# Electronic Nose Evaluation of the Effects of Canopy Side on Cabernet franc (*Vitis vinifera* L.) Grape and Wine Volatiles

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**Abstract:** The effect of grapevine canopy side (north versus south and east versus west) on grape and wine volatiles of Cabernet franc was evaluated during two growing seasons using two electronic nose systems based on conducting polymers and surface acoustic waves. Data from three sampling dates per season from both electronic noses were compared with physicochemistry and wine aroma sensory evaluations. Univariate and multivariate statistical analyses generally indicated grape physicochemistry indices could not differentiate consistently ($p > 0.05$) between canopy sides across growing seasons and sampling dates. Both electronic nose (ENose) systems provided complete discrimination of canopy sides for grapes and wine using canonical discriminant analysis. On average, the surface acoustic wave-based ENose explained <50% of variation for grapes and <60% for wine using the first principal component, compared to >80% for the conducting polymer-based ENose. Wine aroma sensory evaluation differentiated canopy sides in three of four evaluations.

**Key words:** canopy side, grape volatiles, wine volatiles, electronic nose, Cabernet franc

Fruit from different grapevine canopy locations may have different maturity because of variations in heat and light exposure (Downey et al. 2006), causing altered grape composition (Jackson and Lombard 1993). Several studies have evaluated the effects of management practices on grape composition, using both natural and artificial methods for manipulating light intensity: plastic sheet (Kliewer et al. 1967), waxed bags (Weaver and McCune 1960), shade cloth (Smart et al. 1988), shaded- and light-exposed berries from the same cluster (Price et al. 1995), and canopy sides (Bergqvist et al. 2001). Some studies have shown that increased exposure to sunlight delays ripening by inhibiting sugar accumulation (Bergqvist et al. 2001, Kliewer 1977) and may ripen berries unevenly compared to clusters growing in shade (Kliewer and Lider 1968). In contrast, other studies have shown that the percentage of soluble solids is not affected by light exposure (Crippen and Morrison 1986a, Spayd et al. 2002). Berry weight was higher in shaded berries in some studies (Crippen and Morrison 1986a), but not others (Crippen and Morrison 1986b). Exposed clusters have been shown to have lower titratable acidity (Bergqvist et al. 2001, Crippen and Morrison 1986a, Kliewer and Lider 1968) and pH (Bergqvist et al. 2001) than shaded clusters. The apparently contradictory results on grape composition due to light exposure suggest the need for exploring alternative evaluation tools.

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Electronic nose (ENose) technology has been used in a variety of food industry applications, including quality assurance, process monitoring, study of storage conditions, maturation and aging of wine, and product-package interaction (Mielle 1996a), and also used to evaluate the effect of a vineyard management technique on grape and wine volatiles (Martin et al. 2008). ENose is a chemosensor array-based technology usually consisting of a series of sensors. Upon exposure to chemical vapor, sensors undergo physicochemical changes (Mallikarjunan 2005). Based on the sensor, electronic noses can be classified into the following systems: conducting polymer (CP), quartz microbalance (QMB), metal oxide sensors (MOS), metal oxide semiconductor field effect transistors (MOSFET), and surface acoustic wave (SAW). All systems consist of three major parts: sensors, system controls, and data processing units (Mallikarjunan 2005). Precision and accuracy of an ENose depend on several characteristics, including sensor selectivity, operating temperature, humidity, sensor drift, and sensitivity to a particular compound. Hence, the use of a particular sensor could be limited to certain applications. CP, SAW, and MOS electronic noses are the most commonly used due to sensor drift over time (Mielle 1996).

Conducting polymer-based systems consist of several sensors. A change in the resistance of each sensor is stored as a "smell print" during introduction of standard samples, and an unknown sample is compared with the available smell prints for identification (Cyrano Sciences 2000). CP sensors are composed of different polymers: polyaniline, polypyrrole, polythiophene, polyacetylene, and polyindole at different oxidation-reduction states to provide selectivity to different compounds (Mallikarjunan 2005, Pinheiro et al. 2002). The ability of a CP ENose to measure grape volatiles nondestructively has been demonstrated (Athamneh et al. 2008). SAW-based systems consist of a single sensor, which simulates a virtual sensor array as if consisting of 100 orthogonal sensors

(Mallikarjunan 2005). The commercial zNose uses SAW-based sensors and operates as a miniature fast-reading gas chromatography (GC) unit (Mallikarjunan 2005). Samples are drawn into the sampling port and sent through a column. Identification of volatile compounds is based on peak retention time in the column and quantification is determined by frequency shifts of the quartz crystal detector, which correspond to the amount of material deposited (Electronic Sensor Technology 2001). The data obtained from this system can be analyzed using chromatographic or spectroscopic approaches (Lammertyn et al. 2004, Mallikarjunan 2005). Primary problems reported with the use of CP sensors for wines are the influence of ethanol (Ragazzo-Sanchez et al. 2006) and water vapor. However, an ethanol baseline with a conducting polymer ENose system has been used to minimize the ethanol interference with sensor readings, basing discrimination on wine aroma volatiles (Santos et al. 2004). Sensitivity generally varies according to sensory type and polymer type for CP ENose systems. Reported sensitivity is in the µg/L to ng/L range (Mallikarjunan 2005).

In this study, we sought to determine the ability of CP and SAW electronic nose systems to discriminate grapevine canopy sides, compared to traditional analyses.

