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Sensory, Chemical, and Electronic Tongue Assessment of Micro-oxygenated Wines and Oak Chip Maceration: Assessing the Commonality of Analytical Techniques

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Micro-oxygenation (MOX) was conducted in the presence and absence of oak chips at rates to mimic oxygen ingress during barrel maturation of red wine. Following MOX, wines were analyzed for chemical attributes pertaining to phenolic composition and assessed by a trained sensory panel. An electronic tongue (ET) was also used to assess the wines. Variations in chemical attributes were found to be mostly influenced by vintage, followed by oak chip maceration accounting for 48% and 16% of variation within the data set, respectively. MOX treatment accounted for 11% of variability within the physicochemical data set, with attributes pertaining to anthocyanin polymerization and levels of sulfur dioxide in the finished wine being most significantly influenced. A generalized Procrustes rotation and alignment of the chemical, electronic tongue, and sensory data sets followed by PLS1 regressions showed good prediction of the sensory characters *oak*, *pencil shavings*, *stewed plum*, *vegetal*, and *spice* over the range of sensory scores from the ET data; *bitterness* and *astringency* could also be predicted from the physicochemical data with good precision.

KEYWORDS: Micro-oxygenation; Shiraz; sensory assessment; electronic tongue; chemometrics; Procrustes

INTRODUCTION

Sensory analysis is indispensable for the assessment of food flavor characteristics to identify the significant sensory and quality contributors to food quality and consumer preference. However, it can be slow and expensive and involves considerable training and maintenance of the sensory panels. The limited number of samples that can be subjected to comprehensive sensory evaluation, quantitative descriptive analysis for instance, impedes the use of descriptive sensory studies in the evaluation of novel approaches or changes to food production procedures. For this reason, the establishment of correlations between chemical or instrumental measurements of specific compositional attributes and the sensory characteristics of food, such as flavor, is of interest. The establishment of such correlations can also lead to a better understanding of the relationship between compositions and sensory properties. This is a complex task, as most foodstuffs contain potentially thousands of components that impact upon taste and aroma. The quantification of all compounds that contribute to the sensory properties of foods and modeling their interactions may be unrealistic. Therefore, there is value in using

analytical instruments producing a range of partially selective signals such as multisensor systems or spectrometers for correlating with human perception.

The electronic tongue multisensory systems (ET) are instruments with potential for correlating food composition with flavor assessments. ETs comprise an array of sensors with a nonselective response to a range of inorganic and organic substances, coupled with chemometric data processing tools (1). Most of the developed systems are based on potentiometric and voltammetric chemical sensors, although there are no limitations as to the types of sensors that can be incorporated into the ET. As the design of the ET attempts to imitate the structure of human olfaction and gustation systems, the instrument is expected to be able to reproduce their behavior as well. An ET based on an appropriate set of sensors should therefore be able to respond to a range of compounds and take into account interactions such as suppression and synergetic effects, so that sensor responses can be correlated to human perception. Several applications of the ET to the assessment of specific taste and flavor attributes of foods and wines have been reported. Astringency and bitterness of oenological tannins in model wine solutions have been correlated using potentiometric (2) and ion selective field effect transistor (3) sensors. An amperometric electronic tongue together with an

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electronic nose consisting of metal oxide sensors and spectrophotometric measurements was used for the prediction of sensory attributes of 15 Italian wines (4), and an ET with 29 potentiometric sensors was used to predict 20 sensory attributes of beer (5).

The deliberate and controlled exposure of red wine to oxygen is a technique exploited by winemakers to improve the sensorial qualities of the wine. Traditional exposure of wine to oxygen arises from deliberate vigorous wine transfers, from splashing and racking operations during alcoholic fermentation, and during the maturation phase when wine is stored in wooden barrels (6, 7). Micro-oxygenation (MOX), a technique originally developed in the mid 1990s to improve the astringent sensation of Tannat wines (8, 9), has rapidly been adopted by wine makers worldwide in an attempt to impart the positive sensorial changes that arise in wine and that are attributed to oxygen exposure, in a cost-effective way (10, 11). MOX is defined as the controlled addition of oxygen to wine in a manner designed to ensure that complete mass transfer from gaseous to the dissolved state occurs, with addition rates less than the ability of the wine to chemically consume the oxygen (12).

Anecdotal evidence from wine makers regarding the perceived organoleptic changes and sensorial improvements to wine arising from the use of MOX technologies are frequently the most substantial evidence used for deciding the appropriateness or otherwise of this technology for a specific wine. Several researchers have reported changes in the sensorial qualities of wines that have undergone MOX, with difference in color, astringency, and vegetal aromas being the most commonly reported observations (8, 13, 14). MOX has also been used in combination with oak chip maceration to emulate barrel maturation of red wines (15). However, the variability of the wine matrix and the rate and timing of oxygen additions make interpretation and extrapolation of results to all winemaking situations difficult. Presently there is no simple or reliable means to determine the suitability of a specific wine to be deliberately exposed to oxygen and often winemakers make the decision to use MOX based upon gustatory assessments and with consideration to the perceived historical quality of wines derived from similar parcels of fruit that have been subjected to MOX. The technology and outcomes of MOX in the production of red wine have recently been reviewed, and the reader is directed elsewhere for a more detailed discussion of MOX applications (16).

This study extends prior investigations in which phenolic compounds in MOX-treated wines were analysed using an electronic tongue (12). The purpose of this investigation was 2-fold: first, to determine sensorial changes in Shiraz wine exposed to MOX at a rate intended to mimic barrel maturation in a controlled and replicated study with and without oak chip maceration and, second, to assess the correlations between the sensory perceptions and physicochemical analyses of the wine. An ET based on potentiometric chemical sensors has been studied, and the possibility of using instrumental and/or chemical data for rapid assessment of wine organoleptic properties is presented.

