribeira Sacra and non-Ribeira Sacra wines. The use of Li and Fe alone resulted in a satisfactory level of correct classification of the two wine groups. The use of Li, Fe and Rb enabled a more accurate determination of origin (Rebolo *et al.*, 2000). Kallithraka *et al.* (2001) showed that the elemental content of 33 red and white Greek varietal wines varied substantially, which indicates that elemental content can be employed as a reliable indicator for differentiation of wines from various regions. Trace and ultra trace element concentrations in wines originating from the Okanagan Valley and the Niagara Peninsula have provided verification of vineyard origin (Taylor *et al.*, 2002). Furthermore, Taylor *et al.* (2003) established that analysis

of Sr, Rb, Mn, U, Al, V, Zn, Mo, Sb and Co could discriminate between Niagara and Okanagan vineyards with 100% accuracy.

The majority of the studies were conducted in Mediterranean countries, such as Spain, France, Italy and Greece, owing to their interest in wine authenticity. In South Africa, however, the regional differentiation between varietal wines of known origin by means of routine chemical analysis has not been addressed. There are certain measures, however, which have been taken by SAWIS (South African Wine Information and Systems) to ensure the authenticity of grape origin, variety and quantity of wine in South Africa before certification. In addition, the national authorities also provide strict guidelines, which must be adhered to in regard to the quality of wine, since the production of quality wines is of economic importance to South Africa. These guidelines include official tasting (organoleptic properties), chemical analyses such as ethyl alcohol concentrations, fructose and glucose content, sulphur dioxide levels (bound and free), pH and volatile acid determinations. Although these guidelines are strictly enforced and do, to a certain extent, guarantee the quality of wine, they cannot be considered a substitute for chemical analyses to determine the origin of wine. The aim of this study was to investigate the use of element analysis by ICP-AES to differentiate between the geographic origins of wines produced in the Western Cape (Breede River Valley and Coastal Regions).

MATERIALS AND METHODS

Wine samples

Wine collected for use in this study is listed in Table 1, and included the following: 8 Pinotage, 19 Merlot, 9 Shiraz, 12 Cabernet Sauvignon, 15 Sauvignon blanc, 25 Chardonnay and 8 Chenin blanc samples. These single varietal wines were collected between 2000 and 2001, directly from estate cellars in sealed, labelled bottles. More than one vintage was included wherever possible to facilitate data comparison. A laboratory number was allocated to each wine (sample), after which it was packed into crates and stored at 4°C until required for analysis.

Instrumental

Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)

A Varian (Liberty series II) ICP-AES equipped with a Varian grating (1800 lines/mm for the sequential mode in the Paschen-Runge configuration), a Varian auto-sampler (Model SPS-5) and a concentric silica torch with a V-groove nebuliser were used to analyse the elemental composition of wine samples. The system was managed by the Varian "Plasma 96" software version.

Operating conditions

Operating conditions were as follows: pump rate: 15 rpm; forward radio frequency power: 1000 W; argon flow in the plasma and nebuliser: 2 L/min; spray chamber temperature: ambient; observation height: 10 mm above load coil; sample size: 1.5 ml; sample uptake rate: 3.0 ml/min; purge time: 0.5 min; rinse time: 15 seconds; signal integration time: 0.167 min; wash cycle: 0.5 min (rinsing solution: de-ionised water).

Reagents used

The multiple element solution (Merck, catalogue no. 10365) and ethyl alcohol (Merck, catalogue no. 100983), both analytical grade, were supplied by Merck/NT Laboratories SA.

TABLE 1

Wines used in this study, with origin, grape variety and vintage.

Region	District	Ward	Cellar	Grape variety	Vintage	
Breede River Valley	Worcester	Goudini	Deetlefs	Pinotage	99/00	
	Robertson	Le Chasseur	Le Grand Chasseur	Chardonnay Shiraz	00/01 00/01	
		Bonnievale	Van Zylshof	Chardonnay	00/01	
		No ward	Zandvliet	Shiraz	98/99/00	
Coastal	No district	Constantia	Groot Constantia	Merlot	99/00	
	Paarl	No ward	De Zoete Inval	Sauvignon blanc	99/00/01	
				Cabernet Sauvignon	97/98	
	Wellington	Hildenbrand	Chardonnay	Chardonnay	99/00	
				Cabernet Sauvignon	99/00	
	Franschhoek Valley	La Motte	Chardonnay	Chardonnay	97/98	
				Shiraz	97/98	
	Franschhoek Valley	L'Ormarins	Sauvignon Blanc	Sauvignon Blanc	99/00/01	
				Cabernet Sauvignon	95/96/97	
	No ward	Rhebokskloof	Chardonnay	Chardonnay	98/99/00	
				Merlot	98/99	
	No ward	Ruitersvlei	Chenin blanc	Chenin blanc	00/01	
				Stellenbosch	Devon Valley	Clos Malverne
	Stellenbosch	Jonkershoek	Klein Gustrouw	Merlot	00/01	
				Cabernet Sauvignon	00/01	
		Bottelary	Hazendal	Chardonnay	Chardonnay	98/99/00
					Merlot	99/00/01
No ward		Klawervlei	Chenin blanc	Chenin blanc	96/98/01	
				Merlot	00/01	
No ward		Meerlust	Chardonnay	Chardonnay	96/97/98	
				Merlot	95/96/97	
Bottelary		Mooiplaas	Sauvignon blanc	Sauvignon blanc	98/99/00/01	
				Pinotage	98/99/00	
Simonsberg-Stellenbosch		Morgenhof	Chenin blanc	Chenin blanc	98/99/00	
				Merlot	98/99	
No Ward		Neethlingshof	Chardonnay	Chardonnay	00/01	
				Merlot	00/01	
Stellenbosch		Nietvoorbij	Chardonnay	Chardonnay	97/98/00	
	Pinotage			97/98/99		
No ward	Vredenheim	Cabernet Sauvignon	Cabernet Sauvignon	92/93/97		
			Stellenbosch	Warwick	Chardonnay	98/99/00
Stellenbosch	Warwick	Merlot	Merlot	98		
			Polkadraai Hills	Zevenwacht	Shiraz	Shiraz
Sauvignon blanc	00/01					

