

DEVELOPMENT OF PREDICTIVE MODELS FOR ASTRINGENCY FROM ANTHOCYANIN, PHENOLIC AND COLOR ANALYSES OF BRITISH COLUMBIA RED WINES

DÉVELOPPEMENT DE MODÈLES PRÉDICTIFS POUR L'ASTRINGENCE DES VINS ROUGES DE COLOMBIE BRITANNIQUE PAR L'ANALYSE DES ANTHOCYANES, DES COMPOSÉS PHÉNOLIQUES ET DE LA COULEUR

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Abstract: One-hundred and eighty-nine commercial red wines from four vintages (1996-1999), four varieties (Pinot noir, Merlot, Cabernet franc, Cabernet Sauvignon) and 13 vineyard locations within the Okanagan Valley of British Columbia were analysed for total phenolics, anthocyanins, flavonols, tartaric esters, free SO₂, pH and titratable acidity, as well as copigmented-, monomeric-, polymeric- and total- anthocyanins (absorbance values). Color was evaluated using color density, hue, Hunter-color (L, a, b) and chroma values. Statistics (means, standard deviations) and discriminant analysis were used to explore the response patterns in the compositional analyses among the vintages, varieties and vineyard locations. Color density was highly correlated to the monomeric- and polymeric- anthocyanins for all varieties. Discriminant analysis revealed that some wine vintages could be differentiated using the flavonols, anthocyanins, copigmented anthocyanins, hue and L values. Phenolic concentrations were lower in 1996 and 1997 vintages compared to 1998 and 1999. Discriminant analysis showed that the varieties Pinot noir, Cabernet franc and Merlot/Cabernet Sauvignon could be differentiated using the monomeric-, polymeric- and total- anthocyanins, as well as color density, hue and L values. Cabernet Sauvignon wines formed a subset within the Merlot grouping. Discriminant of wines from the vineyard locations revealed that there was a considerable overlap among the regions, but that the groupings were generally consistent with geographic location. Sensory analysis was used to determine the intensity of astringency and astringent aftertaste in a subset of 35 wines from 1998. Multiple linear regression was used to relate the sensory and compositional analyses. A two-variable model predicted astringency (R=0.77) from total phenolics and copigmented anthocyanins; whereas, a one-variable model was developed to predict astringent aftertaste (R=0.74) from total phenolics. Sensory data collected on an additional 25 red wines were used to validate the appropriateness of the models.

Résumé: Cent quatre-vingt-dix vins rouges de 1996 à 1999, issus de quatre cépages différents (Pinot noir, Merlot, Cabernet franc et Cabernet Sauvignon) et provenant de 13 vignobles distincts de la Vallée de l'Okanagan de Colombie Britannique, ont été analysés : teneurs en composés phénoliques, anthocyanes, flavonols, esters tartriques, SO₂ libre, acidité, anthocyanes totales, copigmentées, monomériques et polymériques. La couleur a également été évaluée en déterminant l'intensité colorimétrique, la teinte et les valeurs L, a, b. Moyennes, écart-types et analyses discriminantes ont été utilisés pour explorer les résultats selon les millésimes, les cépages ou encore les vignobles étudiés. L'intensité colorimétrique était très corrélée aux quantités d'anthocyanes monomériques et polymériques pour tous les cépages. L'analyse discriminante par rapport aux millésimes révèle que les quatre années étudiées peuvent être différenciées par rapport au contenu en flavonols, anthocyanes, anthocyanes copigmentées des vins ainsi que par la teinte et la valeur L. On remarque que les concentrations en polyphénols sont plus faibles pour les vins des années 1996 et 1997 que pour ceux des années 1998 et 1999. L'analyse discriminante visant à expliquer les différences entre les variétés de raisins montre que les cépages Pinot noir, Merlot et Cabernet Franc peuvent être différenciés en fonction des quantités d'anthocyanes monomériques, polymériques et totales ainsi que par l'intensité colorimétrique, la teinte et la valeur L. Par contre, les Cabernet Sauvignon se confondent avec les Merlots. Enfin, l'analyse discriminante visant à distinguer les divers vignobles révèlent que ces derniers sont relativement imbriqués les uns dans les autres, on arrive cependant à faire des regroupements géographiques pertinents. Une analyse sensorielle a été utilisée pour déterminer l'astringence, son intensité et son arrière goût, d'après un échantillon de 35 vins de 1998. Une régression linéaire multiple a permis de relier les résultats sensoriels aux résultats analytiques de la composition des vins. Un modèle à deux variables corrèle l'astringence (R=0,77) avec le contenu de polyphénols totaux et d'anthocyanes copigmentées ; alors qu'un modèle à une variable a été développé pour corrélérer l'arrière goût de l'astringence (R=0,74) avec la quantité de polyphénols totaux. Des données sensorielles supplémentaires qui ont été collectées à partir de 25 vins rouges valident ces modèles.

Key words: astringency, anthocyanin, phenols, red wine, discriminant analysis.

INTRODUCTION

Although the British Columbia (BC) wine industry dates back to the mid 1900's, it has only been recognized as a producer of premium *Vitis vinifera* wines for the past 15 years. Before the signing of the North American Free Trade Agreement (NAFTA), a protected BC market supported an industry that was largely based on French hybrid varieties. The industry responded to NAFTA by pulling out hybrid grapes and replanting *Vitis vinifera* varieties and by establishing stringent wine standards which are enforced through a quality assurance program known as the Vintners Quality Alliance (VQA). The resulting increase in quality of wines combined with an effective collective marketing program has produced a high level of consumer confidence and generated a rapid industry expansion. Between 1989 and 1999, the industry increased the plantings of *Vitis vinifera* grapes from 1,100 acres (BC WINE INSTITUTE, 1995) to more than 4,200 acres (BC WINE INSTITUTE, 2001) and is continuing to expand. In addition the industry has begun to establish an international reputation capturing 709 medals in international competitions in 2000 (BC WINE INSTITUTE, 2001).