MATERIALS AND METHODS

Winemaking and MOX. Shiraz grapes were harvested from a single vineyard located in the Yarra Valley, Victoria, Australia, during the 2004 and 2005 vintages. Approximately 25 tons of grapes were processed each year in a single batch. Alcoholic fermentation was induced by inoculation with *Saccharomyces cerevisiae*. At the completion of alcoholic fermentation, the wine was pressed off the skins, transferred to a tank, and inoculated for MLF using *Oenococcus oeni*. At the completion of MLF, the wine was chilled, allowed to settle, and taken off gross lees and a

50 mg L⁻¹ addition of sulfur dioxide was made. From this commercial-scale fermentation a 5 kL parcel of wine was used for the MOX trials.

Wine was transferred to six stainless steel tanks 36 cm diameter and 3 m high with a calculated capacity of 305 L for oxygen additions. Control tanks consisted of six variable-capacity tanks with dimensions of 77 cm by 45 cm with a calculated capacity of 110 L. An additional tank of wine was retained and used for topping all tanks and barrels during the trial. Three MOX and three control tanks were chosen at random for each vintage and had oak chip (Boise, France) additions at a total rate of 14 g L⁻¹. Four types of oak chips were used in combination at the following rates: fresh (2 g L⁻¹), single toast assorted (10 g L⁻¹), double toast 180 (1 g L⁻¹), and double toast 210 (1 g L⁻¹). These rates were chosen following discussion with the chip supplier and were intended to replicate the oak flavor extraction derived from new French barriques. Oxygen addition was done at a rate of 2 mL L⁻¹ month⁻¹ using Oenodev micro-oxygenation controllers modified in accordance with supplier instructions by insertion of a reduced volume dosing chamber into each controller to enable accurate oxygen delivery to this wine volume. Thus, four treatments for each vintage were designated as MOX + no oak; MOX + oak; no MOX + no oak; no MOX + oak. Full details of winemaking, MOX, and preparation of wine for packaging are described in ref 12.

Sensorial Analysis: Difference Testing. Duo-trio tests were conducted to determine significant differences between treatment replicates (17). A conservative α level of 0.05 was adopted for data analysis. Following statistical analysis collapse of the experimental design enabled descriptive sensorial analysis to be conducted using one replicate per treatment.

Descriptive Sensorial Analysis. The approach for descriptive sensorial analysis followed that of Blackman and Saliba (18). Panel members were selected on the basis of interest and availability from the National Wine and Grape Industry Centre and had previous wine-tasting experience. Initial training sessions involved the sensorial assessment of several wines of each treatment with participants instructed to describe perceived dominant attributes and descriptors. Descriptors were collated at the end of the first session and compiled into groups of similarity. In subsequent training sessions participants were exposed to a range of aroma and mouthfeel standards to represent the wine attributes chosen by the panel. Aroma and mouthfeel standards were prepared in order to represent a sensorial ranking of approximately 5 on a 9 point scale: i.e., recognizable by the majority of panel members but not overpowering relative to the wines for assessment. Panel feedback was sought at each training session for the appropriateness of each aroma and mouthfeel standard and adjustments made on the basis of overall panel ratings. The final aroma and mouthfeel standards used for sensorial training and wine assessments are described in Table S1 (Supporting Information). A total of eight sessions were used for panel training.

During both training and test phases, panelists were instructed to sniff and to rinse their mouths with water between samples and to wait 30 s before tasting the next sample. This was carried out to remove residual tastes and astringency. The formal descriptive evaluation of the wines was undertaken over four sessions held over 2 days with at least a 3 h break between sessions. Each wine representing the four treatment levels and three replicates for each treatment was assigned a three-digit random number by Compusense 5.0, and this was transcribed onto International Standard Organisation XL-5 glasses. The order of presentation of the wines to the panelists was determined using a randomized unbalanced block design. Each panelist was presented with only three wines at each session; these were presented in the random order determined by the Compusense 5.0 program. The panelists were instructed to rate the wines using the 1–9 scale for the following attributes: *oak*, *spice*, *pencil shavings*, *vegetal*, *astringency*, *bitterness*, *cherry*, and *stewed plums*. Results were entered directly into the Compusense 5.0 program at individual panelist terminals. All evaluations were conducted under white fluorescent lights at ambient temperature (approximately 22 °C) in individual tasting booths.

Chemical and Instrumental Analysis. A set of physicochemical parameters related to the phenolic compositions was measured on all wine samples. An emphasis was made on phenolics, as both MOX treatment and maceration with oak chips are expected to affect primarily this group of compounds. Condensed tannin concentration was determined by methyl cellulose precipitation (19), red wine color and phenolic measurements were determined using the Somers methods (20), and total

Table 1. Coding for Physicochemical Attributes of Wines

ID	attribute
1	total phenols (Folin)
2	non-flavonoids (Folin)
3	flavonoids (Folin)
4	CIE-X
5	CIE-Y
6	CIE-Z
7	CIE-L
8	CIE-a
9	CIE-b
10	tannin concn
11	color density
12	color hue
13	total phenolics
14	total anthocyanins
15	flavylium cation concn
16	anthocyanins in cation form
17	anthocyanins in cation form SO ₂ corrected
18	chemical age 1
19	chemical age 2
20	anthocyanin polymerization
21	anthocyanin copigmentation
22	acetic acid
23	molecular SO ₂
24	free SO ₂
25	total SO ₂
26	ratio free:total SO ₂
27	pH
28	titratable acidity

phenol, flavonoid, and non-flavonoid fractions were determined using the Folin method (21). Calculations for wine color density, wine color hue, total phenolics, total anthocyanins, ionized anthocyanins, percentage of anthocyanins in ionized form, and percentage of ionized anthocyanins in the absence of sulfur dioxide bleaching and chemical age were done according to ref 22. Glucose, fructose, and acetic acid were measured by enzymatic procedures (Roche Boehringer) in miniaturized format using a Biotek μ Quant microplate reader. Wine spectral measures were determined using a Shimadzu UV-1700 scanning spectrophotometer running UVProbe version 2.21 with transmission between 250 and 800 nm recorded and CIELab color coordinates calculated using UVPC Color Analysis Version 3.00. Physicochemical parameters are identified in accordance with **Table 1**.