De-ionised water (conductivity between 0.06 and 0.08 mS/m) was prepared by passing distilled water (single distilled water and two ion exchange filters) through a Millipore milli-R020 system (Microsep South Africa). Water purity was verified monthly.

All glassware used in the procedure was rinsed with de-ionised water, washed with 3% nitric acid solution, rinsed three times with de-ionised water and allowed to dry in a drying oven at 80°C.

Calibration

All blank and standard solutions were prepared by means of a

solution of de-ionised water and ethanol. An ethanol concentration of 12% (v/v) was used for matrix matching of the alcohol content of the undiluted wine samples. Calibration curves were linear over four to five orders of magnitude, with a correlation coefficient of between 0.9974 and 0.9999. Calibration plots were obtained using standard solutions of 100, 200, 500, 1000 and 2000 mg/L for potassium; 10, 20, 50, 100 and 200 mg/L for sodium; and for the remaining elements: 0.01, 0.1, 1, 10 and 100 mg/l. Each standard solution was analysed twice to establish a mean value. A 12% ethanol solution was used as a sample blank.

Reference standards

Water samples of known composition, supplied by Agrilasa (Private Bag X79, Pretoria, 0001), were used as reference samples in the absence of appropriate reference material for wine samples. The water reference samples were analysed at intervals of ten wine samples.

Wine analysis

Samples were obtained by first shaking the sealed bottles, which were inverted three to four times, before the capsule and cork were removed by means of a corkscrew. The bottleneck was wiped clean by means of a paper towel and the wine (± 50 ml) was poured directly into an ICP glass sample tube after the first few millilitres of wine ("rinsing" the bottle neck) were discarded. All glass tubes as well as the sample racks were coded. The initial number of elements analysed (35) and the atomic emission lines used to determine each element are listed in Table 2. The selected elements and atomic lines were chosen in accordance with Eschnauer *et al.* (1989). The selected atomic lines are also those most frequently used for routine analysis in a variety of matrices (R. Maartens, personal communication, 2003).

All wine samples were initially subjected to qualitative analysis. After visual examination of the results, 12 elements were eliminated due to having values below the detection limits indicated as negative values (non-detection). The wine samples were re-analysed, quantifying the remaining 23 elements (Table 2, indicated in bold). Quantitative analysis was performed in duplicate. A typical analysis batch comprised 48 wine samples, one water reference sample after every tenth wine sample and one blank sample at the beginning of each batch. The quantitative data were submitted for statistical analysis. Table 3 lists the concentration levels of selected elements in South African red and white wine samples.

Statistical methods

Each variety was considered as a data set on its own. In each data set, univariate procedures (normal probability plots and Shapiro-Wilk tests) were used to test the normality assumption in each variable (element). Two-dimensional scatter plots were used to verify bivariate (elliptical shape) and multivariate normalities. These analyses indicated that normality assumption was valid.

Stepwise discriminant analysis (SDA) was used to select a subset of variables from the initial 23 variables. The subset of vari-

TABLE 2
Selected elements with atomic lines for qualitative and quantitative analysis.

Element	Atomic line (nm)	Element	Atomic line (nm)	Element	Atomic line (nm)
Ag	328.07	Fe	259.94	Pt	265.94
Al	396.15	K	769.90	Sb	252.85
As	188.97	La	408.67	Se	196.09
Au	267.59	Li	670.78	Si	251.61
B	208.95	Mg	285.21	Sn	189.92
Ba	455.51	Mn	257.61	Sr	407.77
Be	234.86	Mo	202.03	Tl	334.94
Ca	317.933	Na	589.59	V	292.46
Cd	214.43	Ni	231.60	Y	371.03
Co	228.61	P	214.91	Zn	213.85
Cr	267.71	Pb	220.35	Zr	343.82
Cu	324.76	Pd	340.45		

TABLE 3
Mean concentrations of selected elements in South African red and white wines (including minimum, maximum and standard deviations).