Early successes in the BC Wine Industry were with Germanic style white wines. However, as the industry grew and the market evolved, there was interest and need to produce a full complement of wines, including red wines. In BC, this was particularly challenging because of the cool climate conditions and the requirement to produce quality products that would be competitive in an international marketplace.

Quality red wines require mature grapes that have been grown in a manner that optimizes the development of anthocyanins, phenolics and flavor compounds (JACKSON and LOMBARD, 1993). Anthocyanins impart color to the grapes and consequently to the wine. The composition and distribution of anthocyanins are complex and vary with cultivar (MAZZA, 1995; GAO *et al.*, 1997) maturity (KATALINIĆ and MALE, 1997), vintage (KATALINIĆ and MALES, 1997), region and yield (JACKSON and LOMBARD, 1993). Anthocyanins and other phenols contribute to astringency, bitterness, body and finish; all important components in the enjoyment of a red wine (BAKKER *et al.*, 1986).

The type of canopy management (ZOECKLEIN, *et al.*, 1995, REYNOLDS *et al.*, 1994, PRICE *et al.*, 1995), as well as enological practice (GIRARD *et al.*, 1997, GIRARD *et al.*, 2001, RIBÉREAU-GAYON *et al.*, 2000a) and the use of barrels (RIBÉREAU-GAYON *et al.*, 2000b) affect the nature and concentration of the phenolic and color constituents in the finished wine.

In addition to the viticultural and enological practices, the area where the grapes are grown, including soil types, climatic conditions and exposure influences the phenolic profiles. Established wine growing areas have conducted studies over many years to examine the link between the viticultural, climatic and soil parameters and the composition of the wines. Several researchers (ARAZARENA *et al.*, 2000; KWAN and KOWALSKI, 1978; MORET *et al.*, 1980) have used multivariate statistics to classify wines according to their composition. However, there are no reports to establish these linkages in the BC wine industry. Accordingly the objectives of this research were: 1) to establish a database of compositional data (anthocyanin, phenolic and color analyses) for commercial BC red wines, 2) to document the perceived astringency for a subset of commercial BC red wines, 3) to relate the sensory and analytical data sets, and 4) to evaluate the database for patterns and compositional differences among vintages, varieties and vineyard locations.

MATERIALS AND METHODS

I- WINES

One-hundred and eighty-nine commercial wines were assayed from 32 wineries in the Okanagan Valley of British Columbia. The wines consisted of 4 varieties (Pinot noir, Merlot, Cabernet franc and Cabernet Sauvignon) and 4 vintages (1996 to 1999). In each case, the cork was pulled out partially and two needles from 60 mL syringes were inserted alongside the cork. One syringe was empty and allowed for collection of the sample and the other was filled with N₂ to fill the headspace created by removal of the sample. Sampling in this way permitted utilization of the wine at a later date without oxidation. Enough wine was sampled so that 50 mL could be used for SO₂ determination, 50 mL for pH / titratable acidity determination and 10 mL could be filtered through a 0.45 µm PVDF Acrodisc syringe tip membrane for color and phenolic analyses. Sample containers were flushed with N₂ and refrigerated at 4 °C.

II- ANALYTICAL DETERMINATIONS

1) Free SO₂ Determination

Free SO₂ was determined using the aeration-oxidation method of AMERINE and OUGH (1980). In this method, a 20 mL wine sample was acidified with 10 mL of 25 p. cent phosphoric acid, and the SO₂ was stripped using an air flow of 2000 mL/min for 15 minutes. SO₂ was trapped in a solution of 10 mL of 0.3 p. cent hydrogen peroxide containing three drops of indicator (methyl red and methylene blue) and one drop of 0.01 N NaOH to change the color to emerald green. The H⁺ produced was titrated with 0.01 N

NaOH; the volume added in mL was multiplied by 32 to obtain the mg/L free SO₂.

2) pH and tartaric acid measurements

The pH and titratable acidity (TA) were measured using a Metrohm 686 Titrprocessor and a 665 Dosimat (Metrohm Ltd., Switzerland). For TA, a solution of 10 mL of sample was titrated with 0.1N NaOH to an end point of pH 8.1 and expressed as tartaric acid equivalents.

3) Analysis of phenolics

Phenolics were analyzed as described by MAZZA *et al.* (1999). In this method filtered samples were diluted 1:10 with 10 p. cent ethanol. Total phenolics, anthocyanins, flavonols and tartaric esters were determined by vortexing the diluted sample with 0.25 mL of 0.1 p. cent HCl (in 95 p. cent ethanol) and 4.55 mL of 2 p. cent HCl. After 15 min, absorbance values at 280 (A₂₈₀), 320 (A₃₂₀), 360 (A₂₈₀), and 520 (A₂₈₀) nm were read on a spectrophotometer. The A₂₈₀, A₃₂₀, A₃₆₀, and A₅₂₀ were used to determine total phenolics (GLORIES, 1978) (here thereafter referred to as phenolG), tartaric esters, flavonols, and anthocyanins, respectively. Standards for the total phenolics, anthocyanins, flavonols, and tartaric esters were gallic acid (in 10 p. cent ethanol), malvidin-3-glucoside (in 10 p. cent ethanol), quercetin (in 95 p. cent ethanol), and caffeic acid (in 10 p. cent ethanol) respectively.

