

Multielement Analysis of Canadian Wines by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Multivariate Statistics

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Trace element fingerprints were deciphered for wines from Canada's two major wine-producing regions, the Okanagan Valley and the Niagara Peninsula, for the purpose of examining differences in wine element composition with region of origin and identifying elements important to determining provenance. Analysis by ICP-MS allowed simultaneous determination of 34 trace elements in wine (Li, Be, Mg, Al, P, Cl, Ca, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Mo, Ag, Cd, Sb, I, Cs, Ba, La, Ce, Tl, Pb, Bi, Th, and U) at low levels of detection, and patterns in trace element concentrations were deciphered by multivariate statistical analysis. The two regions were discriminated with 100% accuracy using 10 of these elements. Differences in soil chemistry between the Niagara and Okanagan vineyards were evident, without a good correlation between soil and wine composition. The element Sr was found to be a good indicator of provenance and has been reported in fingerprinting studies of other regions.

KEYWORDS: Wine analysis; fingerprinting; provenance; trace element; inductively coupled plasma mass spectrometry; multivariate analysis

INTRODUCTION

Various studies indicate that trace element patterns can be used to fingerprint wines and that these patterns, at least in part, reflect the provenance, or region of origin, of wines (1–7). Given that many countries, including Canada, have labeling requirements that certify the geographic origin of grapes used in wine, fingerprinting could have both legal and regulatory utility. The ability to discriminate wines by region suggests trace element composition is influenced by regional environmental factors such as soil chemistry and regional geology, although viticultural practices and processing methods also have a strong effect on the concentrations of some elements (8, 9).

The two major wine-growing regions in Canada are the Niagara Peninsula in Ontario and the Okanagan Valley in British Columbia. The Vintner's Quality Alliance (VQA) is an Appellation of Origin system in which British Columbia and Ontario wines are certified and labeled according to region of origin, vineyard of origin, and grape variety. This study of wine provenance by fingerprinting Canadian wines was intended to further verify the use of trace element patterns for regional identification. The relationship between trace element composi-

tion and provenance was further examined by identifying important fingerprint elements in this and other studies and by examining the relationship between soil chemistry and wine composition.

Although higher precision instruments have been used for trace element (10, 11) and isotope ratio (12–14) determination in wine, quadrupole ICP-MS analysis of wine samples allows the determination of multiple elements with sufficiently low detection limits. Problems with plasma instability related to the ethanol content in wine were minimized by a simple 1:1 dilution with HNO₃ (1), eliminating the loss of volatile elements that would occur when samples are digested. The use of multivariate statistics has been reported in several studies (1–7) and provides a sophisticated discrimination of wine regions compared to the use of single-element concentrations.

MATERIALS AND METHODS

Materials. A sample set of 95 wines was obtained, 59 samples from 26 vineyards in the Okanagan Valley and 36 samples from 17 vineyards on the Niagara Peninsula. All of the wines sampled for the study were made from grapes grown on a single plot of land, and the soil was sampled from the corresponding vineyard plots. To reduce the effects of varietal differences, wines made from the most commonly grown varieties of white *Vitis vinifera* grapes were chosen preferentially, which include Riesling, Pinot Blanc, Chardonnay, and Gewurztraminer, but due to limitations of sampling, other varieties were also included. Vineyard soils from the Niagara region are classified as alfisols, which

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Table 1. Optimal ICP-MS Operating Conditions for Analysis of Diluted Wine Samples

instrument parameter	condition
RF power	1500 W
carrier gas (inner)	1.00 L/min
auxiliary gas (intermediate)	0.82 L/min
plasma gas flow (outer)	14 L/min
peristaltic pump (sample uptake)	0.4 mL/min
spray chamber temperature	2 °C
extract 1	-220 V
extract 2	-98 V
einzel 1,3	-100 V
einzel 2	-38 V
quadrupole focus	9 V

have a subsurface layer of silicate clay accumulation. Soils from the more arid Okanagan region are classified as inceptisols, due to their weakly developed subsurface horizons, with some mollisols, which are grassland soils, in the north of the valley.