## Materials and Methods

**Field design.** This study was performed during 2007 and 2008 on Cabernet franc grapes grown on a Ballerina training system in Charlottesville, Virginia. Heat summation for 2007 and 2008 was 1370.6°C and 1154.4°C, respectively. Mean monthly precipitation from April through October was 81 mm and mean relative humidity was 75% in September. Both vineyards were dry farmed. Grapevine rows with canopy sides facing true north/south (±5°) and true east/west (±5°) were planted in 2003 on 16187.43 $m^2$ and 4046.86 $m^2$ plots, respectively. Vines were clone 4 grafted onto 101-14 rootstock. Vines on both plots were spaced 2.13 x 3.05 m apart. In 2007, 10 grapevines were selected using a randomized block design for both the east/west- and north/south-oriented plots. Fruit was sampled based upon canopy side on three sampling dates postbloom (once per week) in both seasons. Sampling was conducted on weeks 12, 14, and 15 postbloom in 2007, and weeks 14, 15, and 17 postbloom in 2008. The last sampling date for both seasons was at commercial harvest.

Degrees Brix by refractometer (model 10430; AO Scientific Instruments, Keene, NH), %RH by digital hygrometer (model 4187; Traceable, Control Company, Friendswood, TX), and temperature by infrared thermometer (model 42529; Extech Instruments, Waltham, MA) were measured on both sides within the vine canopy on all sampling dates, between 0800 and 1100 hr. At the end of the growing season, ~80.0 kg of fruit was harvested from each canopy side. Several components of yield were determined: shoots/meter, clusters/vine, clusters/shoot, cluster weight, berry weight, fruit weight/vine, and fruit weight/canopy side.

**Laboratory analysis.** Twenty-five berries per vine were randomly collected from each side of each vine at each sampling date, processed, and analyzed immediately. Berry samples were crushed in a commercial blender (Waring model 13BL91; New Hartford, CT) for one second and placed into a filter bag (model 400; Steward Stomacher Lab System, London, UK). The expelled juice was filtered through 0.45-µm syringe filters (Whatman, Clifton, NJ). Berry weight, Brix, pH, and titratable acidity (TA) were determined as described previously (Zoecklein et al. 1999). Color intensity ($A_{420}$ + $A_{520}$), hue ($A_{420}/A_{520}$), and total phenols ($A_{280}$) were estimated using a Genesys 5 spectrophotometer (Spectronic, Leeds, UK). Yeast assimilable nitrogen was determined enzymatically (Megazyme, Bray, Ireland). The total glycosyl-glucose (TGG) and phenol-free glycosyl glucose (PFGG) analyses were performed as described (Williams et al. 1995) and modified (Zoecklein et al. 2000). For wines, analyses of malic acid, yeast assimilable nitrogen, alcohol concentration, residual sugar, and volatile acidity were also conducted. L-Malic acid was determined enzymatically (R-Biopharm AG, Darmstadt, Germany). Alcohol was determined by FTIR (model FT 120; Foss WineScan, Eden Prairie, MN) and residual sugar concentration by Clinitest (Bayer, Elkhart, IN).

Wine samples for GC-MS analysis were prepared using a 4-mL sample with 1.0 g NaCl in 10-mL clear glass vials sealed with septa (MicroLiter Analytical Supplies, Suwanee, GA), as described (Whiton and Zoecklein 2000). Vials were pre-incubated 30 sec at 30°C with agitation at 250 rpm. A CAR/DVB/PDMS grey SPME fiber (Supelco Sigma-Aldrich, St. Louis, MO) was used to penetrate vials to a 32-mm depth. A GC-MS (model 6890N, Network GC System, 5975B inert MSD; Agilent Technologies, Santa Clara, CA) with injector temperature at 250°C, DB-wax column (30 m x 0.25 mm), and helium carrier gas with a flow rate of 1 mL/min was used. Oven temperature was 40°C with a ramp rate of 6°C/min to 230°C. Thirty-two standard compounds from each wine sample were manually integrated and quantified.

**Processing and fermentation.** Grapes harvested from each canopy side were crushed and destemmed using a Wottle (Anton, Poysdorf, Austria) destemmer-crusher to about 50% berry breakage, estimated visually. Fruit was distributed into three open-top 60-L Nalgene fermenting bins (Thermo Fisher Scientific, Waltham, MA) of equal height and volume for each canopy side. Each bin was treated with 250 mg/L Velcorin (Scott Laboratories, Petaluma, CA) dimethyl-dicarbonate. Bins were held for 24 hr at 7°C in a cooler, followed by a 25 mg/L potassium metabisulfite addition. Grapes were cold soaked for 6 days at 7°C, with daily punching of the must. Must juice analysis was then performed, following addition of 0.24 g/L FermAid K (Lallemand, Blagnac, France).

*Saccharomyces cerevisiae* ICV-D254 yeast (Lallemand) (0.24 g/L) was inoculated following the cold-soak treatment. Go-Ferm (Lallemand) yeast nutrient was prepared according to manufacturer instructions and added during yeast rehydration. After inoculation, caps were punched three times daily. Fermentation was monitored by hydrometer and carried out at 25 ± 2°C until dryness (<1% residual sugar), as determined by Clinitest (Bayer). Following fermentation, wines were dejuiced using a Willmes press (model 100; Bensheim, Germany) to 0.5 bar. Free run and press run fractions were

combined and placed into sanitized, carbon dioxide-filled glass carboys. Wine was kept at 7°C for 24 hr, racked into 3.80-L glass bottles, and stored at 12°C.