Total phenolics were also determined using the Folin-Ciocalteu method (SINGLETON and ROSSI, 1965) (here thereafter referred to as phenolF). This method consists of vortexing 0.20 mL of diluted wine (1:10) or standard, 1.8 mL of distilled water, 10 mL of diluted Folin-Ciocalteu reagent and 8 mL of Na₂CO₃ (75 g/L) solution. After two hours, absorbance at 765 nm was measured in a 1 cm cuvette using a spectrophotometer.

4) Color measurement

The absorbance of filtered wine samples was recorded at 420 (A₄₂₀), 520 (A₅₂₀), and 700 (A₇₀₀) nm in a 1 mm cuvette. Values were corrected for a 1 cm cuvette. Color density and hue were calculated as follows (WROLSTAD, 1976): color density = [(A₅₂₀ - A₇₀₀) + (A₄₂₀ - A₇₀₀)] and hue/tint = [(A₄₂₀ - A₇₀₀) / (A₅₂₀ - A₇₀₀)]. A CIELAB program for the spectrophotometer was used to measure L, a and b values, which have recently been proposed as a better measurement for evaluation of wine color (BAKKER *et al.*, 1986).

5) Copigmented anthocyanins

Copigmented-, monomeric-, polymeric-, and total-anthocyanins were determined using the procedure described by MAZZA *et al.* (1999). In this procedure, 20 µL of 10 p. cent (v/v) acetaldehyde was added to 2 mL of filtered wine and the absorbance at 520 nm (A_{acet}) was determined. To another 2 mL sample, 160 µL of 5 p. cent (w/v) SO₂ was added and the absorbance at 520 nm (A^{SO₂}) was determined. The absorbance of wine at 520 nm (A^{wine}) was also determined. All measurements were carried out in 1 mm cuvettes and readings were converted to 1 cm cuvettes. From these readings, the analyses were expressed in absorbance: copigmented anthocyanins = (A_{acet} - A^{wine}); monomeric anthocyanins = (A^{wine} - A^{SO₂}); polymeric anthocyanins = (A^{SO₂}); and total anthocyanins = (A_{acet}).

III- SENSORY ANALYSES

Thirty-four 1998 wines (16 Merlot, 8 Pinot noir, 6 Cabernet franc and 4 Cabernet Sauvignon) were evaluated for perceived astringency and astringent after-taste. Six panelists evaluated the wines in random order, in a total of three sessions. Each session containing two sets, one containing six wines and the other containing five wines. Wine samples (40 mL) were served in 210 mL ISO wine glasses labeled with 3-digit random numbers. Panelists took a one hour break between sessions. Panelists were wine writers with extensive experience in international wine tasting.

Judges evaluated perceived astringency and astringent aftertaste on 9-point scales from low (1) to high (10) and short (1) to long (10), respectively. Scales were anchored with written definitions. A wine with «low astringency» (1) was defined as being «light» with few tannins and extract; whereas, a wine with «high astringency» (10) was considered «robust» with high tannins and extract. A wine with a «short astringent aftertaste» disappeared quickly; whereas a wine with a «long astringent aftertaste» had a lingering drying aftertaste. Data was used to develop linear regression models to relate sensory and compositional analyses.

A «validation» data set was collected using 12 judges and 25 wines (1998 vintage) (7 Merlot, 6 Pinot noir, 6 Cabernet franc and 6 Cabernet Sauvignon). Judges evaluated the wines in duplicate, in a total of five sessions. At each session, judges evaluated two trays with five wines. Samples (40 mL) were served according to a completely randomized design, in 210 mL ISO glasses labeled with 3-digit random numbers. Judges assessed the first set, took a short break, and then evaluated the second set. The second

TABLE I
Analytical values (\pm standard deviations) for phenolic and color in BC commercial red wines for the different vintages.

Résultats des analyses (\pm écart type) pour la couleur et les composés phénoliques des millésimes de la Colombie britannique

Compound	Units	1996 (n=28)	1997 (n=60)	1998 (n=85)	1999 (n=16)
free sulfur dioxide	mg/L	6.2 \pm 5.6	11.7 \pm 10.3	16.1 \pm 10.9	20.3 \pm 12.1
pH	-	3.7 \pm 0.1	3.7 \pm 0.1	3.8 \pm 0.1	3.8 \pm 0.1
titratable acidity	g tartaric acid/L	4.3 \pm 1.8	6.1 \pm 0.9	5.9 \pm 0.6	6.0 \pm 0.9
total phenolics ¹ (phenolG)	mg gallic acid/L, 280 nm	957.8 \pm 243.6	863.5 \pm 157.9	980.8 \pm 224.4	930.9 \pm 195.1
tartaric esters	mg caffeic acid/L, 320 nm	139.8 \pm 25.5	144.7 \pm 37.3	176.1 \pm 40.1	141.1 \pm 36.4
flavonols	mg quercetin/L 360 nm	44.6 \pm 26.8	64.8 \pm 26.6	99.2 \pm 34.1	72.4 \pm 26.4
anthocyanins	mg malvidin-3-3-glucoside/L, 520 nm	51.1 \pm 28.3	82.6 \pm 54.1	202.6 \pm 85.6	185.1 \pm 77.5
total phenolics ² (phenol F)	mg gallic acid/L	2201.1 \pm 486.8	2074.3 \pm 369.4	2199.1 \pm 535.1	2115.9 \pm 483.6
copigmented anthocyanins	absorbance units	0.2 \pm 0.2	0.4 \pm 0.3	0.6 \pm 0.5	0.8 \pm 0.6
monomeric anthocyanins	absorbance units	1.2 \pm 0.6	1.1 \pm 0.6	1.5 \pm 0.7	1.4 \pm 1.0
polymeric anthocyanins	absorbance units	1.3 \pm 0.5	1.4 \pm 0.6	1.7 \pm 0.7	1.1 \pm 0.4
total anthocyanins	absorbance units	2.7 \pm 0.7	2.7 \pm 1.0	3.8 \pm 1.4	3.2 \pm 1.4
color density	absorbance units	4.6 \pm 1.3	4.4 \pm 1.6	5.7 \pm 2.1	4.2 \pm 1.9
hue	absorbance units	0.9 \pm 0.1	0.9 \pm 0.1	0.9 \pm 0.1	0.9 \pm 0.1