Analytical Methods. Wines were diluted 1:1 with 0.2 mol/L HNO₃ and analyzed for 34 elements using a quadrupole ICP-MS (4500 series, Agilent, U.K.) with a concentric nebulizer, following a procedure similar to that of Baxter et al. (1). The dilution reduces the concentration of ethanol from 10–12% in the wine to 5–6%, diminishing matrix effects and plasma instability associated with introducing ethanol into the plasma (15), but maintains the concentrations of most elements above instrument detection limits. Optimal operating conditions of the ICP-MS are given in **Table 1**. The high radio frequency power (1500 W) helped maintain a stable plasma in the presence of ethanol (16), and the plasma gas flow rate was increased to 14 L/min because of the higher power used. Replicate analyses of two in-house reference wines monitored precision over a 5 month period, and five water reference materials [T-123, T-127, T-129, and T-135 (USGS) and AMW-3(DFC)] were matrix matched to the wine samples (0.1 mol/L HNO₃ and 6% ethanol) to monitor precision and accuracy, which were <5% for Cd, Sb, Ba, Tl, Pb, and U; <10% for As, Rb, Sr, Mo, Cs, La, Ce, and Th; <15% for V, Mn, Fe, Cu, Zn, Ag, and Bi; <20% for Mg, Al, Ca, Co, Ni, and Br; <25% for Li, Be, Ti, Se, and I; and 27% for Cl and P. The limit of detection (LOD) was estimated as 3 times the standard deviation (SD) of the blank divided by sensitivity and mean sample dilution factor.

Soil was sampled from five to eight sites within each vineyard plot at a depth of 0.3–0.5 m. The subsoil was sampled to reduce the effects of fertilizers and variable organic matter content in the topsoil on trace element concentrations. Soils were air-dried, sieved to <2 mm grain size, and combined by weight to form a composite sample of each vineyard plot. A subsample was then sieved (unground) to <0.074 mm grain size (200 mesh) for each vineyard. This size fraction contains primarily clay-size particles, which strongly adsorb trace elements, and was analyzed to accentuate patterns in wine fingerprint elements. For 20 samples, the <2 mm sample was ground to 0.074 mm and analyzed as well, to ensure biases were not imposed by different particle size distributions in the two regions. Both grain sizes were prepared as pressed pellets and analyzed by X-ray fluorescence for 30 elements (Na₂O, MgO, Al₂O₃, SiO₂, P₂O₅, S, Cl, K₂O, CaO, Sc, TiO₂, V, Cr, MnO, Fe₂O₃, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Zr, Nb, Ba, Ce, Pb, Th, and U) according to the procedure (17), which provides an efficient method of determining total concentrations of multiple elements in soil. The XRF instrument was a Fisons/ARL model 8420+ sequential wavelength-dispersive X-ray spectrometer, with an Rh anode end-window X-ray tube operated at 3 kW, with the instrument conditions shown in Longerich (17). Precision and accuracy were monitored with geological reference materials [AGV-1 (andesite, USGS), DNC-1 (diabase, USGS), JG-2 (granite, JGS), and BCR-1 (basalt, USGS)] and are better than ±2% for all elements except Cl, As, and Pb, which are better than ±5%.

Data Analysis. Wine element concentrations were examined by graphical and statistical analysis to discriminate wine by region. Scatterplots of element concentrations in wines were made for the entire data set to determine which elements were important to a regional fingerprint. Multivariate statistical analysis was then performed with

Systat version 6.1. Because multivariate statistical methods, which were used in the fingerprint analysis, assume a normal data distribution and are easily skewed by outliers (18), element concentrations in wines were log transformed to better fit a normal distribution and reduce the extremity of outliers. For the untransformed data the relative standard deviation is constant, but with log transformation the standard deviation becomes constant, which meets the assumptions of parametric statistical analyses. Log transformation also reduces the relative distribution of data, so that elements of higher abundance are brought into the same range as elements of lower abundance, which is important when elements of different abundance are included in the same analysis.

Principal component analysis (PCA) was used to examine structures in the wine data. With this analysis, matrix decomposition reduces a large number of variables into a smaller set of dimensions by analyzing the interrelationships between variables. The components give the best linear combination of variables, that is the combination of variables which accounts for more of the variance than any other combination (19). The value of the loading in a component (between 0 and 1) describes the magnitude of the contribution of the component (e.g., element), whereas the sign (positive or negative) of the loading describes whether the variable is positively or negatively correlated to the component (20).

