Using Elemental Analysis For Discrimination Of Pinot Noir Wines From Six Different Districts In An Ava

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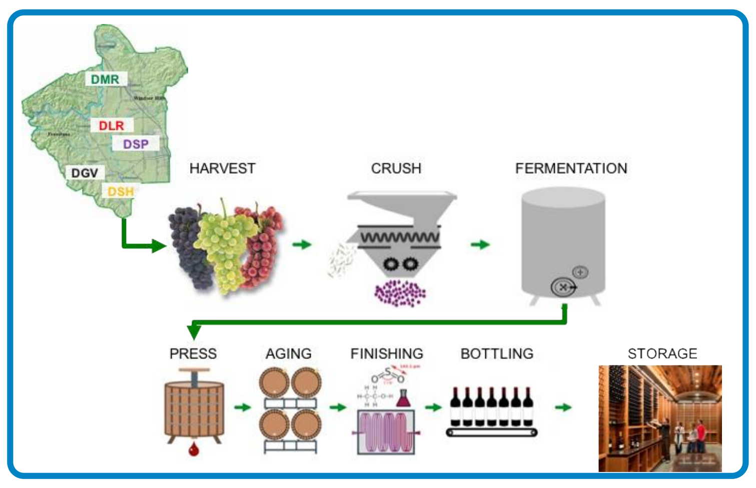
Introduction

- For U.S. wine consumers place of origin on a region, county and state level are very important decision criteria for wine purchase [1].
- Wine consumers associate information about the wine region with higher quality [2], and they are willing to pay premium prices for wines from well-known regions.
- The determination of geographical origin of wine is gaining increased interest by researchers and federal agencies around the world, partially due to increased fraud with regards to place of origin labeling.
- For wine, multi-elemental profiling of macro, micro, and trace elements has been proposed for determination of authenticity.
- To successfully determine the geographical authenticity of wine, one needs to
    - i. understand the variability in elemental concentrations and ratios within and across countries, states, regions and sub-regions
    - ii. connect results from controlled studies to commercial real world practices
    - iii. study how cultivars and/or wine styles impact the elemental fingerprint
- Past studies looked at elemental differences between countries and wine regions [3-9], however, limited information is available for elemental differences of wines made from the same cultivar and coming from within one wine region under commercial practices



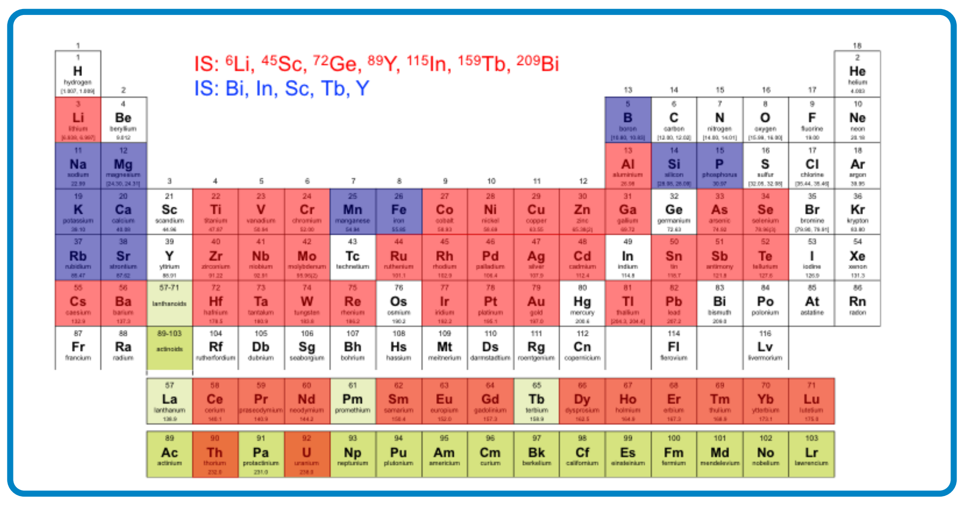
Experimental

Samples

- 25 Pinot noir wines from single vineyard plots from one of 5 neighborhoods within one American Viticultural Area (AVA).
- Fermented in separate containers without significant additions other than yeast and nutrients
- With minimal oak contact
- From the same vintage (2016)
- Part of multi-year *Neighborhood Initiative*

Sample Preparation

- For ICP-MS: 1:3 dilution in 5% HNO_3; matrix-matched calibration 0 - 500 µg/L (4% ethanol, 5% HNO_3) for 40 elements; IS mix
- For MP-AES: 1:3 dilution in 5% HNO_3; matrix-matched calibration 0 - 50 mg/L (4% ethanol, 5% HNO_3) for 11 elements; IS mix
- 5 spiked wine samples (2 concentrations)



Data Collection

8800/8900 ICP-MS/MS (Agilent)