The electronic tongue used for measurements comprised 26 potentiometric chemical sensors. Responses of the sensors were measured versus conventional Ag/AgCl reference and pH electrodes (Metrohm, Switzerland). All sensors used in this study, except the reference and pH electrodes, were produced at the Laboratory of Chemical Sensors of St. Petersburg University (1). Potentiometric measurements were carried out using a custom-made high input impedance multichannel voltmeter connected to a computer. Before each measuring session, sensors were conditioned for 10 min in red table wine and then washed with distilled water until stable potential readings were achieved. Three replicated measurements were run in each sample with a measurement time of 8 min per sample.

After the measurements were completed, sensor responses were checked for reproducibility. Nine sensors were found to have low reproducibility of the potential or be drifting during the period of the measurements and were therefore removed from the data set. An array comprising 17 sensors was used for further data processing consisting of 10 plasticized PVC sensors, of which 7 were anion-sensitive displaying response to organic anions, in particular phenols (A1–A7), and 3 were cation-sensitive (C1–C3), 6 were chalcogenide glass sensors displaying redox response (G1–G6) and a conventional glass pH electrode.

Data Processing. The chemical attributes related to wine color and anthocyanin and phenolic composition from each vintage were analyzed by principal components analysis (PCA) using the singular value decomposition in the PLS Toolbox (Eigenvector Research Inc., Wenatchee, WA, Version 5.0) in Matlab (The Mathworks R2007a, Natick, MA). Prior to PCA, data were mean centered and variances standardized.

Sensory panel data intrinsically have a three-dimensional structure, as each judge produces a table of scores for a range of attributes for the sample set. Therefore, instead of principal component analysis its multi-dimensional analogue PARAFAC (23) was used for data exploration. An important property of PARAFAC is that it can handle missing data, which were present in this data set as each of the assessors tasted 10 samples out of 12. Scores for the sample from the parallel tasting sessions were averaged. No data preprocessing was used. The number of components for the PARAFAC model was determined using the core consistency diagnostic computing PARAFAC models with one, two, and three components. The optimum was found to be two components with a core consistency of 98%. PARAFAC was computed on the sample sets from the vintages 2004 and 2005 separately and then on the combined data set using the N-way toolbox for MATLAB (24). Similar results were obtained in all three cases; therefore, only results for the combined data set are presented here.

Further evaluation of the influence of MOX, maceration with oak chips, vintage, and sensory panelist performance was done using ANOVA (25, 26). To assess the effects of MOX, oak and sensory panelist ANOVA was performed on the data sets from vintages 2004 and 2005 separately.

Averaging of the panel scores was necessary prior to the further calculations. As differences in the panelist performance were detected by both PARAFAC and ANOVA, simple averaging was considered inadequate. Instead, a consensus average for the sensory responses was calculated using Procrustes rotation, as described below, prior to reapplying ANOVA and applying PLS regression. It is important to note that differences in use of some attributes have been reported even for trained conventional panels (27).

A consensus average of sensory scores was determined using a generalized Procrustes rotation to correct for difference between assessors in the use of scales and interpretation of the meaning of the attributes (28). A variant of the Procrustes rotation algorithm that mitigates for confusion of attributes and differing use of sensory scales by panelists (29) was used in the present study, which consists in iterative scaling with the aim to minimize the differences between each combination of two assessors (30). As this algorithm does not support missing values, they were replaced by the average scores of the samples with the same settings of experimental factors (i.e., MOX and oak). Procrustes rotation is known for producing artifacts: i.e., a consensus average for random data can sometimes be obtained (31). Therefore, it is necessary to perform significance testing of the calculated consensus. A permutation test was used for this purpose (32). After calculation of the consensus average a percentage of variation explained by this consensus compared to the total variation of the initial raw data was calculated. Samples were permuted within score tables of each assessor independently 1000 times. Comparison of the distribution of the permuted data variance with the value for the initial data allows an estimate for the significance of the consensus. The Procrustes rotation algorithm and permutation testing was conducted in MATLAB. ANOVA was then conducted on the averaged scores for both vintages separately with MOX treatment, oak chip maceration, and interactions modeled.

PLS2 regression was used to study the relationship between the sensory attributes and instrumental, i.e. physicochemical and ET, data sets using full cross-validation. Physicochemical data were considered as independent variables for which a set of dependent variables, i.e. sensory attributes, was predicted. Calibration models for predicting individual sensory attributes from the instrumental data were calculated using PLS1 regression. Individual calibration models for each attribute were produced with either physicochemical or ET data being considered as the independent variable. All calibration models were validated using segmented cross-validation. PLS regression was conducted with The Unscrambler (Camo, Norway, version 7.9).