**Electronic nose analysis.** Two electronic nose (ENose) systems, a conducting polymer (CP) (Cyranose 320, Smiths Detection, Pasadena, CA; used in the field and in the laboratory) and a surface acoustic wave (SAW) (ZNose 730, Electronic Sensor Technology, Newbury Park, CA; laboratory only) were used to determine volatile differences between canopy sides in grapes and in wine produced from those grapes.

The CP ENose optimization method was as described in an earlier study on the impact of field variables in our climatic region, such as heat and humidity, on the CP system (Athamneh et al. 2006). Optimization of the wine evaluation method for the CP ENose was as described previously (Gardner 2009). Optimizations involved evaluations of sample temperature, incubation time, pump speed, purge, and individual sensor response. Canonical projection plots showed no separations between replications, indicating minimum sensor drift.

The optimum sample temperature was 30°C. Ethanol standard solutions (three standards per treatment) were used to create an ethanol baseline to evaluate the impact on polymer-based sensor response and to minimize differences in alcohol concentrations among wine samples while using the ENose. Concentrations for ethanol standards were based on the alcohol concentration recorded for each wine treatment.

For field analysis, two clusters (one from each canopy side) were chosen at random from each of 10 selected vines. Clusters were bagged with an HDPE bag (Inteplast, Livingston, NJ) and equilibrated for 45 min. In 2007, additional clusters from neighboring vines were collected for laboratory analysis. Clusters were placed into individual 1.50-L glass jars in a water bath at 30°C for 20 min and then analyzed by CP ENose. Berry analysis was also performed, using 50 g of berries picked from the cluster and placed in a 200-mL glass Mason jar.

Wines were analyzed twice: immediately postfermentation and again 6 months postfermentation. Five replicates of 20-mL wine samples were placed in 40-mL GC clear glass vials sealed with teflon/silicone 3-mm septa (MicroLiter Analytical Supplies). The samples were placed in a water bath at 30°C for 20 min and subsequently analyzed by CP ENose.

For the SAW ENose, the default settings of the DB-5 column system were used, except for the sensor temperature of 45°C. The system was tuned with C6 to C14 alkane standards each day. The same sampling technique for the CP ENose wine analysis was used for this system.

**Sensory analysis.** Triangle difference tests on wine aroma were conducted under standard conditions 6 months postfermentation as described (Meilgaard et al. 2007), comparing east versus west and north versus south. Wines were prescreened for sulfur-like off odors and assigned a randomized 3-digit code. Panelists were given three samples and asked to identify the odd sample. Standard ISO glasses were filled with 10 mL wine, covered with a plastic petri dish, and presented to untrained consumer panelists at 19°C under a red light. Each year, 32 panelists with ages between 21 and 27 years were used ($\alpha = 0.05$, $\beta = 0.30$, $\rho d = 40\%$, 16 correct responses required for significant difference). Approximately equal numbers of male and female panelists were selected, with a prerequisite of wine consumption at least once a week. Written instructions were provided and panelists received two 20-min sessions outlining the procedures. Panelists smelled two sets of samples at different times.

**Statistical analysis.** The physicochemistry, CP ENose, and SAW ENose data were analyzed and compared using univariate (one-way analysis of variance [ANOVA] and least significant difference [LSD]) and multivariate (canonical discriminant analysis [CDA] and principal component analysis [PCA]) statistical methods using SAS JMP version 7 software (SAS Institute, Cary, NC). The SAW ENose data was analyzed using the GC chromatographic approach as described (Lammertyn et al. 2004). For the sensory data, the significance of the number of correct responses was determined as described (Meilgaard et al. 2007).

## Results and Discussion

Components of yield at harvest did not differ among grapevine canopy sides for either season, with the exception of berry weight in 2008 (Table 1). Canonical discriminant analysis (CDA) of seven grape physicochemistry indices (Brix, berry weight, pH, TA, color intensity, hue, and total phenols) demonstrated that the ability of these measures to identify grapevine canopy side increased with weeks postbloom (Table 2). However, these indices did not consistently predict canopy side on any sampling date, unlike both ENoses. CDA plots of the physicochemistry data for 2007 and 2008 generally illustrated that these indices could not differentiate both East from West and North from South (Figure 1). Such plots represent the multivariate mean of the data points as circles whose size indicates the 95% confidence limit for the mean. Nonintersecting circles indicate significant differences.