White wine (n = 50)					Red wine (n = 53)				
Element	Mean (mg/L)	S. D.	Min. (mg/L)	Max. (mg/L)	Element	Mean (mg/L)	S. D.	Min. (mg/L)	Max. (mg/L)
Mg	67.9557	18.143	38.481	101.150	Na	8.226	4.191	0.655	18.855
B	0.297	0.087	0.166	0.492	Mg	67.382	13.132	43.890	95.32
Al	0.392	0.147	0.215	0.886	K	1605.127	286.354	730.300	2449.23
Se	0.225	0.172	0.020	0.990	Sr	0.391	0.145	0.159	0.720
Sn	0.067	0.092	0.011	0.620	Fe	0.260	0.189	0.065	0.578
Ba	0.053	0.022	0.025	0.119	Cu	0.096	0.076	0.001	0.289
					Zn	0.310	0.192	0.030	0.571
					P	2.282	0.706	0.656	4.082
					Al	0.329	0.149	0.018	0.648
					Ba	0.095	0.058	0.033	0.251

S. D. = standard deviation; Min. = minimum; Max. = maximum; n = number of samples.

ables contained those elements which best differentiate or discriminate between geographic origins. SDA is considered a preliminary analysis and the resulting subset of elements from SDA was used in canonical discriminant analysis (CDA) and linear discriminant analysis (LDA).

Canonical discriminant analysis is a parametric dimension-reduction technique related to principal component analysis. CDA discriminates between a given set or group (geographic origin), based on a few linear combinations of variables (elements). These linear combinations are known as canonical variables, which can be plotted on an axis to obtain a two-dimensional graph, which depicts the discrimination between groups. The first two canonical variables are normally plotted against each other, since they account for the most significant discrimination between groups. CDA was applied to data for each variety using the subset of discriminating variables identified by SDA.

Linear discriminant analysis is also a parametric technique used to differentiate between groups. LDA provides a discrimination function, which makes it a useful tool for classification purposes (Srivastava & Carter, 1983). LDA was performed on the same data set as the CDA, using the same variables. Where discrimination between groups is possible, LDA will classify the data into the correct groups, and consequently obtain its classification accuracy.

All the statistical analyses in this study were done using Statistical Analysis System (SAS) Base and Stats, version 8.2 (SAS Institutes, 1999).

RESULTS AND DISCUSSION

Quality control

Regular participation in an inter-laboratory water, soil, and plant (leaf) quality assurance scheme (also known as "Agrilasa"-Private Bag X79, Pretoria, 0001) confirmed the competency of the laboratory and the reliability of results.

Statistical analysis

SDA identified thirteen discriminant elements (variables) which had the most effective discriminatory powers and that provided the best combinations for subsequent analysis (Table 4). According to Krzanowski (1987), the F-values could be used as indicators for inclusion in the subset, even though the probabilities of the F-values are not significant. Krzanowski suggests using the largest F-values for inclusion. It is known that key elements among chemical data sets may offer an increased reliability. Usually, a sample-to-variable ratio higher than 3 is ideal (Kwan & Kowalski, 1978). Owing to the low ratio in this study, selecting those which had exhibited high F values, determined by the initial one-way analysis of variance, reduced the number of variables.

The selected variables of all seven varieties were subjected to CDA and LDA to establish whether discrimination between wines regions could be achieved. Results of CDA are discussed for each variety separately.

Canonical discriminant analysis

Pinotage

Total dispersion of 100% was defined with the first two canonical functions. (Eigenvalues for the two functions were 29.5744 and 2.5158 and the canonical correlations were 0.98 and 0.85, respectively). The total canonical structure coefficients of the two func-

tions were: K (canonical variable 1 (Can 1) = 0.410373 and canonical variable 2 (Can 2) = -0.220561); Mg (Can 1 = 0.475670 and Can 2 = 0.000039); Zn (Can 1 = 0.453714 and Can 2 = -0.088616); Fe (Can 1 = -0.162982 and Can 2 = 0.634389).

The discriminant analysis was carried out taking into account the elements evaluated for Pinotage and the graphical representation shown in Figure 1 yielded a pattern of point-distribution in which it distinguished three groups, corresponding to the wine cellars within the three localities. Magnesium and Zn had the highest total canonical structure coefficients on the first canonical variable, and were most likely responsible for the discrimination between geographic origins in the direction of canonical variable 1. Iron had the highest total canonical structure coefficient on the second canonical variable and was therefore most likely responsible for the discrimination between geographic origins in the direction of canonical variable 2.

Merlot

Canonical variables 1 and 2 explained 74.56% of the total dispersion. (Eigenvalues for the two functions were 16.1816 and 6.3011 and the canonical correlations were 0.97 and 0.93, respectively.) The total canonical structure coefficients of the two functions were: Na (Can 1 = 0.00781 and Can 2 = -0.341289); Ba (Can 1 = 0.797452 and Can 2 = 0.089579); K (Can 1 = -0.385510 and Can 2 = 0.614726); Cu (Can 1 = 0.515097 and Can 2 = -0.318446); P (Can 1 = -0.387246 and Can 2 = -0.456687); Zn (Can 1 =

TABLE 4

Summary of the variables (including F, R² and P-values) that best discriminate between wine regions, districts and wards for each grape variety obtained from SDA for use in CDA and LDA.