Rotation of the component matrix redistributes the variance to achieve a different component pattern, ideally where loadings are high for a few variables and low for all other variables in the analysis, to give a clear grouping of variables. Varimax rotation was used to maximize the variance of the normalized component loadings. The total variance explained by each component is determined by an eigenvalue, which is reported as a percentage.

Discriminant analysis was applied to the data, where region (Okanagan or Niagara) was defined as the dependent categorical variable, and log transformed element concentrations were used as the independent variables. Discriminant analysis derives linear combinations of the independent variables that best discriminate between the defined groups, by maximizing between-group variance relative to within-group variance. Discriminant analysis using a low ratio of samples to variables creates an unstable model, and analysis is also weakened by the inclusion of correlated elements, which cause the model to become less robust. The statistical significance of each variable's (element's) ability to distinguish between groups (wine regions) is indicated by an *F* statistic, and the correlation of each variable to all other variables in the model is indicated by a tolerance value. A small tolerance value indicates that the variable is redundant, or highly correlated with other element(s) in the matrix, in which case matrix ill-conditioning problems can occur (18). An element was eliminated from the model if the corresponding *F* statistic was low or if the tolerance value (between 0 and 1) was small.

Regional differences in soil composition were determined by scatterplots of element concentrations. Pearson's *R* correlations between element concentrations in wine and soil were determined and examined graphically, to aid in the interpretation of the geological source of the fingerprints.

RESULTS AND DISCUSSION

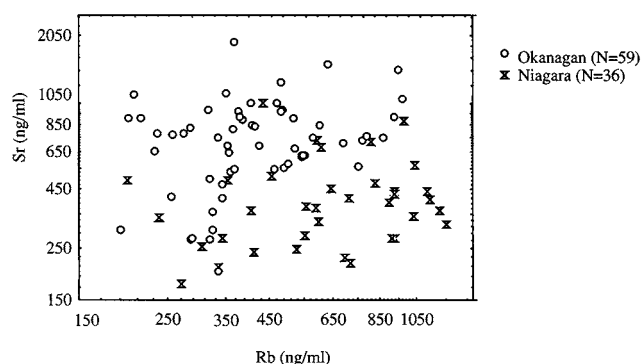
Mean element concentrations, with standard deviations, for the two wine regions are given in **Table 2**, along with method limits of detection. There is some overlap in the range of all wine element concentrations between the two regions (**Table 1**), although scatterplot analysis of element concentrations shows the elements Sr and Rb to be discriminating of wine region (**Figure 1**). These elements have been found to be useful discriminating elements in other regions [Sr (1, 3, 7) and Rb (2, 5)]. Isotope ratios of Sr in wine have also been used as an indicator of provenance and reflect Sr ratios of the soil (12, 14), which suggests the isotope ratios of this element are insignificantly affected by wine-processing practices.

Principal component analysis (PCA), using VARIMAX rotation, was applied to the log transformed element concentrations to analyze the correlation between elements in wine, with

Table 2. Limits of Detection (LOD) and Mean Concentrations (in Parts per Billion except As Noted) and Standard Deviations (SD) of Elements in Wine from the Okanagan Valley and Niagara Peninsula