The *p* values for the analyses of nine physicochemistry indices (PFGG, TGG, and the seven indices listed above) were

**Table 1** Components of yield of different canopy sides for Cabernet franc grapes at harvest in 2008.

| Canopy side | Shoots/meter | Clusters/side | Fruit wt (kg) | Cluster wt (kg) | Berry wt (g) |
|---|---|---|---|---|---|
| East | 20.60 ± 1.02 a[a] | 16.40 ± 3.55 a | 3.12 ± 1.09 a | 0.18 ± 0.04 ab | 1.77 ± 0.07 ab |
| West | 17.40 ± 1.02 a | 17.40 ± 3.55 a | 2.32 ± 1.09 a | 0.13 ± 0.04 b | 1.63 ± 0.07 b |
| North | 18.80 ± 1.02 a | 23.00 ± 3.55 a | 5.50 ± 1.09 a | 0.27 ± 0.04 a | 1.97 ± 0.07 a |
| South | 17.20 ± 1.02 a | 22.80 ± 3.55 a | 5.23 ± 1.09 a | 0.23 ± 0.04 ab | 1.89 ± 0.07 a |
| *p* value | 0.11 | 0.43 | 0.15 | 0.07 | 0.03 |

[a]Columns with different letters indicate a 95% significant difference between treatments.

determined (Table 3). Pairwise comparison (*t*-test) results showed that Brix (2007), TA (2008), and pH (both seasons) values were not significantly correlated with canopy side on most sampling dates, similar to previous results (Athamneh et al. 2008). However, differences between canopy sides were evident for Brix (2008) and TA (2007). Berry weight was differentiated between canopy sides in both seasons for all sampling dates. Fruit color intensity showed canopy differences in 2007, but not in 2008. In general, the physicochemistry indices did not show consistent differences between canopy sides across both seasons.

Canonical plots demonstrated the ability of the CP ENose to distinguish canopy sides at most maturity stages evaluated in the field (Figure 2). The ability to minimize the environmental variables of heat and humidity was confirmed by comparing the CP field results with CP laboratory analyses, which demonstrated exactly the same trends (data not shown). Based on the ANOVA of in-field CP ENose data, most sensors were sensitive ($p < 0.05$) to Cabernet franc grape volatiles, with the exceptions of S19, S24, and S32 (data not shown). The canonical plots of the SAW ENose data on canopy sides of fruit from three sampling dates in 2008 are shown (Figure 3). This data is representative of both seasons and demonstrated that the SAW system showed similar ability to discriminate canopy side.

**Table 2** Canonical discrimination of Cabernet franc grapes at three times postbloom; physicochemistry and conducting polymer-based (CP) in 2007 and 2008 and surface acoustic wave-based (SAW) ENose in 2008.

| Sampling date | Chemistry[a] | CP ENose | SAW ENose |
|---|---|---|---|
| **2007** | | | |
| Week 12 | 80% | 100% | na[b] |
| Week 14 | 90% | 100% | na |
| Week 15 | 95% | 100% | na |
| **2008** | | | |
| Week 14 | 80% | 100% | 100% |
| Week 15 | 85% | 100% | 100% |
| Week 17 | 95% | 100% | 100% |

[a]Values indicate the percentage of correct predictions of east vs west and north vs south.
[b]na indicates data not available.

Principal component analysis (PCA) of physicochemistry and CP and SAW ENose data showed that, for each data source, the first three components together explained 100% of the variation (Table 4). CP ENose data explained most of the variation (>90%) in a single (PC1) axis, while physicochemistry and the SAW ENose data explained similar variation using PC1 and PC2. PCA is a multivariate statistical method

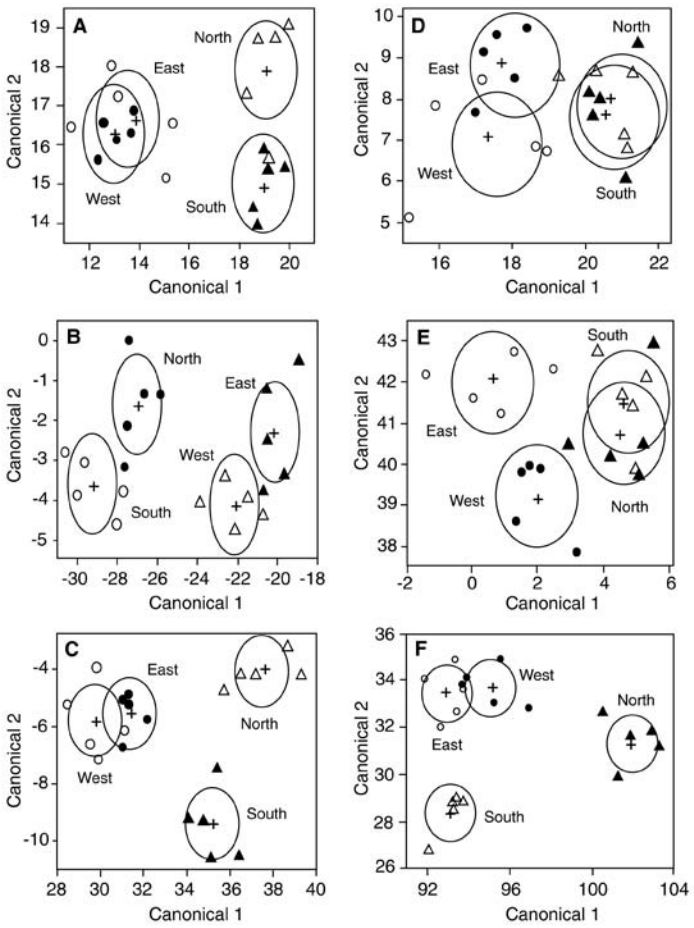


**Figure 1** Canonical distribution of differences detected by physicochemistry analyses of Cabernet franc juice on three sampling dates during 2007 postbloom weeks 12 (**A**), 14 (**B**) and 15 (**C**), and 2008 postbloom weeks 14 (**D**), 15 (**E**), and 17 (**F**). Significant differences at $\alpha = 0.05$ are indicated by nonintersecting circles.