Cultivar	Discriminating variables	R ²	F-values	P-values
Chardonnay	B	0.7858	10.40	<0.0001
	Sn	0.4835	2.03	0.1343
Chenin blanc	Sn	0.9602	120.77	0.0001
	Mg	0.8933	50.21	0.0004
	Ba	0.8889	32.01	0.0048
Sauvignon blanc	B	0.9473	65.91	<0.0001
	Al	0.8909	27.22	<0.0001
	Mg	0.6045	4.59	0.0327
Cabernet Sauvignon	Mg	0.8696	11.67	0.0032
	K	0.7974	4.92	0.0553
	Fe	0.7178	3.81	0.0709
	Ba	0.6961	7.45	0.0024
Merlot	Cu	0.6364	4.81	0.0172
	K	0.6074	4.464	0.0170
	P	0.5849	3.52	0.0483
	Zn	0.5719	3.01	0.0785
	Fe	0.5503	2.45	0.1309
	Sr	0.5191	2.16	0.1645
	Mg	1.000	Infy	<0.0001
Pinotage	K	1.000	Infy	<0.001
	Zn	1.000	31006	0.004
	Fe	1.000	89129	0.0024
	Al	0.9999	73.74	0.0053
Shiraz	K	1.000	52.09	0.0012
	Mg	0.9533	188.53	0.0053

R² = R squared; P = probability of the F-value;
F = statistics of decision-making criteria.

-0.256775 and Can 1 = 0.529199); Fe (Can 1 = 0.190121 and Can 2 = -0.189791); Sr (Can 1 = 0.281895 and Can 2 = -0.000647).

The discriminant analysis, carried out considering the elements evaluated for Merlot, with graphical representation shown in Figure 2, yielded a pattern of point-distribution in which it distinguished four groups, corresponding to the wine cellars within the four localities. Barium and Cu had the highest total canonical structure coefficients on the first canonical variable, and were most likely responsible for the discrimination between geographic origins in the direction of canonical variable 1. Potassium and Zn had the highest total canonical structure coefficients on the second canonical variable and were therefore most likely responsible for the discrimination between geographic origins in the direction of canonical variable 2.

Shiraz

Total dispersion of 99.68% was defined in the first two canonical functions. (Eigenvalues for the two functions were 569.5975 and 12.9652 and the canonical correlations were 0.99 and 0.96, respectively.) The total canonical structure coefficients of the two functions were: Al (Can 1 = 0.882429 and Can 2 = 0.449864); K (Can 1 = 0.958163 and Can 2 = -0.207922); Mg (Can 1 = 0.755006 and Can 2 = 0.620423); Na (Can 1 = 0.650768 and Can 2 = 0.285703).

The discriminant analysis was carried out taking into account the elements evaluated for Shiraz. The graphical representation shown in Figure 3 yielded a pattern of point-distribution in which it distinguished four groups, corresponding to the wine cellars within the four localities. Aluminium and K had the highest total canonical structure coefficients on the first canonical variable, and were most likely responsible for the discrimination between geographic origins in the direction of canonical variable 1. Although Mg showed the highest total canonical structure coefficient on the

second canonical variable, the first eigenvalue indicated that the discrimination was primarily on the first canonical variable.

Cabernet Sauvignon

Canonical variables 1 and 2 explained 99.70% of the total dispersion (Eigenvalues for the two functions were 27.2419 and 3.3529 and the canonical correlations were 0.98 and 0.87, respectively.) The total canonical structure coefficients of the two functions were: Mg (Can 1 = 0.941335 and Can 2 = 0.088585); Fe (Can 1 = 0.749908 and Can 2 = 0.334620); K (Can 1 = 0.622417 and Can 2 = 0.614181).

The discriminant analysis was carried out taking into account the elements evaluated for Cabernet Sauvignon. The graphical representation shown in Figure 4 yielded a pattern of point-distribution in which it distinguished five groups, corresponding to the wine cellars within the five localities. Magnesium and Fe had the highest total canonical structure coefficients on the first canonical variable, which were most likely responsible for the discrimination between geographic origins in the direction of canonical variable 1. Note that the Stellenbosch cellars can only be distinguished by the second canonical variable, which was most likely due to the relatively high canonical structure coefficient of K.

Sauvignon blanc

Canonical variables 1 and 2 explained 99.95% of the total dispersion (Eigenvalues for the first canonical variable was 82.9891 and 3.997 for the second and the canonical correlation was 0.99 and 0.89, respectively.) The total canonical structure coefficients of the two functions were: Al (Can 1 = 0.572483 and Can 2 = 0.791756); B (Can 1 = 0.888081 and Can 2 = -0.458201); Mg (Can 1 = 0.968144 and Can 2 = -0.089245).