- Concentric micromist, quartz double-glass spray chamber at 2°C
- 1550 W RF power, 1.8 V RF matching voltage, 10 mm sampling depth, 1.02 mL/min Ar carrier gas
- He flow (4.3 mL/min), high energy He (10 mL/min for As), O_2 (0.6 mL/min for Se)

4200/4210 MP-AES (Agilent)

- Concentric micromist, double pass cyclonic spray chamber at RT
- 2,000 mg/L ionization buffer mixed with sample

Experimental

Data Analysis

- Isotopes selected based on LOD, instrument detection limits, BEC, past studies and recoveries
- Uni- and multivariate Analysis of Variance ((M)ANOVA) with main effect *neighborhood* to determine discriminating elements and elemental ratios ($P < 0.05$)
- Canonical Variate Analysis (CVA) for classification by *neighborhood*

Results and Discussion

Analytical Method

- 49 elements were detected above LOD (**Table 1**)
- Recoveries (2 concentrations, 5 samples)
    - ICP-MS from 73% (Se) - 107% (Pb)
    - MP-AES from 99% (Ca) – 118% (Si)

Table 1 *Detected elements with limits of detection (LOD) and ranges for the 5 neighborhoods for the MP-AES and ICP-MS.*

	LOD [mg/L]	Range [mg/L]				
		DGV	DLR	DMR	DSH	DSP
B 249.677 nm	0.055	2.87-7.12	4.73-6.96	5.65-14.20	1.83-5.97	4.61-13.38
Ca 396.847 nm	0.061	41.3-70.5	32.4-53.6	33.8-68.3	43.7-53.5	43.6-53.0
Fe 371.993 nm	0.148	0.243-2.255	0.438-1.489	0.380-1.858	0.616-1.41	0.492-1.53
K 769.897 nm	0.216	343-577	380-610	409-696	371-639	503-712
Mg 285.213 nm	0.029	128-147	144-158	118-155	119-167	111-165
Mn 403.076 nm	0.162	1.51-5.97	1.94-3.86	1.10-2.18	2.06-3.30	1.04-3.87
Na 589.592 nm	0.491	10.8-62.3	9.32-37.7	5.83-26.3	4.47-32.2	9.91-27.1
P 214.915 nm	43.9	192-376	259-349	227-329	172-382	257-428
Rb 780.027 nm	0.084	0.519-2.75	0.673-4.05	0.356-1.03	0.617-2.04	1.75-3.82
Si 251.611 nm	0.343	13.6-35.2	9.05-27.5	11.3-22.5	16.5-22.7	19.2-35.7
Sr 421.552 nm	0.025	0.794-1.26	0.622-1.43	0.423-1.46	0.806-2.38	0.447-0.873
	[µg/L]	Range [µg/L]				
^{7}Li	1.15	1.42 - 13.2	ND - 10.1	ND - 9.8	ND - 7.1	2.93 - 24.4
^{27}Al	2.82	107 - 547	129 - 231	126 - 277	119 - 359	150 - 325
^{47}Ti	1.09	4.13 - 7.65	3.19 - 7.71	3.69 - 9.60	3.08 - 6.58	4.49 - 9.57
^{51}V	0.041	0.098 - 0.855	0.099 - 0.305	0.144 - 1.20	0.120 - 0.475	0.278 - 0.901
^{52}Cr	0.512	1.80 - 11.0	3.42 - 4.98	3.10 - 10.0	1.54 - 11.0	3.05 - 8.4
^{59}Co	0.015	1.85 - 15.8	5.95 - 13.2	1.20 - 3.57	2.39 - 10.7	2.25 - 6.01