**Table 3** *p* Values (ANOVA) of canopy side differences in Cabernet franc juice detected by physicochemical analyses during 2007 and 2008 on three sampling dates (postbloom weeks 12, 14, and 15 in 2007, and weeks 14, 15, and 17 in 2008).

| | 2007[a] | | | 2008[a] | | |
|---|---|---|---|---|---|---|
| **Physicochemistry indices** | **Week 12** | **Week 14** | **Week 15** | **Week 14** | **Week 15** | **Week 17** |
| Brix | 0.81 | 0.76 | 0.76 | 0.04 | 0.03 | 0.00 |
| Berry weight (g) | 0.00 | 0.00 | 0.00 | 0.03 | 0.02 | 0.03 |
| pH | 0.03 | 0.06 | 0.28 | 0.19 | 0.17 | 0.00 |
| Titratable acidity (g/L) | 0.00 | 0.18 | 0.00 | 0.39 | 0.03 | 0.52 |
| Color intensity ($A_{420}+A_{520}$) | 0.01 | 0.01 | 0.03 | 0.94 | 0.71 | 0.62 |
| Hue ($A_{420}/A_{520}$) | 0.04 | 0.47 | 0.14 | 0.35 | 0.00 | 0.50 |
| Total phenols ($A_{280}$) | 0.20 | 0.57 | 0.05 | 0.16 | 0.16 | 0.52 |
| PFGG (μM) | 0.02 | 0.32 | 0.01 | na | na | 0.11 |
| TGG (μM) | 0.24 | 0.00 | 0.01 | na | na | 0.00 |

[a]*p* values ≤ 0.05 indicate significance; na indicates data not available.

in which the variation of data is summarized in the form of principal components. This method explains the variation in data by replacing the larger set of variables correlated with canopy side with a smaller set of uncorrelated variables.

The conducting polymer-based system discriminated better between canopy sides than the surface acoustic wave-based system (Table 4). This could be attributed to the types of data sets in the two systems. Better discrimination can be observed with a larger data set (Vandeventer and Mallikarjunan 2003). Based on biplot ray lengths for physicochemistry data in 2007 and 2008, Brix was the least-effective parameter in detecting canopy side difference, followed by TA and hue (data not shown). Wine chemistry parameters (PFGG, TGG, color intensity, hue, and total phenols) of fruit from

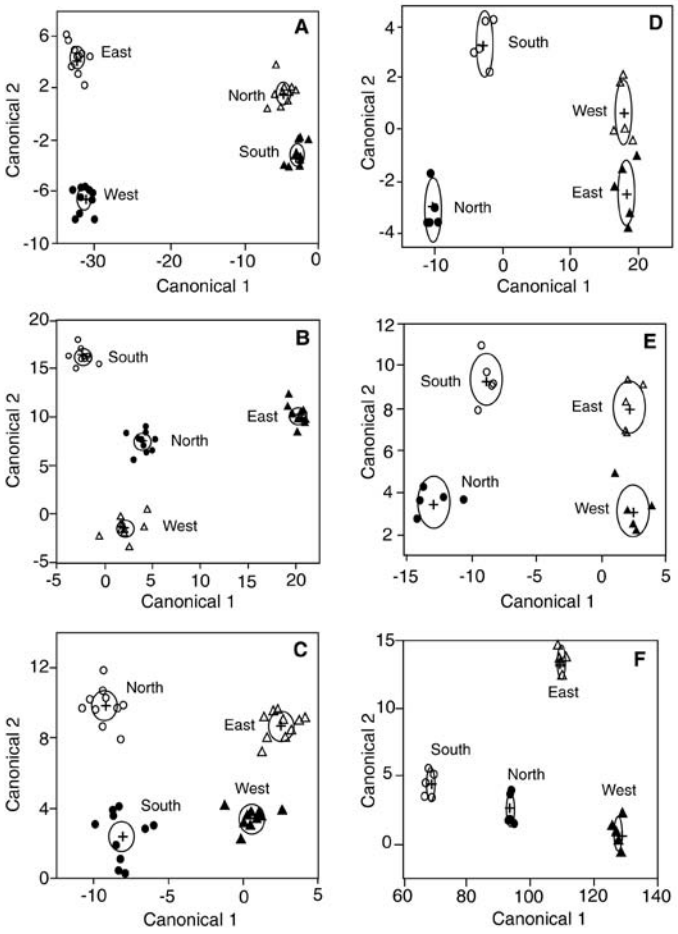


**Figure 2** Canonical plots of canopy side differences for Cabernet franc grape berries, detected by conducting polymer-based ENose in the field, in 2007 postbloom weeks 12 (**A**), 14 (**B**), and 15 (**C**), and 2008 postbloom weeks 14 (**D**), 15 (**E**), and 17 (**F**). Significant differences at $\alpha = 0.05$ are indicated by nonintersecting circles.