RESULTS AND DISCUSSION

Chemical Analysis. Data for chemical attributes are presented in Table S2 (Supporting Information). Biplots of PCA components 1, 2, and 3 with loadings of the chemical data are shown in **Figure 1**. Samples are distinctly separated by vintage (PC1) on the basis of wine color attributes, including CIE color coordinates,

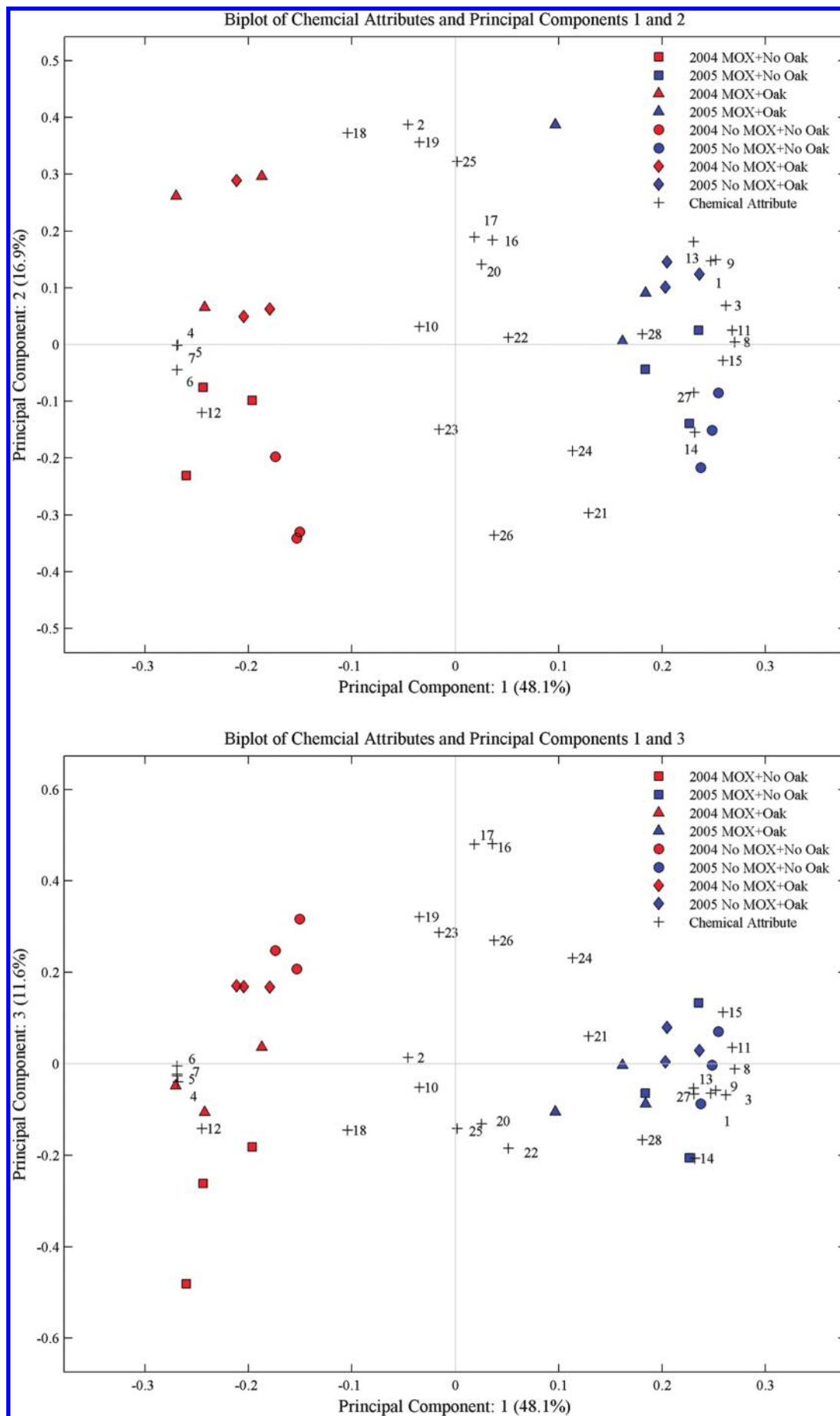


Figure 1. Biplot of chemical attribute loadings and PCs 1 versus 2 and PCs 1 versus 3. Physicochemical attributes are given in Table 1.

wine color density and hue, flavonoid concentration, total phenols, flavylum ion concentration, pH, and titratable acidity. Nonflavonoid phenolic concentration, copigmentation, and chemical age attributes are important determinants and are influenced by the presence of oak chips (PC2), while MOX treatment has an influence on the chemical age of the wine and the levels of free and molecular sulfur dioxide (PC3). Chemical age attributes indicate the degree that polymeric pigments have replaced monomeric anthocyanins in the contribution to wine color (22), and this attribute could be expected to be highly influenced by the production of stable chromophores that are reported with MOX (13), while acetaldehyde production during MOX will rapidly bind to sulfur dioxide (33), leading to decreased ratios of free to total sulfur dioxide in the finished wines. In the present investigation chemical attributes of the wines appear to be more highly influenced by vintage and oak chip maceration rather than MOX.

Sensory Analysis. Duo–trio testing of treatment replicates did not show any significant differences across replicates for all treatments and vintages at an α value of 0.05. Therefore, quantitative descriptive analysis was conducted on a single replicate for each treatment and vintage. Median scores and distributions for sensory attributes are illustrated for each vintage in box plots that show lower, median, and upper quartile ranges (Figure S1, Supporting Information). Extending from each box are whiskers indicating the interquartile range.

Evaluation of panelist performance was necessary to determine consistency and appropriate use of the sensory scales. Very often panelists differ in the use of a scale or in the sensitivity to some of the attributes (34). In these cases calculation of the average scores as a simple arithmetic mean is inadequate and weighting and scaling should be employed (29). Therefore, assessment of the individual differences between panelists was carried out first. Two-factor PARAFAC analyses of the sensory data produced three sets of loadings corresponding to the samples, attributes, and judges. Loadings for the first and second factors for the samples, attributes and judges are plotted in Figure 2. Consistent with analytical chemical data, separation according to vintage and oak chip maceration was evident in the plot of sample loadings (Figure 2A). No separation according to the MOX treatment for either vintage was observed. Comparing loading plots of samples and sensory attributes, it is possible to conclude that the main influence of the oak treatment was on such wine flavor attributes as *oak*, *pencil shavings* and *vegetal*. The sensory attributes *oak* and *pencil shavings* have higher values in oak-treated wines, which was expected, and the sensory attribute *vegetal* is lower in wines with oak maceration.