1: total phenolics by the Glories method (Glories, 1978) ; 2: total phenolics by the Folin-Ciocalteu method (Singleton, 1965)

set consisted of the duplicate assessment that had different order and codes.

Sessions took place in the morning on five consecutive days. Ten of the 12 judges were employees of the Pacific Agri-Food Research Centre (PARC), who had considerable experience with wine evaluation and two were members of the local wine industry.

Perceived astringency and astringent aftertaste were assessed on 10 cm linear line scales, anchored at 1 and 9 cm with the terms low and high, or short and long, respectively. Definitions of the terms and anchors were as described above.

IV - STATISTICAL ANALYSIS

Means and standard deviations were calculated for all analytical variables using Excel (Microsoft, Seattle WA).

Discriminant analysis (DA) was used to explore differences among the groups (vintages, varieties, vineyard locations) using the analytical variables. Data from all 189 wines were used for the DA for vintage and variety; however, DA of the vineyard locations was performed on 161 wines because 28 wines could not be designated to a given vineyard location. Discriminant analysis used a combination of the original variables to describe the differences between the classes (vintage, variety or location) (KLECKA, 1980). It created new variables, called discriminant functions,

to maximize the separation of the classes. Analyses were conducted using the SAS procedure CANDISC (SAS Institute Inc., Cary, NC). All plots were produced using Excel (Microsoft, Seattle WA). For clarity on the DA plot, the vineyard locations were identified by geographical region within the Okanagan Valley as north, central and south Okanagan.

Multiple regression was used to relate the sensory and analytical evaluations. Multiple linear regression models (NETER *et al.*, 1989) were developed using forward stepwise selection (SAS Institute Inc, Cary, NC) in order to select analytical variables which would successfully predict astringency and astringent aftertaste. The models were confirmed (validated) with data from a second sensory evaluation on an additional 25 wines, using: a) a «plot» of predicted and observed values, b) the «correlation coefficient» between the predicted and observed values, c) the square root of the «prediction error» $[\sum(\text{predicted}-\text{observed})^2/n]$ for the predicted and observed values, d) the «test of bias», which evaluated the difference between the mean of the predicted and observed values and e) the «test of regression coefficient» that assessed if the observed and predicted values fit the following equation (observed = 0 + 1*predicted).

RESULTS AND DISCUSSION

I- VINTAGE

Mean compositional values for the different vintages are shown in table I. As expected, free SO₂ concentrations were lower in the wines from the older vintages, due to the binding of free SO₂ with time. In general, the 1996 and 1997 vintages, and the 1998 and 1999 vintages, appeared to have a similar compositional profile (table I). The 1998 vintage had the highest levels of total phenols, flavanols, anthocyanins, color density, b and chroma. This was consistent with the fact that the 1998 growing season had an exceptional number of growing-degree-days and sunshine hours (ENVIRONMENT CANADA, 2000). In contrast, the 1996 vintage with a much lower number of growing-degree-days, had the lowest levels of titratable acidity, tartaric esters, flavonols, anthocyanins and copigmented anthocyanins. The lower titratable acidity was not consistent with the «poor» season and suggests that wines may have been deacidified sometime during vinification. The response pattern among vintages was not always readily apparent. For example, one would expect copigmented anthocyanins to increase with aging and show a trend with vintage date. In this database, the reverse was true. The values are influenced by not only known variables (vintage, variety, location), but unknown variables such as vine age, method of fermentation, duration of extraction, alcohol content of the wine, etc., all of which were uncontrolled and would have contributed to a range of values. Therefore, mean values should be interpreted with caution.

For the most part, discriminant analysis was able to distinguish among the four vintages (figure 1). The first two discriminant (DISCRIM) variables represented 64.3 and 22.1 p. cent of the variability in the data, respectively. Most of the vintage separation occurred along DISCRIM I which was positively correlated with anthocyanin, flavonols and copigmented anthocyanins and negatively correlated with L and hue. These variables, in combination with one another, explain the differences among the vintages, especially the difference between the 1998 and 1996 wines. In contrast, DISCRIM II was positively correlated with color density, tartaric esters and polymeric anthocyanins and negatively correlated with L and titratable acidity. These variables accounted for differences between the 1996 and 1997 wines, as well as the differences between the 1998 and 1999 wines.