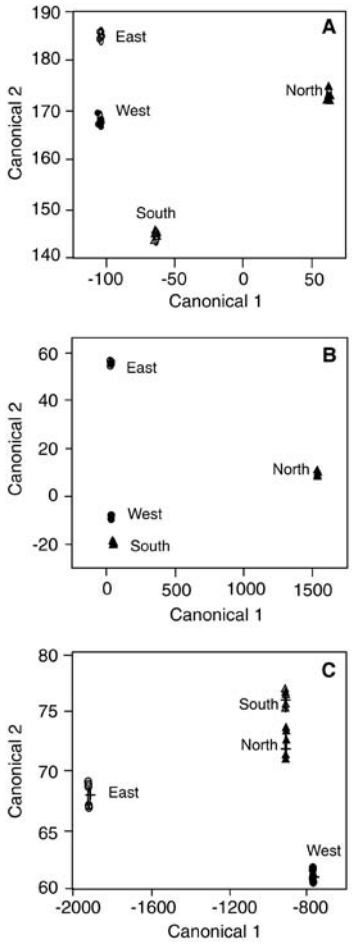


**Figure 3** Canonical plots of canopy side differences for Cabernet franc grape juice, detected by surface acoustic wave-based ENose in the laboratory, in 2008 postbloom weeks 14 (**A**), 15 (**B**), and 17 (**C**). Significant differences at $\alpha = 0.05$ are indicated by nonintersecting data groups.

**Table 4** Principal component analysis of Cabernet franc juice, showing the difference between canopy side detected by physicochemical analyses, conducting polymer-based (CP) ENose in 2007 and 2008 and surface acoustic wave-based (SAW) ENose in 2008.

| 2007[a] | | | | 2008[a] | | | | |
|---|---|---|---|---|---|---|---|---|
| Sampling date | Physico-chemistry | CP ENose | SAW ENose | Sampling date | Physico-chemistry | CP ENose | SAW ENose | Principal component |
| **Week 12** | 81.1 | 99.7 | na | **Week 14** | 66.5 | 92.6 | 72.6 | PC1 |
| | 18.1 | 0.2 | na | | 26.0 | 4.8 | 23.5 | PC2 |
| | 0.8 | 0.1 | na | | 7.5 | 2.6 | 3.9 | PC3 |
| **Week 14** | 72.4 | 97.6 | na | **Week 15** | 69.5 | 58.8 | 54.9 | PC1 |
| | 20.3 | 2.1 | na | | 27.2 | 39.8 | 30.1 | PC2 |
| | 7.3 | 0.3 | na | | 3.3 | 1.4 | 15.0 | PC3 |
| **Week 15** | 76.9 | 99.7 | na | **Week 17** | 49.3 | 95.6 | 42.9 | PC1 |
| | 12.7 | 0.1 | na | | 42.1 | 3.5 | 36.9 | PC2 |
| | 10.3 | 0.1 | na | | 8.6 | 0.9 | 20.2 | PC3 |

[a]Values indicate the percentage of variation explained by principal components 1, 2, and 3; na indicates data not available.

**Table 5** Pairwise comparison data of 2008 Cabernet franc wine chemistry indices.

| Treatment | Color intensity ($A_{420}+A_{520}$) | Hue ($A_{420}/A_{520}$) | Total phenols ($A_{280}$) | PFGG (μM) | TGG (μM) |
|---|---|---|---|---|---|
| East | 0.717 ± 0.03 b[a] | 0.469 ± 0.01 c | 2.673 ± 0.03 c | 62.7 ± 5.30 a | 1388 ± 36.30 b |
| West | 0.520 ± 0.03 c | 0.560 ± 0.01 b | 2.454 ± 0.03 d | 28.2 ± 5.30 bc | 1323 ± 36.30 b |
| North | 0.886 ± 0.03 a | 0.605 ± 0.01 b | 3.344 ± 0.04 a | 36.8 ± 5.30 b | 1608 ± 36.30 a |
| South | 0.811 ± 0.03 a | 0.663 ± 0.01 a | 3.192 ± 0.04 b | 15.2 ± 5.30 c | 1598 ± 36.30 a |

[a]Different letters within columns indicate a 95% significant difference between treatments.

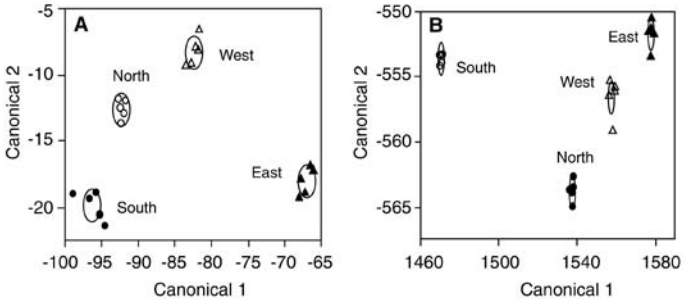


**Figure 4** Canonical plots of canopy side differences for Cabernet franc wine, detected by conducting polymer-based ENose in the laboratory, in 2008 immediately postfermentation (**A**), and 6 months postfermentation (**B**). Significant differences at $\alpha = 0.05$ are indicated by nonintersecting circles.

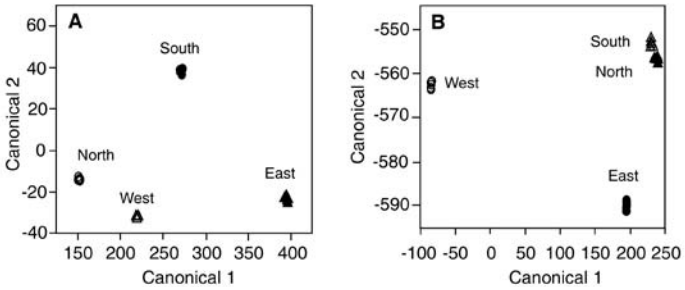


**Figure 5** Canonical distribution of 2008 Cabernet franc wine 6 months postfermentation, using (**A**) surface acoustic wave-based ENose and (**B**) GC-MS. Significant differences at $\alpha = 0.05$ are indicated by nonintersecting data groups.