element	LOD	Okanagan mean concn (N = 59)	SD	Niagara mean concn (N = 36)	SD
Li	0.017	7.42	5	6.64	6.79
Be	0.002	0.27	0.27	0.48	0.4
Mg ^a	0.01	61	24	55	11
Al	1.4	307	280	834	440
P ^a	0.15	116	80	116	75
Cl ^a	2.5	15	13	30	24
Ca ^a	0.06	76	40	90	32
Ti	0.24	7.1	5	18.3	11
V	0.03	10	20	50	52
Mn ^a	0.0001	0.7	0.3	1.42	0.74
Fe ^a	0.004	1.08	0.8	2.55	1.57
Co	0.002	2.27	1.2	4.02	1.82
Ni	0.16	21	28	25	12
Cu	0.26	55	80	133	229
Zn	0.45	463	300	787	488
As	0.05	2.97	2.7	7.89	6.7
Se	0.8	1.51	1.6	1.34	0.71
Br	0.1	179	70	313	192
Rb	0.08	446	190	680	296
Sr	0.013	766	320	420	194
Mo	0.03	7.9	9	12.4	15.4
Ag	0.013	0.014	0.012	0.021	0.03
Cd	0.004	0.47	0.9	0.67	0.54
Sb	0.005	0.39	0.3	1.42	1.22
I	0.09	2.29	1.5	5.56	3.68
Cs	0.005	1.25	0.8	3.15	2
Ba	0.05	140	100	115	57
La	0.0004	0.37	0.5	1.33	1.57
Ce	0.0005	0.77	1.0	2.56	3.16
Tl	0.002	0.111	0.00	0.225	0.1
Pb	0.03	11.8	9	28.2	22.1
Bi	0.008	0.238	0.4	0.172	0.159
Th	0.001	0.106	0.13	0.147	0.193
U	0.001	0.57	1.2	0.69	0.63

^a Concentration in parts per million.

**Figure 1.** Regional discrimination of Sr and Rb concentrations in wine, using a logarithmic scale.

the component loadings given in **Table 3**. The number of components was chosen by examination of a scree plot (eigenvalues vs components), where components were retained until the decrease in eigenvalue with component number became insignificant. Six elements (P, Cl, Ca, Fe, Br, and La) were excluded from the analysis because they did not contribute significantly in any of the components, had a high analytical uncertainty, or had concentrations that are expected to be strongly influenced by processing, making the element a poor discriminator of region. Five of these elements, P, Cl, Br, Ca, and Fe, loaded moderately high in several components and were removed from the analysis. These elements had a poor precision

in the ICP-MS determination, due to low ionization potential (Cl and Br) and the presence of polyatomic background species of the same mass (P, Ca, and Fe). The halide elements can also be introduced into wines from antiseptics and anion exchangers (21), Fe concentrations are increased when wine is processed in stainless steel vats (8), and Ca concentrations are affected by precipitation from wine during aging by the formation of calcium tartrate crystals, known as “wine diamonds” (22). Due to the expected high correlation ($R = 0.99$) between Ce and La, inclusion of both elements in the analysis was redundant, and La, having the lower concentration, was removed.

Examination of the component loadings (**Table 4**) shows the first component is influenced strongly by the variables U, Ce, Th, Ti, Be, V, Bi, Al, Sb, Pb, and Co and explains 21% of the overall variance. The second component shows strong loading of the elements Zn and Cd, which reflects the similar geochemical mobilities of these elements (23) due to similar electron configurations. Component 3 shows intercorrelation between Li, Mg, and Sr, component 4 groups Tl, Cs, and Rb, and Ba and Sr load high in component 5. These elements are classified as soluble cations by their ionic potential (ratio of ionic charge to ionic radius), and the loading of these components reflects element mobility (24) and periodic similarities. Element grouping is less clear in the last five components, which contain less of the total variance. Component 6 groups Mo, As, and V; component 7 groups Se and I, and in component 8 only the element Mn loads high. Component 9, which explains 8.8% of the total variance, groups the transition metals Ni and Cu, for which concentrations in wine may be influenced by processing in stainless steel (25). The heavy metals Bi and Pb are grouped by component 10. Many of the elements grouped by PCA have similar solubility, particularly the soluble cations grouped in components 3–5, suggesting wine element concentrations are influenced by the mobility of the element in the environment.

The important elements for discriminating wine regions were determined by examining the element scatterplots and by exploratory statistics. A discriminant function was derived that classified the Niagara and Ontario wines with 100% success rate (eq 1), where elements represent log transformed concentrations.

$$14.09 + 0.54U - 0.54V - 0.90Al - 0.70Sb + 1.01Co - 0.82Zn + 1.94Sr - 1.32Rb + 0.49Mo - 1.24Mn \quad (1)$$

Wines were plotted according to this function in **Figure 2**. Elements were included and removed from the model in an iterative manner, based on their F statistics and tolerance values. The F statistics and tolerance values for the derived discriminant function (eq 1) are given in **Table 5**, examination of which shows the most important discriminating element to be Sr.