^{60}Ni	0.346	15.1 - 45.4	29.9 - 87.3	9.77 - 39.2	33.5 - 47.9	33.6 - 86.9
^{65}Cu	1.25	16.1 - 58.2	11.4 - 37.7	11.0 - 75.3	10.1 - 71.4	4.08 - 107
^{66}Zn	1.01	298 - 986	589 - 1826	151 - 1233	392 - 741	528 - 1000
^{71}Ga	0.014	0.023 - 0.273	0.026 - 0.088	0.018 - 0.164	ND - 0.076	0.056 - 0.150
^{75}As	0.053	0.423 - 4.14	0.624 - 1.62	0.176 - 1.19	0.393 - 1.88	0.461 - 1.13
^{78}Se	0.016	0.172 - 1.07	0.119 - 0.318	0.075 - 0.260	0.152 - 0.680	0.200 - 0.983
^{90}Zr	0.059	0.310 - 1.99	0.119 - 1.30	0.072 - 0.580	0.161 - 1.92	0.175 - 2.06
^{98}Mo	1.60	ND - 7.61	ND - 1.94	ND	ND - 2.11	ND
^{101}Ru	0.020	0.493 - 7.79	ND - 0.814	ND - 0.444	0.142 - 1.39	0.185 - 1.76
^{103}Rh	0.007	0.113 - 0.352	0.098 - 0.233	ND - 0.161	0.108 - 0.225	0.036 - 0.162
^{105}Pd	0.068	ND - 0.024	ND - 0.058	ND	ND- 0.048	ND - 0.015
^{111}Cd	0.014	0.661 - 16.2	1.25 - 5.87	0.712 - 14.5	0.699 - 4.11	3.70 - 28.4
^{125}Te	0.001	183 - 445	213 - 625	109 - 418	101 - 460	308 - 740
^{133}Cs	0.027	0.021 - 0.153	0.011 - 0.151	0.012 - 0.050	0.019 - 0.056	0.019 - 0.116
^{137}Ba	0.179	ND - 0.029	ND - 0.025	ND	ND	ND - 0.023
^{140}Ce	0.008	ND - 0.025	ND - 0.026	ND	ND - 0.024	ND - 0.033
^{141}Pr	0.012	0.015 - 0.073	0.012 - 0.060	ND - 0.024	ND - 0.026	ND - 0.055
^{147}Sm	0.011	ND - 0.035	ND - 0.048	ND	ND	ND - 0.041
^{148}Nd	0.012	0.012 - 0.038	ND - 0.042	ND - 0.015	ND - 0.027	ND - 0.063
^{157}Gd	0.016	ND - 0.014	ND	ND	ND	ND - 0.014
^{163}Dy	0.012	0.013 - 0.052	ND - 0.041	ND	ND - 0.027	ND - 0.049
^{165}Ho	0.011	0.023 - 0.089	0.017 - 0.060	ND - 0.024	ND - 0.061	0.017 - 0.075
^{166}Er	0.010	ND - 0.029	ND - 0.026	ND	ND - 0.025	ND
^{172}Yb	0.017	ND - 1.43	ND - 1.03	ND - 0.534	ND - 1.48	ND - 0.503
^{175}Lu	0.021	0.045 - 0.432	ND	ND	ND - 0.078	ND - 0.074
^{178}Hf	0.195	0.104 - 0.384	ND - 0.140	ND - 0.431	0.074 - 0.181	0.081 - 0.910
^{181}Ta	0.033	ND	ND - 0.012	ND - 0.013	ND - 0.014	ND
^{182}W	0.071	ND - 0.029	ND	ND	ND	ND
^{185}Re	0.004	0.467 - 6.92	ND - 1.23	ND - 1.52	0.240 - 2.57	0.224 - 4.41
^{195}Pt	0.009	0.075 - 1.41	0.149 - 0.499	0.075 - 0.184	0.147 - 1.10	0.198 - 0.788
^{197}Au	0.216	1.85 - 12.9	1.64 - 5.78	0.543 - 2.96	1.49 - 9.87	1.91 - 3.96
^{205}Tl	0.004	ND	ND	ND - 0.015	ND - 0.019	ND - 0.020
$^{1/3*(206+207+208)}$Pb	0.077	1.42 - 13.2	ND - 10.1	ND - 9.8	ND - 7.1	2.93 - 24.4
^{238}U	0.012	107 - 547	129 - 231	126 - 277	119 - 359	150 - 325