**Table 6** Pairwise comparisons and ANOVA on 2008 east, west, north, and south Cabernet franc wine volatiles 6 months postfermentation.

| | Concentration (μg/L) | | | | |
|---|---|---|---|---|---|
| Compound | East | West | North | South | *p* value |
| Ethyl acetate | 24.88 ± 0.45 a[a] | 24.13 ± 0.45 a | 25.53 ± 0.45 a | 25.17 ± 0.45 a | 0.2326 |
| 2-Methyl propanol | 23.07 ± 0.81 a | 22.44 ± 0.81 a | 22.92 ± 0.81 a | 24.03 ± 0.81 b | 0.5932 |
| Isoamyl acetate | 3004.95 ± 95.28 c | 2781.96 ± 95.28 c | 4069.96 ± 95.28 a | 3702.57 ± 95.28 b | <0.0001 |
| *n*-Butanol | 9.12 ± 0.02 ab | 9.13 ± 0.02 a | 9.09 ± 0.02 ab | 9.08 ± 0.02 b | 0.1128 |
| 3-Methyl butanol | 75.26 ± 2.13 ab | 71.77 ± 2.13 b | 81.58 ± 2.13 a | 82.18 ± 2.13 a | 0.0232 |
| Ethyl hexanoate | 216.73 ± 5.98 b | 194.05 ± 5.98 c | 240.05 ± 5.98 a | 236.82 ± 5.98 a | 0.0021 |
| Hexyl acetate | 4.17 ± 0.08 a | 1.47 ± 0.08 d | 3.54 ± 0.08 b | 2.61 ± 0.08 c | <0.0001 |
| Ethyl heptanoate | 5.01 ± 0.11 b | 5.05 ± 0.11 b | 5.14 ± 0.11 b | 6.27 ± 0.11 a | 0.0001 |
| *n*-Hexanol | 1.54 ± 0.03 b | 1.69 ± 0.03 a | 1.04 ± 0.03 c | 0.99 ± 0.03 c | <0.0001 |
| Ethyl octanoate | 109.93 ± 2.54 b | 109.39 ± 2.54 b | 144.98 ± 2.54 a | 144.42 ± 2.54 a | <0.0001 |
| 2-Ethyl-1-hexanol | 6.60 ± 0.24 b | 8.14 ± 0.24 a | 6.22 ± 0.24 b | 5.36 ± 0.24 c | 0.0002 |
| Ethyl nonanoate | 24.13 ± 0.03 c | 24.29 ± 0.03 ab | 24.32 ± 0.03 a | 24.22 ± 0.03 b | 0.0043 |
| 1-Octanol | 106.82 ± 2.51 b | 255.91 ± 2.51 a | 68.72 ± 2.51 c | 58.05 ± 2.51 d | <0.0001 |
| Terpinene-4-ol | 13.17 ± 0.35 c | 41.86 ± 0.35 a | 17.22 ± 0.35 b | 9.13 ± 0.35 d | <0.0001 |
| Ethyl decanoate | 59.04 ± 1.53 d | 82.00 ± 1.53 c | 116.22 ± 1.53 a | 109.95 ± 1.53 b | <0.0001 |
| Isoamyl octanoate | 36.21 ± 0.05 d | 36.57 ± 0.05 c | 38.04 ± 0.05 a | 37.66 ± 0.05 b | <0.0001 |
| Nonanol | 7.92 ± 0.14 b | 12.01 ± 0.14 a | 6.82 ± 0.14 c | 5.58 ± 0.14 d | <0.0001 |
| Isovaleric acid | 2.23 ± 0.06b c | 2.05 ± 0.06 c | 2.40 ± 0.06 ab | 2.57 ± 0.06 a | 0.0014 |
| Diethyl succinate | 341.11 ± 9.19 a | 275.90 ± 9.19 b | 345.39 ± 9.19 a | 338.10 ± 9.19 a | 0.0020 |
| Methionol | 1.56 ± 0.04 a | 1.57 ± 0.04 a | 1.48 ± 0.04 a | 1.57 ± 0.04 a | 0.4287 |
| Citronellol | 10.17 ± 1.20 c | 19.82 ± 1.20 a | 15.34 ± 1.20 b | 18.65 ± 1.20 ab | 0.0019 |
| Phenethyl acetate | 93.22 ± 2.44 ab | 88.60 ± 2.44 b | 100.95 ± 2.44 a | 100.90 ± 2.44 a | 0.0175 |
| β-Damascenone | 24.91 ± 0.41 b | 26.85 ± 0.41 a | 14.96 ± 0.41 c | 14.99 ± 0.41 c | <0.0001 |
| Hexanoic acid | 1.04 ± 0.08 a | 0.98 ± 0.08 a | 1.05 ± 0.08 a | 1.13 ± 0.08 a | 0.6676 |
| Ethyl dodecanoate | 26.42 ± 0.41 b | 27.09 ± 0.41 b | 40.47 ± 0.41 a | 41.43 ± 0.41 a | <0.0001 |
| Benzyl alcohol | 137.62 ± 4.60 b | 150.74 ± 4.60 b | 166.67 ± 4.60 a | 172.38 ± 4.60 a | 0.0027 |
| Phenethyl alcohol | 21.12 ± 0.85 b | 20.96 ± 0.85 b | 22.71 ± 0.85 ab | 24.71 ± 0.85 a | 0.0450 |
| γ-Nonalactone | 0.08 ± 0.00 b | 0.09 ± 0.00 a | 0.07 ± 0.00 c | 0.07 ± 0.00 c | <0.0001 |
| Ethyl myristate | 41.18 ± 0.16 a | 40.02 ± 0.16 b | 39.74 ± 0.16 b | 40.04 ± 0.16 b | 0.0010 |
| Octanoic acid | 1.63 ± 0.21 a | 1.63 ± 0.21 a | 1.62 ± 0.21 a | 1.65 ± 0.21 a | 0.9998 |
| Ethyl palmitate | 89.01 ± 0.66b c | 87.61 ± 0.66 c | 90.06 ± 0.66 b | 96.95 ± 0.66 a | <0.0001 |