The loading plot for the judges (Figure 2C) reveals two separate clusters with one of the tasters (G) well separated from other assessors, indicating differences in panelist performance. Individual differences between judges were further assessed using ANOVA with the effects taster, MOX and oak treatments, and vintage found to be significant. Since differences between vintages were not of interest for the purposes of the present study, data from each vintage were analyzed by ANOVA separately. Three main effects, MOX, oak treatments, and tasters, were estimated, and *P* values are shown in Table 2. The effects of oak treatment and sensory panelist were significant for both vintages 2004 and 2005. Analysis of the univariate results revealed that oak chip maceration was significant for all attributes except *cherry*, *stewed plum*, and *bitterness* for both vintages. Maceration with oak chips increased the intensity of *oak*, *spice* and *pencil shavings*, slightly increased *astringency* and *bitterness*, while *vegetal* and *H₂S* characters were decreased in the treated wines. This is as expected, as oak contact with wine imparts considerable spicy aromas,

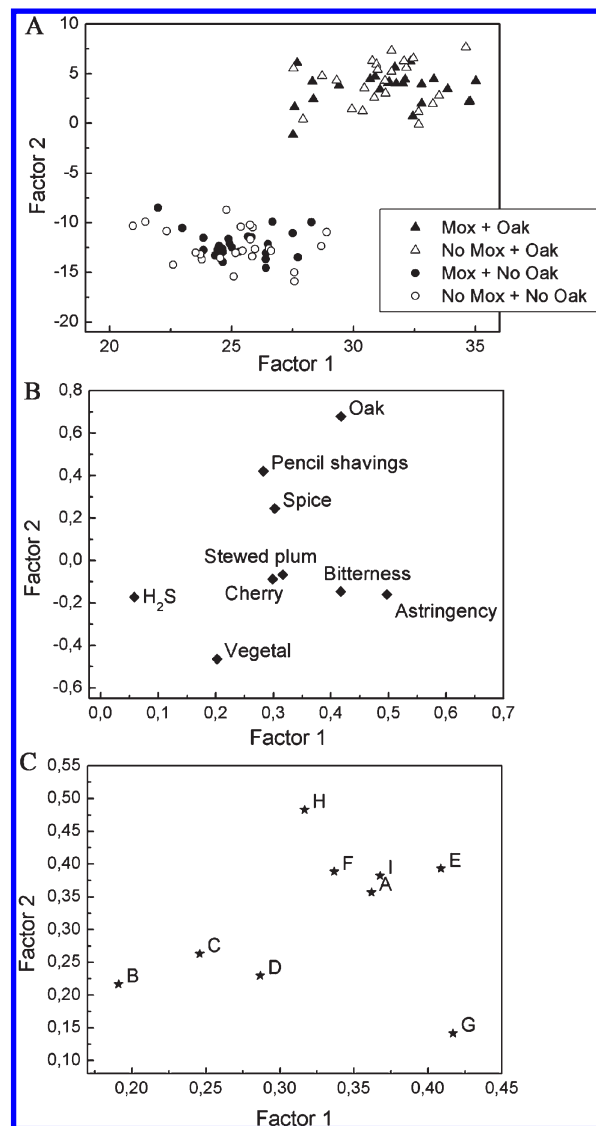


Figure 2. PARAFAC loadings for the samples (A), sensory attributes (B), and judges (C) for the first two factors.

Table 2. Significant Sources of Variation in the ANOVA Model of the Raw Sensory Data

	vintage 2004			vintage 2005		
	effect			effect		
	taster	MOX	oak	taster	MOX	oak
total	0.000	0.314	0.000	0.000	0.001	0.000
bitterness	0.000	0.415	0.040	0.000	0.253	0.793
astringency	0.000	0.069	0.005	0.000	0.609	0.013
cherry	0.000	0.681	0.050	0.000	0.003	0.753
oak	0.000	0.247	0.000	0.000	0.849	0.000
pencil shavings	0.000	0.629	0.000	0.000	0.475	0.000
vegetal	0.000	0.272	0.000	0.000	0.009	0.000
stewed plum	0.000	0.556	0.481	0.000	0.293	0.067
spice	0.000	0.257	0.000	0.000	0.334	0.000
H ₂ S	0.000	0.810	0.000	0.000	0.001	0.000

potentially masking the presence of sensory characteristics that are close to threshold, whereas the extraction of hydrolyzable tannins may impart a higher level of perceived astringency and bitter character (35, 36).

The effects of MOX treatment were significant for the sensory attributes *cherry* (increased), *vegetal* (increased) and *H₂S*

Table 3. Significant Sources of Variation in the ANOVA Model of the Sensory Data after Averaging

	2004			2005		
	effect			effect		
	MOX	oak	MOX*oak	MOX	oak	MOX*oak
total	0.558	0.048	0.516	0.235	0.023	0.163
bitterness	0.267	0.008	0.752	0.806	0.446	0.870
astringency	0.589	0.003	0.908	0.589	0.008	0.637
cherry	0.069	0.379	0.680	0.054	0.363	0.008
oak	0.081	0.000	0.056	0.399	0.000	0.708
pencil shavings	0.160	0.000	0.151	0.094	0.000	0.025
vegetal	0.324	0.000	0.882	0.015	0.000	0.139
stewed plum	0.290	0.000	0.706	0.199	0.000	0.293
spice	0.008	0.000	0.254	0.149	0.000	0.016
H ₂ S	0.874	0.031	0.886	0.013	0.000	0.003

(decreased) for the 2005 vintage wines. It is important to note that the magnitude of the effect of the MOX treatment on wine properties was small compared to that of maceration with the oak chips. The main effect of taster was significant for all attributes for both vintages, indicating once more that there were disagreements between the panelists. Therefore, application of scaling for calculation of the average scores was considered appropriate.