II- VARIETY

Mean compositional analyses for the different varieties are shown in table II. On average, Cabernet Sauvignon, Cabernet franc and Merlot wines had similar compositional profiles. They had higher levels of tartaric esters, flavonols, anthocyanins, chroma as well as copigmented-, monomeric-, polymeric- and total-

anthocyanins (absorbance values) than the Pinot noir wines. This was expected since Pinot noir is a lightly pigmented, less astringent cultivar. On average, the varieties did not differ in SO₂, pH, titratable acidity, total phenolics (phenolF), hue, L, a, and b values. As indicated above, mean values should be interpreted with caution. It is more illustrative to evaluate the patterns of responses among varieties using a combination of variables.

Discriminant analysis was successful in distinguishing among two of the four varieties, forming three groups: Pinot noir, Cabernet franc and Merlot/Cabernet Sauvignon (figure 2). The first two discriminant (DISCRIM) variables represented 84.2 p. cent and 10.2 p. cent of the variability, respectively. Most of the vintage separation occurred along DISCRIM I which was positively correlated with total anthocyanins, color density, polymeric- and monomeric- anthocyanins and negatively correlated with hue and L. These variables were most successful in distinguishing between Merlot/Cabernet Sauvignon and Pinot noir wines. Interestingly the range of samples for the Pinot noir wines appear to be greater than that for the other varieties. This is consistent with the diversity of styles and range of compositional values typically found in Pinot noir wines. The Cabernet Sauvignon wines formed a subset within the Merlot wines. DISCRIM II was positively correlated with total phenolics (phenolF) and titratable acidity and negatively correlated with tartaric esters. These variables were most useful in describing the difference between the Cabernet franc and Merlot/Cabernet Sauvignon wines.

III- VINEYARD LOCATIONS

Mean compositional analyses for the different vineyard locations are shown in table III. Although

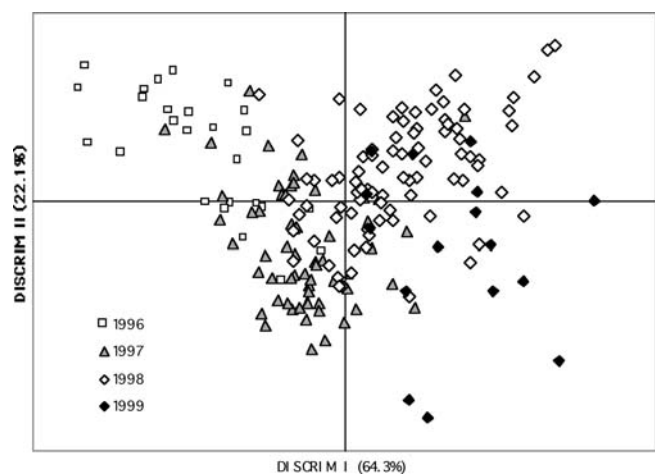


Figure 1 - Discriminant analysis of the wines according to vintage

Analyse discriminante des vins selon le millésime

there was a broad range of compositions for each of the vineyard locations, wines from the north (Mission, Westbank and Summerland) as well as the Similkameen, had lower concentrations of total phenols, tartaric esters, flavonols, anthocyanins and color density than wines from sites located towards the south (Black Sage, east Oliver, west Oliver) as well as Naramata. This phenomenon was expected due to the

longer growing degree day and sunshine hours associated with the south end of the valley.

Discriminant analysis could distinguish effectively among the vineyard locations (figure 3). The first three discriminant (DISCRIM) variables represented 33.4, 18.2 and 13.0 p. cent of the variability, respectively. Most of the location separation occurred along DISCRIM I, which was positively correlated with total phe-

TABLE II
Analytical values (\pm standard deviations) for phenolic and color compounds in British Columbia commercial red wines for the different varieties.

Résultats des analyses (\pm écart type) pour la couleur et les composés phénoliques des cépages de la Colombie britannique

Compound	Units	Cabernet franc (n=29)	Cabernet Sauvignon (n=25)	Merlot (n=60)	Pinot noir (n=75)
free sulfur dioxide	mg/L	14.0 \pm 10.7	13.4 \pm 7.7	13.3 \pm 11.4	3.8 \pm 0.1
pH	-	3.8 \pm 0.1	3.8 \pm 0.1	3.8 \pm 0.1	3.8 \pm 0.1
titratable acidity	g tartaric acid/L	5.4 \pm 1.3	5.8 \pm 1.2	5.7 \pm 1.0	5.8 \pm 1.2
total phenolics ¹ (phenolG)	mg gallic acid/L, 280 nm	955.8 \pm 225.9	915.3 \pm 149.5	918.9 \pm 209.8	896.2 \pm 219.2
tartaric esters	mg caffeic acid/L, 320 nm	181.3 \pm 49.5	172.9 \pm 33.0	167.8 \pm 41.3	136.4 \pm 26.9
flavonols	mg quercetin/L 360 nm	94.4 \pm 36.7	96.0 \pm 36.5	90.9 \pm 37.3	55.7 \pm 22.5
anthocyanins	mg malvidin-3-3-glucoside/L, 520 nm	178.9 \pm 95.0	176.1 \pm 82.9	185.2 \pm 97.4	77.1 \pm 52.2
total phenolics ² (phenolF)	mg gallic acid/L	2006.1 \pm 433.8	2091.8 \pm 393.9	2246.4 \pm 510.1	2147 \pm 483.3
copigmented anthocyanins	absorbance units	0.6 \pm 0.5	0.4 \pm 0.3	0.7 \pm 0.6	0.3 \pm 0.3
monomeric anthocyanins	absorbance units	1.6 \pm 0.8	1.7 \pm 0.7	1.7 \pm 0.7	0.8 \pm 0.3
polymeric anthocyanins	absorbance units	1.6 \pm 0.5	2.0 \pm 0.7	1.9 \pm 0.5	1.0 \pm 0.3
total anthocyanins	absorbance units	3.6 \pm 1.0	4.1 \pm 1.2	4.2 \pm 1.1	2.1 \pm 0.4
color density	absorbance units	5.5 \pm 1.7	6.5 \pm 1.9	6.2 \pm 1.5	3.3 \pm 0.7
hue	absorbance units	0.8 \pm 0.1	0.8 \pm 0.1	0.8 \pm 0.1	1.0 \pm 0.1