Elements that discriminate wine by region are expected to be controlled by regional environment and minimally influenced by wine-processing. Pearson's R correlations between wines and vineyard soils were derived for element concentrations and element ratios, without any strong positive correlations. Because soil data are based on total concentration and not plant-available concentration, it is likely that the speciation of many of the elements contained in the soil is not suitable for plant uptake. There is also the possibility of differential element uptake, in which plants will absorb nutrient elements from the soil preferentially compared to non-nutrient and toxic elements (26). Further complications arise from the fact that roots of grape vines tend to reach depths of several meters, and because soil samples were taken from within the top 0.3–0.5 m of the vineyard, sampling may not be an accurate representation of

Table 3. Factor Loadings Obtained from Principal Component Analysis for Log Transformed Element Concentrations in Wines Using 10 Components and VARIMAX Rotation

total variance: component:	21% 1	6.8% 2	7.4% 3	11% 4	5.6% 5	8.2% 6	5.6% 7	4.8% 8	8.8% 9	3.4% 10
U	0.92	0.11	-0.02	0.01	-0.10	0.11	-0.05	0.00	-0.01	-0.05
Ce	0.85	0.07	-0.05	0.23	0.15	0.01	0.09	-0.01	0.09	-0.01
Th	0.85	-0.04	0.01	0.07	0.01	0.00	0.04	-0.15	-0.03	-0.14
Ti	0.74	0.19	0.21	0.30	0.08	0.35	-0.02	0.20	0.09	0.05
Be	0.68	-0.33	0.17	0.29	0.05	0.08	0.15	0.10	0.31	0.07
V	0.64	0.19	0.04	0.15	0.19	0.49	0.17	0.26	0.06	0.12
Bi	0.60	-0.28	0.14	0.02	0.06	0.02	0.04	-0.04	0.07	-0.55
Al	0.60	0.01	0.04	0.45	-0.05	0.19	0.30	0.20	0.34	0.14
Sb	0.59	0.18	0.10	0.17	0.13	0.54	0.08	0.18	0.26	0.04
Pb	0.56	0.22	-0.01	0.14	-0.08	0.19	-0.04	0.07	0.44	-0.40
Co	0.55	0.06	0.17	0.47	0.09	0.19	0.24	0.10	0.35	0.26
Zn	-0.03	0.83	-0.01	0.18	0.07	0.06	-0.04	0.14	0.19	0.11
Cd	0.16	0.79	0.02	0.12	-0.07	0.02	0.27	-0.02	0.22	-0.07
Li	0.15	-0.12	0.86	0.02	0.03	0.20	0.15	-0.07	-0.03	-0.16
Mg	0.04	0.13	0.84	0.10	-0.30	0.01	-0.01	0.12	0.11	0.15
Sr	-0.16	-0.04	0.53	-0.13	-0.65	-0.01	0.28	-0.10	-0.16	-0.16
Tl	0.24	0.03	-0.07	0.85	-0.05	0.07	0.11	0.15	0.16	0.14
Cs	0.22	0.16	0.02	0.85	-0.04	0.09	0.10	0.05	-0.03	0.02
Rb	0.08	0.17	0.15	0.80	0.06	0.00	-0.05	0.02	-0.17	-0.37
Ba	-0.08	0.01	0.11	0.09	-0.91	0.11	-0.09	0.12	0.16	0.07
Mo	0.08	0.03	0.10	0.02	-0.19	0.88	0.10	-0.07	0.15	-0.10
As	0.39	-0.08	0.15	0.42	0.04	0.60	0.11	0.11	0.32	0.10
Se	0.09	0.13	0.23	0.09	0.04	0.08	0.87	-0.11	0.02	-0.03
I	0.19	0.10	-0.17	0.39	-0.10	0.31	0.54	0.29	0.22	0.09
Mn	0.12	0.15	0.06	0.28	-0.09	0.08	-0.07	0.78	0.31	0.04
Ag	0.37	0.04	0.14	0.06	0.08	0.39	-0.03	-0.51	0.51	0.17
Cu	0.13	0.18	0.10	-0.06	-0.13	0.18	-0.08	0.16	0.77	0.12
Ni	0.03	0.25	-0.11	0.05	-0.01	0.11	0.22	0.09	0.71	-0.18