The consensus average scores calculated using a generalized Procrustes rotation was found to be highly significant with $p < 0.01$ by the permutation test. ANOVA was run on the consensus average scores from the vintages 2004 and 2005 separately with two effects, MOX treatment and oak chip maceration, and with their interaction also modeled. P values from this ANOVA are shown in **Table 3**. Only the effect of oak maceration was significant for this model, comprising all attributes for both vintages. Univariate ANOVA has shown that the effect of oak maceration was significant for all attributes except *cherry* for the vintage 2004 and for all attributes except *cherry* and *bitterness* for the vintage 2005. Similar to the results obtained for the raw sensory data, the intensity of attributes *oak*, *spice*, *pencil shavings*, *astringency*, and *bitterness* increased while *vegetal*, *stewed plum* and *H₂S* decreased in the oak-treated wines. The effect of MOX treatment was significant for the sensory attributes *spice* (increase) for vintage 2004, and *vegetal* (increase) and *H₂S* (decrease) for vintage 2005. Interaction effects of MOX and oak treatments were significant only for the vintage 2005 for the attributes *cherry*, *pencil shavings*, *spice*, and *H₂S*. The effect of MOX treatment was more pronounced in the wines that were not macerated with oak chips. As maceration with oak chips produced greater changes in the wine organoleptic properties in comparison to MOX treatment, it may have masked any effect of the latter.

Correlation of Sensory, Chemical, and Instrumental Data Sets.

Comparison of sensory and instrumental (physicochemical and ET) data sets was performed using PLS2 regression. Instrumental data were used as explanatory or X-variables for predicting sensory attributes. Data from both vintages were combined in one data set. PLS2 models were validated using full cross-validation due to the small number of samples.

A plot of the PLS2 correlation loadings of the physicochemical and sensory data is shown in **Figure 3A**. Circles on the plot correspond to the 50% and 100% of explained variance or the absolute values of the correlation coefficient of 0.7 and 1, respectively. Two significant PCs were extracted, containing 65% of variance in both physicochemical and sensory data sets. Physicochemical parameters are shown by numbers corresponding to the list in Materials and Methods. There was no or little

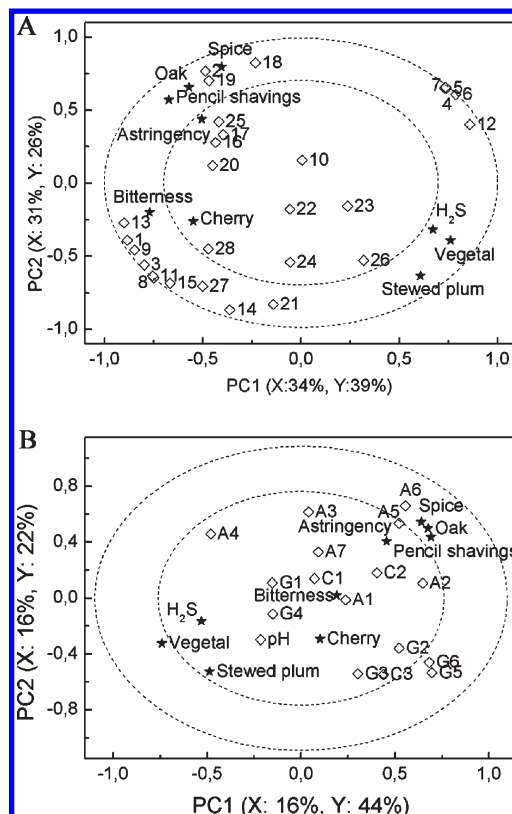


Figure 3. PLS2 loadings for first two principal components for explanatory variables physicochemical (A) and ET (B) data for sensory data (dependent) variables. Physicochemical attributes are given in **Table 1**. Electronic tongue sensors are designated by letter and numeral: (A) anion sensitive; (C) cation sensitive; (G) glass redox responsive.

correlation between physicochemical parameters and sensory attributes *cherry* and *astringency*. *Bitterness* was correlated with total phenolic content (13 and 1). The content of nonflavonoid phenolic compounds (2) and chemical ages 1 (18) and 2 (19) were positively correlated with the sensory attributes *oak*, *pencil shavings*, and *spice* and negatively correlated with *H₂S*, *vegetal*, and *stewed plum*.

A plot of PLS2 correlation loadings of the ET and sensory data is shown in **Figure 3B**. Four significant PCs were extracted, containing 85% and 76% of variance in the ET and sensory data sets, respectively. Similar to the model of physicochemical and sensory data attributes, *oak*, *spice*, *pencil shavings*, and *astringency* were negatively correlated with *vegetal*, *stewed plum*, and *H₂S*. Correlation loadings of the attributes *bitterness* and *cherry* were close to 0, which means that they were not correlated with the ET data. Weak correlation was observed with sensory attributes *astringency* and *H₂S*, which had correlation coefficients of -0.53 and 0.46 , respectively, along the first PC. Responses of the sensors displaying sensitivity to the organic anions and polyphenols in particular were positively correlated with attributes *oak*, *pencil shavings*, and *spice* and negatively correlated with *stewed plum* and *vegetal*.

Calibration models using PLS1 with full cross validation were done with respect to each sensory attribute individually using physicochemical and ET data. Predicted values of the attributes using physicochemical and ET data are shown in **Table 4**. These results are largely in agreement with the results obtained using PLS2. Attributes for which there were no or weak correlations according to PLS2 could not be predicted by any individual PLS1 model. The exception was *astringency*, which could be predicted by physicochemical data.