Results and Discussion

Discriminating Elements & ratios

- In addition to the 49 detected elements (**Table 1**), various elemental ratios were included.
- The elemental ratios were used to study uptake for rootstock, soil and water effects
    - K/(Na+K+Rb+Cs)
    - Na/(Na+K+Rb+Cs)
    - Ca/(Ca+Mg)
    - Mg/ (Ca+Mg)
    - Fe/(Sc+Ti+V+Cr+Mn+Fe+Co+Ni+Cu+Zn)
    - Cu/(Sc+Ti+V+Cr+Mn+Fe+Co+Ni+Cu+Zn)
- Overall significant differences between the elemental composition of the 5 neighborhoods were found by MANOVA (P < 0.05).
- 40 variables were found to discriminate significantly between the 5 neighborhoods (P < 0.05), and were subsequently used in the CVA (**Figure 1-2**).
- Along CV 1, explaining 65% of the discrimination, K, B, Rb, Ni, Cs, Ba vs. Cd, Ta, Pt were the most discriminating elements.
- Along CV 2, explaining additional 22% of the variability, the Fe and K ratios, K, B and V vs. Co, Ni and REEs were the most discriminating elements.

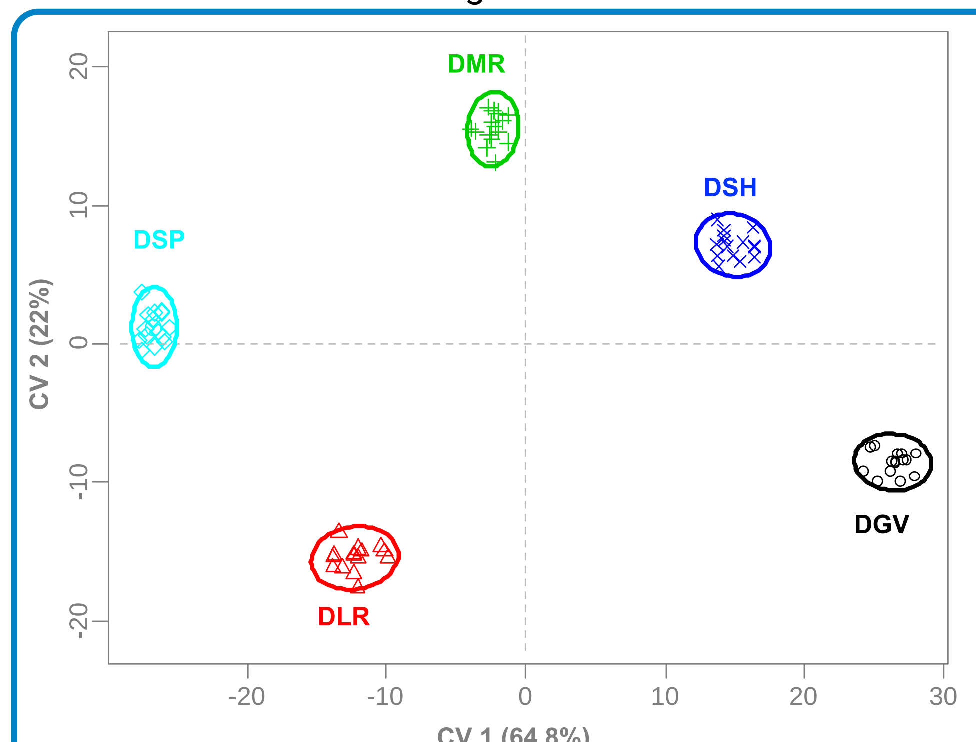


Figure 1 *Separation of the 5 neighborhoods by CVA (95% confidence intervals are shown for each group).*

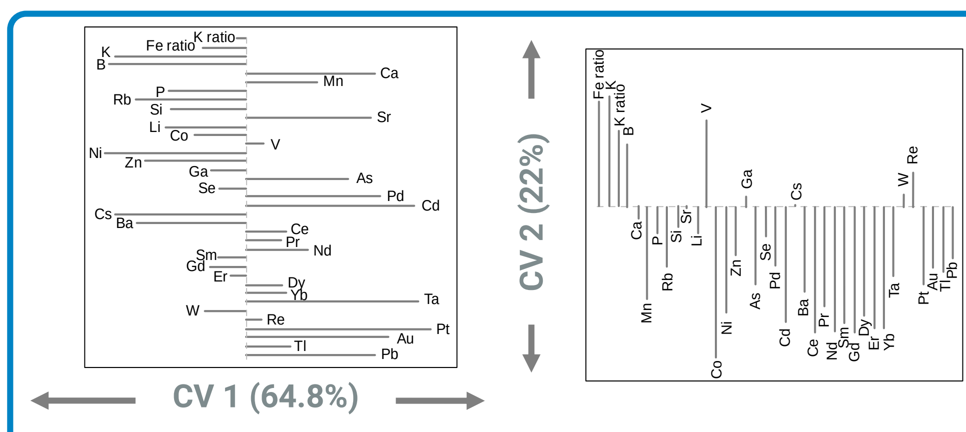


Figure 2 *CVA structures for each CV dimension, showing how each element discriminates among the 5 neighborhoods. (**left**) CV 1 (**right**) CV2.*

Conclusions

- Commercial wines from different wineries in 5 different neighborhoods within one AVA show characteristic elemental fingerprints
- Despite different viticultural and enological practices wines group by neighborhood.
- Macro, micro and trace elements as well as elemental ratios contribute to the observed separation, indicating the involvement of multiple factors and underlying mechanisms, including location and soil composition, elemental uptake by vine and rootstock, viticulture and nutrient management, water sources, and small differences in the different wineries.
- Ongoing research is looking into soil composition, water sources and scion-rootstock information.

Acknowledgments and References

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References

[1] Atkin & Johnson. 2010. IJWBR **22**:42 ; [2] Johnson & Bruwer. 2007. IJWBR **19**:276; [3] Martin et al. 2012. FOCHDJ **133**:1081; [4] Coetzee et al. 2005. JAFC **53**:5060; [5] Castineira Gomez et al. 2004. JAFC **52**:2953; [6] Thiel et al. 2004. ABC **378**:1630; [7] Sperkova & Suchanek. 2005. FOCHDJ **93**:659