The discriminant analysis was carried out taking into account the elements evaluated for Sauvignon blanc. The graphical representa-

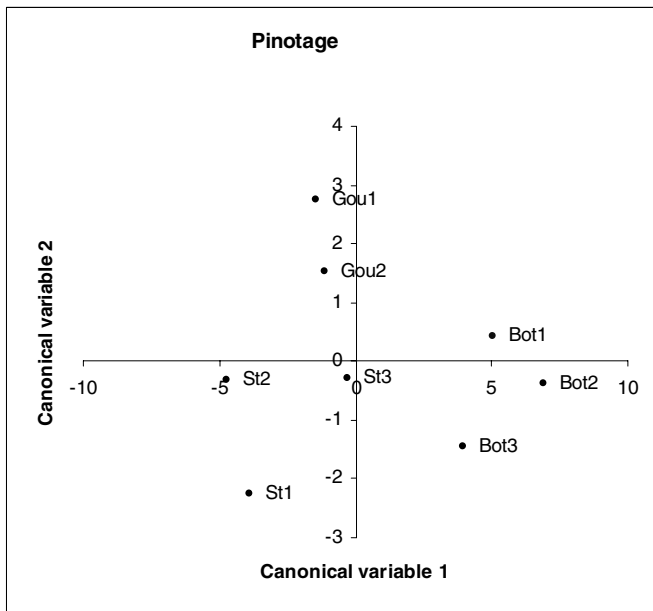


FIGURE 1

Plots of the first two canonical variables for Pinotage showing separation of wines from Bottelary, Goudini and Stellenbosch areas on the basis of Mg, K, Zn and Fe (Bot = Bottelary; Gou = Goudini; St = Stellenbosch, includes Simonsberg-Stellenbosch).

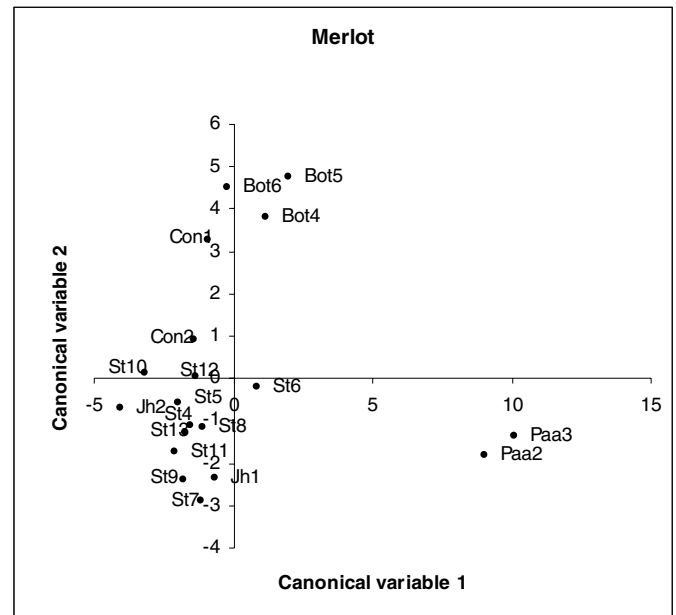


FIGURE 2

Plots of the first two canonical variables for Merlot, showing separation of wines from Bottelary, Constantia, Jonkershoek and Paarl areas on the basis of Na, Ba, K, Cu, P, Zn Fe and Sr (Bot = Bottelary; Con = Constantia; Paa = Paarl, includes Voor-Paardeberg; St = Stellenbosch, includes Simonsberg-Stellenbosch; Jh = Jonkershoek).

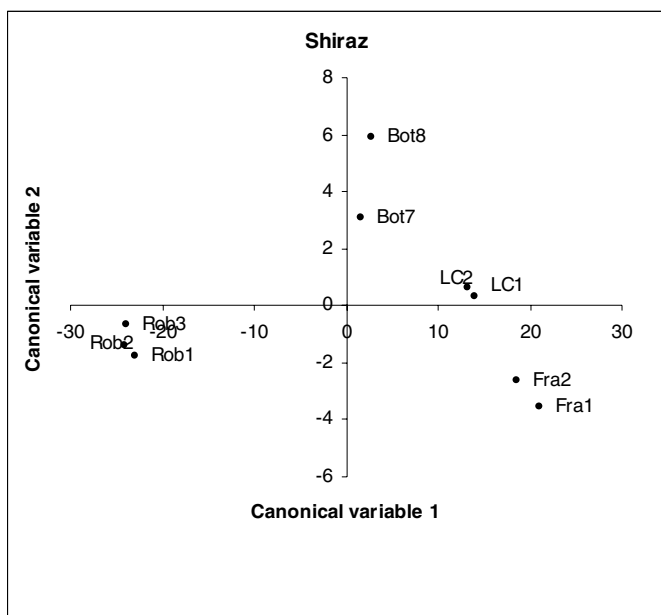


FIGURE 3

Plots of the first two canonical variables for Shiraz showing separation of wines from Bottelary, Franschhoek, Le Chasseur and Robertson areas on the basis of Al, K, Mg and Na (Bot = Bottelary; Fra = Franschhoek; LC = Le Chasseur; Rob = Robertson, includes Ashton).