Table 4. PLS1 Predictive Models for Sensory Attributes with Physicochemical and Electronic Tongue Data

attribute	value range	physicochemical data				electronic tongue data			
		slope	offset	R^2	RMSEP	slope	offset	R^2	RMSEP
bitterness	3.6–4.6	0.80	0.83	0.89	0.14				
astringency	4.3–5.6	0.69	1.60	0.78	0.24				
cherry									
oak	0–5.15	0.91	0.20	0.94	0.72	0.85	0.42	0.87	1.08
pencil shavings	0.3–3.95	0.98	0.04	0.98	0.31	0.72	0.58	0.83	0.81
vegetal	1.3–3.75	0.68	0.75	0.87	0.38	0.82	0.45	0.86	0.39
stewed plum	2.3–3.75	0.84	0.47	0.9	0.22	0.69	0.91	0.78	0.31
spice	0.98–3.92	0.96	0.10	0.96	0.31	0.84	0.37	0.90	0.47
H ₂ S	0.23–1.43	0.51	0.32	0.70	0.24				

The red wine system used in this study, with its combination of vintage, MOX treatment, physicochemical data, ET data, and sensory data, has demonstrated the potential use of analytical data for predicting phenolic effects on sensory responses. Initial statistical analysis showed that vintage variations influencing phenolic composition and wine color attributes accounted for the largest portion of the variability within the chemical data set (48%), oak chip maceration (16%) was found to increase the nonflavonoid concentration and the anthocyanin indices chemical ages 1 and 2, and MOX (11%) influenced anthocyanin polymerization indices and the levels of sulfur dioxide in the finished wine. With respect to sensory analysis, vintage was found to account for the largest sensory differences between the wines and oak chip maceration influenced perceived *bitterness*, *astringency*, *spice*, *oak*, *pencil shavings*, and *H₂S*. The sensory impact of MOX was minor for one vintage, only influencing *cherry* and *vegetal* and the fermentation off-odor *H₂S*. It is not possible to categorically ascribe sensory and chemical variations of the wines to seasonal influences upon grape and, therefore, wine composition or to bottle age affect. The variations within vintage are of lesser importance in comparison to variations between vintages, and the influence of MOX treatments within each vintage accounts for only a minor amount of total variation. Clearly more research is required to determine the impact of MOX across vintages and how long-term wine storage may influence the overall variations attributed to MOX treatment. A generalized Procrustes rotation was employed for the calculation of the average scores, which were further used for calibrating ET and physicochemical data sets. Both data sets identified good commonality with some of the sensory attributes of the wines. These results indicate that appropriate instrumental and physicochemical measurements may be used for the rapid assessment of some aspects of the wine flavor and partly replace sensory panels in routine analysis.

ABBREVIATIONS USED

MOX, micro-oxygenation; MLF, malolactic fermentation; PCA, principal component analysis; PLS, partial least-squares; PARAFAC, parrel factor analysis.

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Supporting Information Available: Table S1, giving sensory descriptors and standards used for panel training and sensorial assessments, Table S2, giving physicochemical attributes of wines for both vintages, and Figure S1, giving box plots of median

scores and distributions for sensory attributes of wines for the 2004 and 2005 vintages. This material is available free of charge via the Internet at <http://pubs.acs.org>.

LITERATURE CITED

- (1) Legin, A.; Rudnitskaya, A.; Lvova, L.; Vlasov, Y., Electronic tongues: new analytical perspective for chemical sensors. In *Integrated Analytical Systems*; Alegret, S., Ed.; Elsevier: Amsterdam, 2003; Vol. 39, pp 437–486.
- (2) Fontoin, H.; Saucier, C.; Rudnitskaya, A.; Legin, A.; Teissedre, P.-L.; Glories, Y., Qualitative discrimination of tannin extracts in model wine solution using the electronic tongue. In *XXXth World Congress of Vine and Wine*; June 10–16, 2007; OIV: Budapest, Hungary, 2007.
- (3) Puech, J.-L.; Prida, A.; Isz, S. Quality Assessment of Oenological Tannins Utilising Global Selectivity Chemical Sensors Array (“Electronic Tongue”). *S. Afr. J. Enol. Vitic.* **2007**, 27 (2), 101–106.
- (4) Buratti, S.; Ballabio, D.; Benedetti, S.; Cosio, M. S. Prediction of Italian red wine sensorial descriptors from electronic nose, electronic tongue and spectrophotometric measurements by means of Genetic Algorithm regression models. *Food Chem.* **2007**, 100 (1), 211–218.
- (5) Rudnitskaya, A.; Polshin, E.; Kirsanov, D.; Lammertyn, J.; Nicolai, B.; Saison, D.; Delvaux, F. R.; Delvaux, F.; Legin, A. Instrumental measurement of beer taste attributes using an electronic tongue. *Anal. Chim. Acta* **2009**, 646 (1–2), 111–118.
- (6) Castellari, M.; Simonato, B.; Tornielle, G. B.; Spinelli, P.; Ferrarini, R. Effects of different enological treatments on dissolved oxygen in wines. *Ital. J. Food Sci.* **2004**, 16 (3), 387–397.
- (7) Moutounet, M.; Mazauric, J. P.; Saint-Pierre, B.; Hanocq, J. F. Gaseous exchange in wines stored in barrels. *J. Sci. Tech. Tonnellerie* **1998**, 4, 131–145.
- (8) Lemaire, T.; Gilis, J. F.; Fort, J.-P.; Ducournau, P., Micro-oxygenation in extended maceration and early stages of red wine maturation—immediate effects and long term consequences. In *Proceedings of the Eleventh Australian Wine Industry Technical Conference*; Blair, R. J., Williams, P. J., Høj, P. B., Eds.; Australian Wine Industry Technical Conference: Adelaide, Australia, 2002; pp 33–43.
- (9) Roig, G.; Yérle, S., Balance y perspectivas de 10 años de micro-oxygenación. In *ACE Enología*; ACE Revista de Enología: Girona, Barcelona, 2003; Vol. 2007.
- (10) Parish, M.; Wollan, D.; Paul, R. Micro-oxygenation - a review. *The Australian and New Zealand Grapegrower and Winemaker* **2000**, 438a (Technical Issue), 47–50.
- (11) Gore, R. Wine maturation alternatives may offer greater cost effectiveness. *Aust. Wine Ind. J.* **2007**, 22 (5), 46–48.
- (12) Rudnitskaya, A.; Schmidtke, L. M.; Delgadillo, I.; Legin, A.; Scollary, G. Study of the influence of micro-oxygenation and oak chip maceration on wine composition using an electronic tongue and chemical analysis. *Anal. Chim. Acta* **2009**, 642 (1–2), 235–245.
- (13) Llaudy, M. D. C.; Canals, R.; González-Manzano, S.; Canals, J. M.; Santos-Buelga, C.; Zamora, F. Influence of micro-oxygenation treatment before oak aging on phenolic compounds composition, astringency, and color of red wine. *J. Agric. Food Chem.* **2006**, 54 (12), 4246–4252.