Table 4. F Statistics and Tolerance Values for Elements Included in the Discriminant Analysis (Equation 1)

element	F statistic	tolerance	element	F statistic	tolerance
Sr	63.97	0.69	V	14.25	0.32
Rb	24.9	0.8	Zn	13.56	0.85
Mn	21.52	0.87	Mo	9.38	0.57
U	20.78	0.37	Sb	9	0.35
Al	18.37	0.36	Co	7.68	0.39

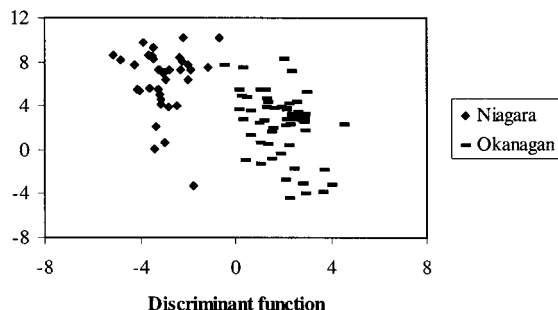


Figure 2. Discriminant analysis of Okanagan and Ontario wines using the discriminant function $14.09 + 0.54U - 0.54V - 0.90Al - 0.70Sb + 1.01Co - 0.82Zn + 1.94Sr - 1.32Rb + 0.49Mo - 1.24Mn$, where element concentrations are log transformed.

where nutrients are absorbed. The overall soil–plant interaction is highly complex, and soil–wine element relationships are further complicated by wine-processing effects.

Vineyard soils sampled from the Okanagan and Niagara regions can be completely differentiated by several of the analytes, particularly the alkaline earth elements (Mg, Ca, Sr, and Ba), which have consistently higher concentrations in Okanagan soils, and Ti, which is consistently higher in Niagara soils (Table 5). Although a linear correlation does not exist between wine and soil concentrations, mean concentrations of

Table 5. T-Test Statistics (Using Separate Variance T Test) and Associated Probabilities for Soil Analytes That Are Significantly Different between the Okanagan and Niagara Regions and Mean Concentrations of Each Analyte in the Two Regions

element	T statistic	probability	Okanagan mean concn (N = 26)	Niagara mean concn (N = 17)
CaO	6.7	<0.001	3.8 ± 1.5	1.47 ± 0.80
TiO ₂	-5.5	<0.001	0.62 ± 0.24	0.98 ± 0.19
Sr	15.1	<0.001	450 ± 104	138 ± 11
Ba	9.8	<0.001	1104 ± 324	465 ± 58

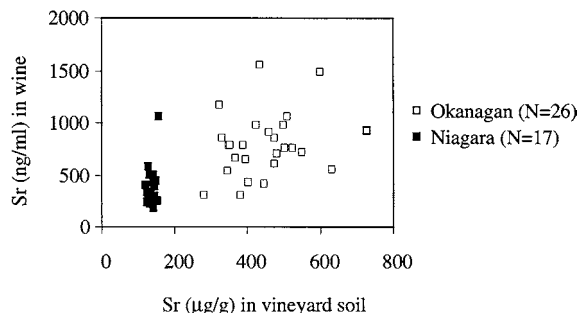


Figure 3. Concentrations of Sr in wines versus Sr in the corresponding vineyard soils.

the soluble alkaline earth elements are higher in Okanagan wines, whereas the mean concentration of Ti in Niagara wines is higher. The relationship between wine and soil Sr is shown graphically in Figure 3, which indicates a clear difference in regional soil concentrations, and more variability in wine concentrations. The difference in mean analyte concentrations in wine suggests that there is a regional influence of soil composition but that there are also other factors which affect wine concentration.

The successful discrimination of wines from two Canadian wine regions gives further evidence of the ability to show provenance using trace element fingerprints. Multielement analysis using ICP-MS requires little sample preparation and gives good precision analysis with low detection limits. The use of multivariate statistics is verified as a powerful tool for the examination of intercorrelations in a chemical data set and fingerprinting wine origin. The element Sr was found to be highly discriminating, in agreement with previous studies (1, 3, 6, 12–14), and the concentrations of Sr were higher in both soils and wine from the same region.

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