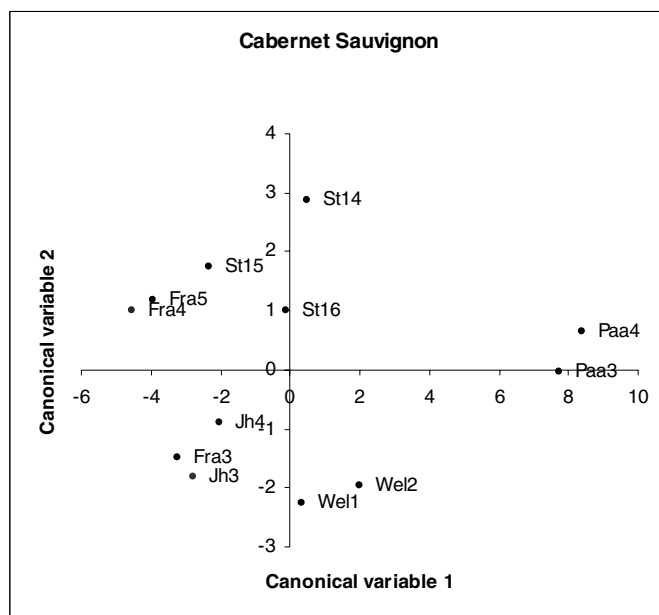


FIGURE 4

Plots of the first two canonical variables for Cabernet Sauvignon showing separation of wines from Paarl, Wellington, Stellenbosch, Franschhoek and Jonkershoek areas on the basis of Fe, K and Mg (Fra = Franschhoek; Paa = Paarl; St = Stellenbosch; Jh = Jonkershoek; Wel = Wellington).

tion shown in Figure 5 yielded a pattern of point distribution in which it distinguished three groups, corresponding to the wine cellars within the three localities. Magnesium and B had the highest total canonical structure coefficient on the first canonical variable, and were most likely responsible for the discrimination between geographic origins in the direction of canonical variable 1.

Chardonnay

Canonical variables 1 and 2 explained 93.32% of the total dispersion (Eigenvalues for the two variables were 8.3059 and 3.9140 and the canonical correlations were 0.94 and 0.89, respectively.) The total canonical structure coefficients of the two functions were: B (Can 1 = -0.202207 and Can 2 = 0.940302); Se (Can 1 = 0.959823 and Can 2 = 0.279584); Sn (Can 1 = 0.118957 and Can 2 = -0.623062).

The discriminant analysis was carried out taking into account the elements evaluated for Chardonnay. The graphical representation shown in Figure 6 yielded a pattern of point-distribution in which it distinguished seven groups corresponding to the wine cellars within the seven localities. Selenium had the highest total canonical structure coefficient on the first canonical variable and was most likely responsible for the discrimination between geographic origins in the direction of canonical variable 1. Boron had the highest total canonical structure coefficient on the second canonical variable and was most likely responsible for the discrimination between geographic origins in the direction of canonical variable 2.

Chenin blanc

Because there were only two origins, there is only one canonical variable for this dataset (eigenvalue for the variable was 2120.3194 and the canonical correlation was 0.99). The total canonical structure coefficients of this one function were: Mg (Can 1 = 0.945342); Sn (Can 1 = 0.225391 and Ba Can 1 =

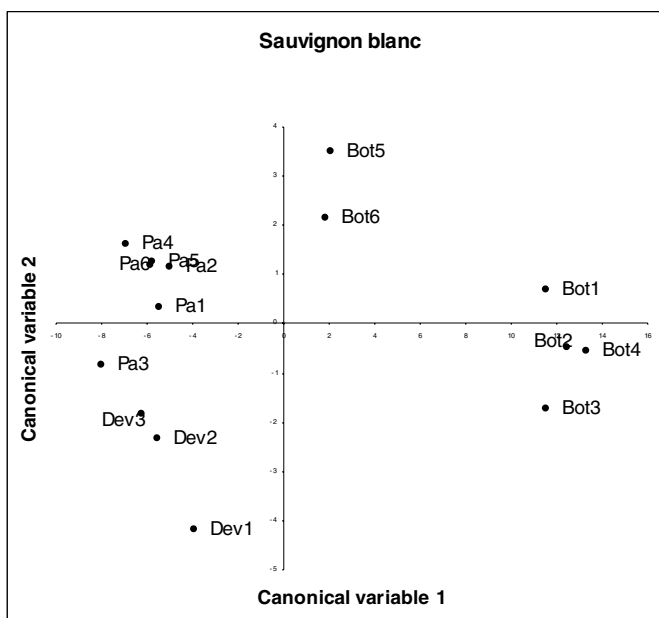


FIGURE 5

Plots of the first two canonical variables for Sauvignon blanc showing separation of wines from Bottelary, Paarl and Devon Valley areas on the basis of Al, B and Mg (Bot = Bottelary; Pa = Paarl; Dev = Devon Valley).