1: total phenolics by the Glories method (GLORIES, 1978); 2: total phenolics by the Folin-Ciocalteu method (SINGLETON, 1965)

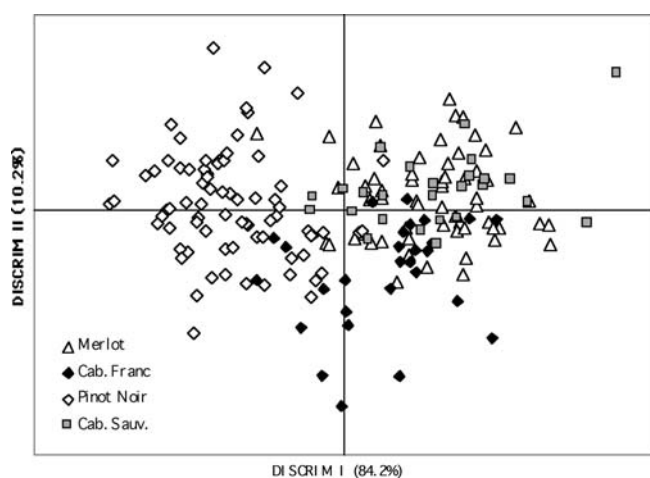


Figure 2 - Discriminant analysis of the wines according to variety.

Analyse discriminante des vins selon le cépage

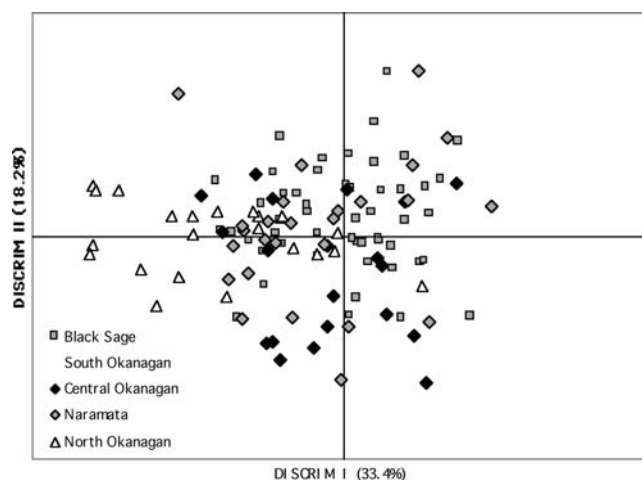


Figure 3 - Discriminant analysis of wines according to vineyard location.

Analyse discriminante des vins selon la localisation du vignoble

TABLE III
Analytical values (\pm standard deviations) for phenolic and color compounds in BC commercial red wines for the different locations
Résultats des analyses (\pm écart type) pour la couleur et les composés phénoliques par vignoble