[a]Different letters within a row indicate a 95% significant difference between treatments.

each canopy side were analyzed using pairwise comparisons and ANOVA. Generally, results indicated minor differences in canopy side each season. For example, in 2008, canopy side differences were seen except for TGG (Table 5). Percentage alcohol (v/v), pH, TA, and malic acid generally illustrated nonsignificant differences between wines produced from the different canopy sides each season (data not shown). Wine volatiles were analyzed both immediately postfermentation and 6 months postfermentation using the CP ENose. These data explained most of the variation along the PCA PC1 axis (>80%), both immediately postfermentation and 6 months postfermentation. Six months postfermentation gave better discrimination of canopy sides (PC1: 97.6%, PC2: 1.7%, and PC3: 0.7%) than did immediately postfermentation (PC1: 81.1%, PC2: 17.9%, and PC3: 1.0%). The SAW ENose analysis performed immediately postfermentation was able to explain <50% variation using PC1 (PC1: 48.4%, PC2: 35.6%, and PC3: 16.0%). However, both CP ENose and SAW ENose analyses of wine volatiles were able to explain 100% of the variation (based on CDA) immediately postfermentation and 6 months postfermentation (Figure 4, Figure 5). ANOVA on CP ENose sensor responses shows that most of the sensors were sensitive to canopy side differences in the wine.

Concentration differences in volatiles were detected in wines produced from different canopy sides using traditional GC-MS 6 months postfermentation (Table 6). CDA and PCA (PC1: 67.5%, PC2: 18.6%, and PC3: 13.9%) explained 100% of the variation in the data across canopy sides. PCA biplot rays indicated that ethyl myristate, citronellol, ethyl nonanoate, and hexyl acetate were the compounds most associated with canopy side differences (data not shown).

Panelists were able to significantly ($\alpha = 0.05$) differentiate wine aroma between east and west (18 and 17, of 32 correct responses, for 2007 and 2008, respectively; Table 7), but between north and south in 2007 only (16 correct responses, compared to 13 of 32 in 2008). These results might have been different if a trained panel had been used, although a trained panel is not necessarily indicative of a consumer response. Lack of differences detected by sensory tests does not always illustrate treatment similarities, since it may involve bias and variability over time (Meilgaard et al. 2007). Although the ENose may produce results similar to sensory analysis (Mallikarjunan 2005), it evaluates both aroma and nonaroma volatiles (Haugen and Kvaal 1998). Additionally, electronic noses have the ability to objectively evaluate volatiles in a complex matrix such as wine.

**Table 7** Cabernet franc wine aroma triangle difference sensory results (n = 32) of east versus west and north versus south treatments for 2007 and 2008.

| Treatment | Correct responses[a] | Signf |
|---|---|---|
| East vs west, 2007 | 18 | yes |
| East vs west, 2008 | 17 | yes |
| North vs south, 2007 | 16 | yes |
| North vs south, 2008 | 13 | no |

[a] $\alpha = 0.05$, $\beta = 0.10$, $\rho_{max} = 40\%$, 16 or more correct responses corresponds to a significant difference.

## Conclusion

A major challenge for the grape and wine industry is to replace time-consuming laboratory analyses with new techniques that are fast, precise, and accurate. A further challenge is to understand the relationships among vineyard management, fruit chemistry, wine chemistry, and sensory response. While most industry practitioners understand the potential differences in grape and, therefore, wine composition that may result from differences in grapevine canopy side, it can be difficult to quantify those differences. Such quantification is required to examine the economics of differential harvest.

This study was performed to determine if conducting polymer-based and surface acoustic wave-based electronic nose systems could distinguish and discriminate between grape and wine volatiles across vine canopy sides. Results were compared with traditional physicochemistry indices. The physicochemistry analyses did not differentiate between canopy sides on most sampling dates and did not show trends across growing seasons. However, this study demonstrated the ability of both ENose systems to distinguish between canopy sides at all maturity stages evaluated. Sensory evaluations of wine aroma also showed canopy side differences. The differences detected by GC-MS for individual wine volatile compounds (25 out of 32) support the variation detected by the ENose systems. Considering the time efficiency and nondestructive procedure, the CP ENose may be more useful than the SAW ENose to differentiate between canopy sides.

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