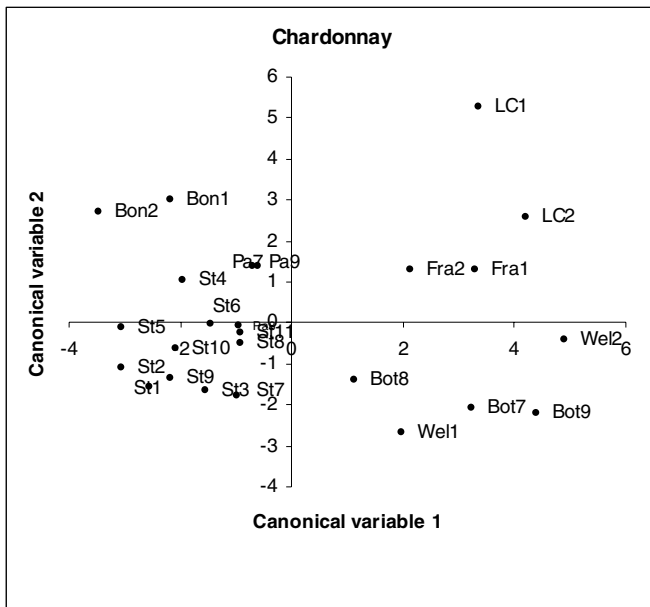


FIGURE 6

Plots of the first two canonical variables for Chardonnay showing separation of wines from Bonnievale, Bottellary, Franschhoek, Le Chasseur, Paarl, Stellenbosch and Wellington areas on the basis of B, Se and Sn (Bon = Bonnievale; Bot = Bottellary; Fra = Franschhoek; LC = Le Chasseur; Pa = Paarl, includes Voor-Paardeberg; St = Stellenbosch, includes Voor-Paardeberg; Wel = Wellington).

0.844440). For graphical representation, we have plotted canonical variable 1 against a constant 1. This plot enables us to see the differentiation between Paarl and Stellenbosch.

The discriminant analysis was carried out taking into account the elements evaluated for Chenin blanc. The graphical representation shown in Figure 7 yielded a pattern of point-distribution in which it distinguished two groups, corresponding to the wine cellars within the two localities. Magnesium and Ba had the highest total canonical structure coefficient on the first canonical variable and were most likely responsible for the discrimination between geographic origins in the direction of canonical variable 1. Tin (Sn) had a high F-value (Table 4), but was not included as a discriminating variable (Figure 7).

To summarise, the CDA results clearly indicate the possibility of separating wines from different geographic origins, using a selected subset of variables. Differentiation between wine regions was also attempted, using LDA on the same set of variables as for CDA.

Linear discriminant analysis

The results of LDA are given in Tables 5 and 6.

Although differentiation accuracies using LDA were poor between certain geographic origins (Tables 5 and 6), LDA has shown the possibility of separating geographic origins.

General

This study has illustrated how a small number of variables related to chemical composition of wines of different varieties can be used to establish a link between element composition and the geographic origin of the wine. On the other hand, the fact that such a differentiation is possible, despite varying cultural practices and winemaking procedures, indicates that even though

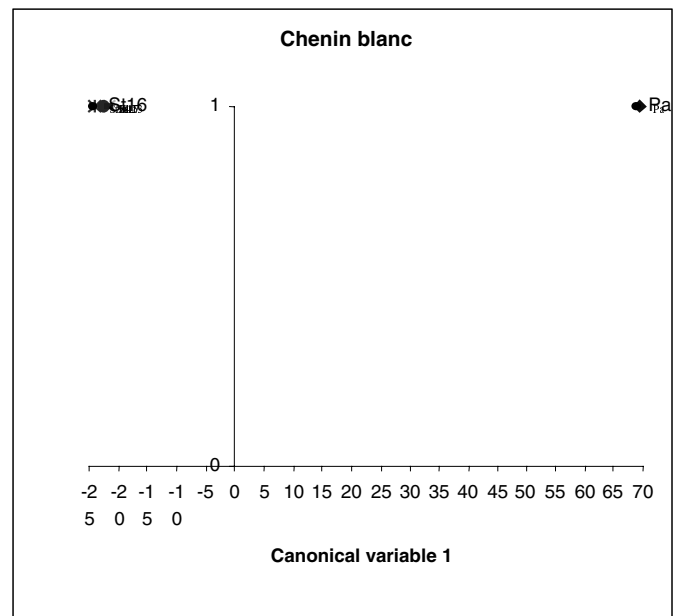


FIGURE 7

Plots of the first two canonical variables for Chenin blanc showing separation of wines from Paarl and Stellenbosch areas on the basis of Mg, Sn and Ba (Pa = Paarl; St = Stellenbosch, includes Simonsberg-Stellenbosch).

these two contributors are important, they do not have a definite influence on wine origin differentiation.

The elements Sn, Mg, K, Zn, Fe and Na were found to be highly discriminative with both CDA and LDA. Organic fertilisers may cause a fluctuation in the content of Na in wines; however the high F-values of Na exclude the influence of individual variations in fertilising practices, but include the possibility of regional differences (Maarse *et al.*, 1987; Latorre *et al.*, 1994). Sodium may therefore be less stable for differentiation purposes in the long term. Maarse *et al.* (1987) mentions the influence of processing conditions on the Fe content of wines. The high F-values of Fe do not indicate a significant variation within regions, due to processing conditions. One cannot expect to find major regional differences in wine processing techniques, which could influence the Fe content of these wines. Consequently, the differences observed in F-values for this element may be ascribed to variations in soil conditions. Similarly, the high F-values for K are not indicative of wine processing techniques, but rather indicate a source of variation in soil type (J. Wooldridge, personal communication, 2005).