Compound	Units	Central Okanagan (n=4)	Mission (n=8)	Westbank (n=6)	Summerland (n=4)	Naramata beach (n=26)	Okanagan falls (n=16)	Similkameen (n=4)	East Oliver (n=27)	West Oliver (n=15)	Black Sage (n=51)
free SO ₂	mg/L	8.5 \pm 5.0	14.1 \pm 9.7	5.8 \pm 3.8	18.7 \pm 5.8	11.1 \pm 10.3	18.5 \pm 11.4	11.8 \pm 9.8	15.9 \pm 16.3	10.4 \pm 7.5	14.2 \pm 8.8
pH	-	3.8 \pm 0.1	3.7 \pm 0.1	3.6 \pm 0.1	3.7 \pm 0.1	3.7 \pm 0.2	3.7 \pm 0.1	3.8 \pm 0.0	3.8 \pm 0.1	3.8 \pm 0.1	3.8 \pm 0.1
titratable acidity	g tartaric acid/L	5.0 \pm 0.3	5.8 \pm 1.3	5.7 \pm 1.5	5.8 \pm 0.6	5.6 \pm 1.4	5.7 \pm 0.9	7.0 \pm 1.3	5.8 \pm 1.0	5.7 \pm 0.6	5.7 \pm 1.5
total phenolics ¹ (phenol(G))	mg gallic acid/L 280 nm	811 \pm 37.4	823.0 \pm 153.7	866.07 \pm 158.1	594.5 \pm 58.2	869.8 \pm 271.8	903.1 \pm 211.5	741.5 \pm 184.9	1073.3 \pm 174.1	983.6 \pm 258.3	945.1 \pm 177.0
tartaric esters	mg caffeic acid/L 320 nm	162.5 \pm 16.0	134.9 \pm 18.3	167.3 \pm 11.8	116.8 \pm 12.4	146.6 \pm 44.3	164.1 \pm 83.2	87.3 \pm 6.7	183.6 \pm 47.4	155.9 \pm 27.6	162.3 \pm 47.6
flavonols	mg quercetin/L 360 nm	84.3 \pm 27.6	59.8 \pm 16.5	65.5 \pm 27.9	48.8 \pm 16.7	74.2 \pm 36.6	80.3 \pm 27.7	35.5 \pm 7.7	99.1 \pm 43.0	81.7 \pm 25.2	74.0 \pm 41.3
anthocyanins	mg malvidin-3- <i>o</i> -glucoside/L, 520 nm	162.0 \pm 33.5	74.3 \pm 34.1	54.3 \pm 41.6	56.8 \pm 27.2	120.2 \pm 91.4	160.1 \pm 69.3	53.5 \pm 15.4	178.9 \pm 97.7	182.9 \pm 106.9	137.0 \pm 108.0
total phenolic ² (phenolF)	mg gallic acid/L	1833.5 \pm 128.1	2116.6 \pm 645.6	2186.7 \pm 348.0	1551.8 \pm 252.4	2127.4 \pm 564.4	2153.1 \pm 589.1	2086.0 \pm 606.8	2372 \pm 393.6	2000.3 \pm 526.0	2182.4 \pm 394.2
copigmented anthocyanins	Absorbance units	0.6 \pm 0.2	0.4 \pm 0.2	0.1 \pm 0.1	0.3 \pm 0.2	0.4 \pm 0.7	0.8 \pm 0.4	0.3 \pm 0.1	0.5 \pm 0.4	0.5 \pm 0.4	0.5 \pm 0.5
monomeric anthocyanins	Absorbance units	1.3 \pm 0.4	0.7 \pm 0.1	0.9 \pm 0.2	0.4 \pm 0.0	1.4 \pm 1.0	1.1 \pm 0.5	0.8 \pm 0.3	1.8 \pm 0.9	1.2 \pm 0.3	1.4 \pm 0.6
polymeric anthocyanins	Absorbance units	1.1 \pm 0.2	1.1 \pm 0.3	1.2 \pm 0.1	0.8 \pm 0.1	1.5 \pm 0.5	1.4 \pm 0.6	1.2 \pm 0.7	1.8 \pm 0.7	1.4 \pm 0.4	1.6 \pm 0.8
total anthocyanins	Absorbance units	3.0 \pm 0.4	2.2 \pm 0.4	2.2 \pm 0.3	1.5 \pm 0.3	3.2 \pm 1.3	3.2 \pm 1.0	2.2 \pm 1.0	3.9 \pm 1.5	3.1 \pm 0.7	3.5 \pm 1.5
color density	Absorbance units	4.2 \pm 0.9	3.4 \pm 0.4	3.8 \pm 0.5	2.3 \pm 0.3	5.1 \pm 1.9	4.5 \pm 1.6	3.5 \pm 1.5	6.4 \pm 2.4	4.7 \pm 1.0	5.3 \pm 2.0
hue	Absorbance units	0.8 \pm 0.1	1.0 \pm 0.1	1.0 \pm 0.1	1.1 \pm 0.1	0.9 \pm 0.2	0.9 \pm 0.1	0.9 \pm 0.1	0.9 \pm 0.1	0.9 \pm 0.1	0.9 \pm 0.1

1: total phenolics by the Glories method (Glories, 1978);

2: total phenolics by the Folin-Ciocalteu method (SINGLETON, 1965)

3: of the 190 wines evaluated only 161 wines could be designated to a given viticultural region.

nolics (phenolG), color density, monomeric anthocyanins and total anthocyanins. This dimension appeared to form a «gradient» of vineyards located north to south in the Okanagan Valley and was generally consistent with geographical location. Wines from Westbank and Mission (identified as north Okanagan) were located to the far left on the plot. These sites are located towards the north end of the valley. Wines from Summerland were also located in this group. In contrast, wines from Okanagan Falls and Naramata (identified as central Okanagan) were located in the center of the plot. Although Summerland and Naramata are located at the same latitude, Naramata has a higher number of growing-degree-days due to its eastern location on Lake Okanagan. Wines from the south end of the valley, from Oliver (identified as south Okanagan) were located to the far right on the plot. However, there was considerable overlap among the regions.

Interestingly Black Sage vineyards, while located in the south, were positioned more centrally on the plot. Wines from this region were closer (more similar) to wines from Naramata and Okanagan Falls than wines from east and west Oliver. Wines from Black Sage and Naramata, despite their geographical distance (25 km), had similar compositional profiles. Presumably this was the result of the combination of climatological, viticultural, and enological practices which result in a similar terroir. DISCIM II was positively correlated with b and a and was most usefully in distinguishing between east and west Oliver.

IV- RELATIONSHIP BETWEEN SENSORY AND ANALYTICAL MEASUREMENTS

Multiple regression generated three possible models to predict astringency from the analytical values: 1) a one-variable model with phenolG (R=0.72), 2) a two-variable model with phenolG and Copig (copigmented anthocyanins) (R=0.77) and 3) a three-variable model with phenolG, Copig and flavonol (R=0.778). Of these models, the two-variable model was simplest and believed the most effective:

$$\text{astringency} = 2.648 + 0.0036 \cdot \text{phenolG} - 0.433 \cdot \text{Copig} \quad (1)$$

Addition of further variables increased the explainable variation, but produced models which were excessively complex.