- (14) du-Toit, W. J.; Lisjak, K.; Marais, J.; du-Toit, M. The effect of micro-oxygenation on the phenolic composition, quality and aerobic wine-spoilage microorganisms of different South African red wines. *S. Afr. J. Enol. Vitic.* **2006**, *27* (1), 57–67.
- (15) Del Álamo, M.; Nevares, I.; Gallego, L.; Fernández de Simón, B.; Cadahía, E. Micro-oxygenation strategy depends on origin and size of oak chips or staves during accelerated red wine aging. *Anal. Chim. Acta* **2010**, *660* (1–2), 92–101.
- (16) Schmidtke, L. M.; Clark, A. C.; Scollary, G. R., Micro-oxygenation of red wine: techniques, applications and outcomes. *Crit. Rev. Anal. Chem.* **2010**, in press, DOI: 10.1080/10408390903434548
- (17) Standards Australia. *Sensory Analysis Method 2.4: Specific Methods-Duo-Trio Test*; SAI Global: Sydney, **2008**; Vol. AS 2542.2.4-2005.
- (18) Blackman, J.; Saliba, A. Sensory characterization of Hunter Valley Semillon using descriptive analysis. *Flavour Fragrance J.* **2009**, *24* (5), 238–244.
- (19) Sarneckis, C. J.; Damberg, R. G.; Jones, P.; Mercurio, M.; Herderich, M. J.; Smith, P. A. Quantification of condensed tannins by precipitation with methyl cellulose: development and validation of an optimized tool for grape and wine analysis. *Aust. J. Grape Wine Res.* **2006**, *12* (1), 39–49.
- (20) Iland, P.; Bruer, N.; Edwards, G.; Weeks, S.; Wilkes, E., *Chemical Analysis of Grapes and Wine: Techniques and Concepts*; Patrick Iland Wine Promotions: Campbelltown, Australia, 2004; p 110.
- (21) Singleton, V. L.; Rossi, J. A., Jr. Colorimetry of Total Phenolics with Phosphomolybdic-Phosphotungstic Acid Reagents. *Am. J. Enol. Vitic.* **1965**, *16* (3), 144–158.
- (22) Zoecklein, B., *Wine Analysis and Production*; Chapman and Hall: New York, 1995; p 621.
- (23) Bro, R. PARAFAC. Tutorial and applications. *Chemom. Intell. Lab. Syst.* **1997**, *38*, 149–171.
- (24) Andersson, C. A.; Bro, R. The N-way Toolbox for Matlab. *Chemom. Intell. Lab. Syst.* **2000**, *52*, 1–4.
- (25) Stahle, L.; Wold, S. Analysis of variance (ANOVA). *Chemom. Intell. Lab. Syst.* **1989**, *6* (4), 259–272.
- (26) Stahle, L.; Wold, S. Multivariate analysis of variance (MANOVA). *Chemom. Intell. Lab. Syst.* **1990**, *9* (2), 127–141.
- (27) Dijksterhuis, G. Assessing panel consonance. *Food Qual. Preference* **1995**, *6* (1), 7–14.
- (28) Gower, J. C. Generalised Procrustes Analysis. *Psychometrika* **1975**, *40*, 33–51.
- (29) Romano, R.; Brockhoff, P. B.; Hersleth, M.; Tomic, O.; Næs, T. Correcting for different use of the scale and the need for further analysis of individual differences in sensory analysis. *Food Qual. Preference* **2008**, *19* (2), 197–209.
- (30) Ten Berge, J. Orthogonal procrustes rotation for two or more matrices. *Psychometrika* **1977**, *42* (2), 267–276.
- (31) Dijksterhuis, G. B.; Heiser, W. J. The role of permutation tests in exploratory multivariate data analysis. *Food Qual. Preference* **1995**, *6* (4), 263–270.
- (32) Wakeling, I. N.; Raats, M. M.; MacFIE, H. J. H., A new significance test for consensus in generalized procrustes analysis. *J. Sens. Stud.* **1992**, *7* (2), 91–96.
- (33) Es-Safi, N. E.; Fulcrand, H.; Cheynier, V.; Moutounet, M. Studies on the acetaldehyde-induced condensation of (-)-epicatechin and malvidin 3-O-glucoside in a model solution system. *J. Agric. Food Chem.* **1999**, *47* (5), 2096–2102.
- (34) Dijksterhuis, G., Procrustes analysis in sensory research. In *Multivariate Analysis of Data in Sensory Science*; Næs, T., Risvik, E., Eds.; Elsevier Science: Amsterdam, 1996; pp 185–220.
- (35) Ferreras, D.; Fernandez, E.; Falque, E. Note: Effects of Oak Wood on the Aromatic Composition of Vitis vinifera L. var. treixadura Wines. *Food Sci. Technol. Int.* **2002**, *8* (6), 343–349.
- (36) Jindra, J. A.; Gallander, J. F. Effect of American and French Oak Barrels on the Phenolic Composition and Sensory Quality of Seyval blanc Wines. *Am. J. Enol. Vitic.* **1987**, *38* (2), 133–138.

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