Frias *et al.* (2003) stated that a number of authors list K, Mg, Mn, Na, Ca, Li, Rb, Cr, Fe, Zn, Ag, P, Co, Cs, Ba, Sr, B, Ti and Al as useful elements for wine classification. It was found that K and Mg were used in five previous studies, Na in four studies, Fe and Zn in three studies, P in two studies, while Ba, Sr and Al were used in one study. Thus, in addition to the elements listed by Frias *et al.* (2003) discriminant analyses resulting from this study indicated that Se, Sn, Zn and Cu could also be used in differentiating between geographical origins. In this study, nine of the elements correspond with Frias' findings. Boron, Mg, Ba, Sn and Se are especially valuable for discriminating between geographical ori-

TABLE 5

Percentage correctly classified Cabernet Sauvignon (with variables; Mg, K, Fe), Shiraz (with variables; Na, Al, K, Mg), Merlot (with variables; Na, Ba, Cu, K, P, Zn, Fe, Sr) and Pinotage (with variables; Mg, K, Zn, Fe), using LDA.

Grape variety	Origin	n	Classification success
Shiraz	¹ Robertson	3	3/3
	Franschhoek	2	2/2
	Bottelary	2	0/2
	Le Chasseur	2	0/2
Total correct classification (%)			55
Merlot	Constantia	2	1/2
	Jonkershoek	2	0/2
	Bottelary	3	3/3
	² Paarl	2	2/2
	³ Stellenbosch	10	7/10
Total correct classification (%)			68
Pinotage	Bottelary	3	1/3
	Goudini	2	0/2
	³ Stellenbosch	3	2/3
Total correct classification (%)			38
Cabernet Sauvignon	Franschhoek	3	2/3
	Paarl	2	1/2
	Stellenbosch	3	2/3
	*Jonkershoek	2	2/2
	Wellington	2	2/2
Total correct classification (%)			75

n=Number of wine samples for each geographic origin; ¹Robertson: includes Ashton; ²Paarl: includes Voor-Paardeberg; ³Stellenbosch: includes Simonsberg-Stellenbosch; *Jonkershoek, which is part of Stellenbosch, was considered a separate origin (Ward) due to its topography.

gins in white wine varieties. This conclusion was drawn from the significantly higher total canonical structure coefficients. Magnesium, Zn, Fe, Ba, Cu, K, Na and Al played the dominant roles in discriminating between geographical origins in red wine varieties. The possibility that Cu and Zn may have originated from fungicides is very unlikely, because grapes are normally sprayed 21 days prior to harvest.

It is unclear as to whether the elements considered, although significant by the classification methods, provide indications of the structure of the population of the region of origin, or only the random samples analysed. However, these results indicate that, under the prevalent conditions at the time of the study, with the relatively small number of samples used, differentiation of Western Cape wines according to geographic origin was possible using element concentrations.

Although the discriminating elements may only be valid for the test set under study, examination of the data does allow a certain number of elements to be identified as common variables.

TABLE 6

Percentage correctly classified Chardonnay (with variables; Se, B, Sn), Chenin blanc (with variables; Sn, Mg, Ba) and Sauvignon blanc (with variables; B, Al, Mg) using LDA.

Grape variety	Origin	n	Classification success
Chardonnay	Bonnievale	2	2/2
	Bottelary	3	2/3
	Franschhoek	2	0/2
	Le Chasseur	2	1/2
	¹ Paarl	3	3/3
	² Stellenbosch	11	9/11
	Wellington	2	0/2
Total correct classification (%)			68
Chenin blanc	Paarl	2	2/2
	² Stellenbosch	2	2/2
Total correct classification (%)			100
Sauvignon blanc	Bottelary	6	6/6
	Devon Valley	3	3/3
	Paarl	6	5/6
Total correct classification (%)			93

n=Number of wine samples for each geographic origin; ¹Paarl: includes Voor-Paardeberg; ²Stellenbosch: includes Simonsberg-Stellenbosch.

CONCLUSIONS

The aim of this study was to differentiate between the geographic origins of wines produced in the Western Cape on the basis of their element composition. Thirteen elements were quantified by means of ICP-AES to classify red and white wines from the Western Cape. Simple inspection of the elemental concentrations could not be used to differentiate the origin; however, multivariate analyses were able to detect similarities between wines according to origin and grape variety. By applying CDA, wines from the Western Cape could be differentiated using only Mg, K, Fe, Zn, Ba, Sn, B, Al, Se, Cu, P, Na and Sr.

The results should be considered as preliminary, due to the small number of samples analysed for certain wine grape varieties and geographic regions. A more comprehensive number of wine samples would facilitate the establishment of the elemental contents which are reproducibly influenced by the factors in vine growth, soil type, grape variety and the wine making processes, and the elements that are not influenced at all.

It would be valuable to both the producers and the authorities to extend this evaluation of the elemental content of South African wines by obtaining completely new and representative samples from additional locations and to establish whether the results can be repeated or improved. In addition, the analysis of the elemental content of wine needs to be applied to wines from other regions, apart from the Western Cape Province, to comprehensively evaluate the statistical procedure.

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