For the prediction of astringent aftertaste, there were two possible models: 1) a one-variable model with phenolF (R=0.74) and 2) a two-variable model with phenolF and antho (anthocyanin) (R=0.76). The one-variable model, which was simplest and explained the

greatest proportion of variation, was considered the most effective:

$$\text{astringent aftertaste} = 3.515 + 0.001 \cdot \text{phenolF} \quad (2)$$

Equations 1 and 2 were «validated» with data from additional sensory analyses. Figure 4 shows the plot of predicted values for astringency compared to the values that were observed on the second sensory evaluation. There was one «outlier» (upper left hand side) for which predicted astringency was extremely high (figure 4). Upon examination of the anecdotal comments from the scorecards, this wine was defective (microbial spoilage) and had a strong atypical aroma and flavor. In retrospect, it should have been dropped from the evaluation. While the correlation is somewhat low (R=0.52), it is acceptable from a sensory perspective. For example, sensory means that differ by less than one unit on a 10-point scale are generally not significantly different. The square root of the prediction error [(predicted-observed) ²/n] provided an estimate of the closeness of the predicted and observed values. For astringency this value was 1.08. This compares favorably with an observed standard error of 0.37, since three times the standard error is roughly equivalent to a Fisher's least significant difference (LSD) (HALL, 1997).

Figure 5 shows the plot of predicted versus observed values for astringent aftertaste. Again the correlation was somewhat low (R=0.42). However the square root of the prediction error (1.25) again compared favorably with an observed standard error of 0.45. There were two wines which could be considered «outliers» on figure 5, one located to the far right and one to the far left. Interestingly, both these wines were Pinot noir wines. One was produced with an extremely «light»

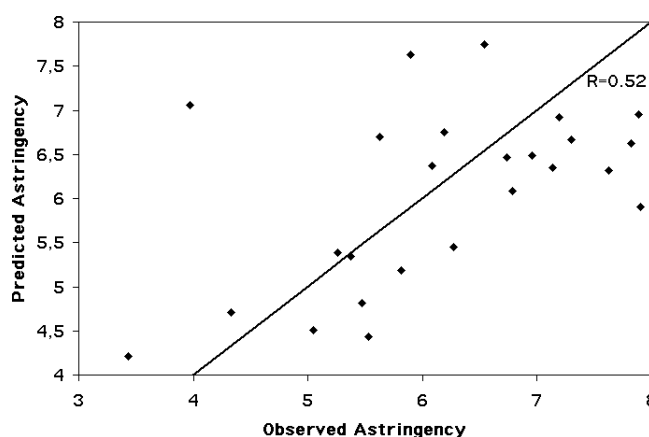


Figure 4 - Predicted versus observed astringency scores. Predicted scores were calculated from the following model (astringency = 2.648 + 0.0036*phenolG - 0.433*Copig).

Corrélation entre l'astringence prédite et mesurée.

Les valeurs prédites ont été calculées selon le modèle (astringence = 2.648 + 0.0036*phénolG - 0.433*Copig).

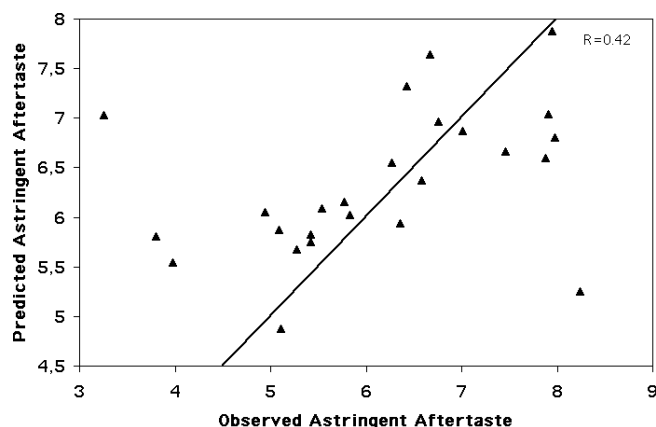


Figure 5 - Predicted versus observed astringent aftertaste scores.

Predicted scores were calculated from the following model (astringent aftertaste = $3.515 + 0.001 * \text{phenolF}$).

Corrélation entre l'arrière goût astringent prédit et mesuré.
Les valeurs prédites ont été calculées selon le modèle (arrière goût astringent = $3.515 + 0.001 * \text{phénolF}$).

style, more typical of a white or rosé wine and the other was produced with an extremely «robust» style, more typical of a Cabernet Sauvignon. Both these wines were atypical for the marketplace, and in retrospect, might not have been appropriate for the validation data set.

Other tests were used to evaluate equations (1) and (2). The «test of bias» evaluated the differences between the mean of the predicted and observed values. Theoretically, it should be zero ($d=0$) when the predicted and observed values are identical. In this research, bias tests were not significantly different from zero, for astringency (-0.124 , $p=0.57$) or astringent aftertaste (0.231 , $p=0.36$), indicating that the predicted values were satisfactory estimates of the actual values.

The «test of regression coefficients» evaluated if the observed and predicted values fit the following equation (observed = $0 + 1 * \text{predicted}$). In figures 4 and 5, the «perfect fit» line was shown with an intercept of zero and a slope of one. In this research, regression coefficients were not significantly different from one, for astringency ($R=0.64$, $p=0.10$) or astringent aftertaste ($R=0.79$, $p=0.55$), confirming that predicted values were satisfactory estimates of actual values.

CONCLUSIONS

Models were successfully developed to predict the sensory attributes, astringency and astringent aftertaste, in BC red wines from compositional analyses. The database of compositional values allowed exploratory data analysis with discriminant analysis, which was useful in identifying analytical components associated with vintage, variety and location differences. In general, the observed patterns were consistent with clima-

tological, enological and viticultural variation. However, data suggested that wines from Black Sage were similar to those from Naramata, despite a geographical separation of 25 km. Results at this stage are considered preliminary and will be verified as additional data become available.

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