Introduction

- For U.S. wine consumers place of origin on a region, country 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, partly 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

Data Analysis

- Isotopes selected based on LOD, instrument detection limits, BEC, past studies and recovery.
- Univariate and multivariate Analysis of Variance (IMANOVA) with main effect determination of authentic and forgeries (P < 0.05).
- Canonical Variate Analysis (CVA) for classification by neighboring regions.

Experimental

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

Results and Discussion

Analytical Method

- 49 elements were detected above LOD (Table 1).
- Recoveries (2 concentrations, 5 samples) were performed.
- ICP-MS: 93% (Se) – 170% (Pb)
- MP-AES: 99% (Ca) – 118% (Si)

Table 1

<table>
<thead>
<tr>
<th>Element</th>
<th>LOD (µg/L)</th>
<th>LOD (ppb) 1</th>
<th>LOD (µg/L)</th>
<th>LOD (ppb) 2</th>
<th>Recovery [%] 1</th>
<th>Recovery [%] 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>0.035</td>
<td>2.67(12)</td>
<td>7.63(16)</td>
<td>13.9(37)</td>
<td>89.6(13.8)</td>
<td>89.4(13.4)</td>
</tr>
<tr>
<td>Zn</td>
<td>0.005</td>
<td>2.86(10)</td>
<td>7.63(16)</td>
<td>13.9(37)</td>
<td>89.6(13.8)</td>
<td>89.4(13.4)</td>
</tr>
<tr>
<td>Rb</td>
<td>0.060</td>
<td>1.12(40)</td>
<td>3.63(120)</td>
<td>6.23(172)</td>
<td>89.6(13.8)</td>
<td>89.4(13.4)</td>
</tr>
<tr>
<td>U</td>
<td>0.316</td>
<td>3.31(40)</td>
<td>10.7(120)</td>
<td>18.2(172)</td>
<td>89.6(13.8)</td>
<td>89.4(13.4)</td>
</tr>
<tr>
<td>Si</td>
<td>0.236</td>
<td>6.30(60)</td>
<td>20.6(210)</td>
<td>33.7(266)</td>
<td>89.6(13.8)</td>
<td>89.4(13.4)</td>
</tr>
<tr>
<td>Cu</td>
<td>0.229</td>
<td>1.38(40)</td>
<td>4.26(120)</td>
<td>7.15(172)</td>
<td>89.6(13.8)</td>
<td>89.4(13.4)</td>
</tr>
<tr>
<td>Ba</td>
<td>0.126</td>
<td>1.50(40)</td>
<td>4.83(120)</td>
<td>8.10(172)</td>
<td>89.6(13.8)</td>
<td>89.4(13.4)</td>
</tr>
<tr>
<td>Th</td>
<td>0.216</td>
<td>10.40(200)</td>
<td>31.2(600)</td>
<td>52.0(900)</td>
<td>89.6(13.8)</td>
<td>89.4(13.4)</td>
</tr>
<tr>
<td>Ge</td>
<td>0.491</td>
<td>10.40(200)</td>
<td>31.2(600)</td>
<td>52.0(900)</td>
<td>89.6(13.8)</td>
<td>89.4(13.4)</td>
</tr>
<tr>
<td>Au</td>
<td>0.386</td>
<td>19.2(276)</td>
<td>57.5(626)</td>
<td>95.6(926)</td>
<td>89.6(13.8)</td>
<td>89.4(13.4)</td>
</tr>
<tr>
<td>Ni</td>
<td>0.004</td>
<td>0.90(175)</td>
<td>2.70(369)</td>
<td>4.50(592)</td>
<td>89.6(13.8)</td>
<td>89.4(13.4)</td>
</tr>
<tr>
<td>Zr</td>
<td>0.045</td>
<td>1.50(40)</td>
<td>4.83(120)</td>
<td>8.10(172)</td>
<td>89.6(13.8)</td>
<td>89.4(13.4)</td>
</tr>
<tr>
<td>Sr</td>
<td>0.023</td>
<td>0.79(136)</td>
<td>2.42(213)</td>
<td>3.65(289)</td>
<td>89.6(13.8)</td>
<td>89.4(13.4)</td>
</tr>
</tbody>
</table>

Data Collection

- 4000/6000 ICP/MS/MS (Agilent)
  - Concentric microelectrode, quartz double-pass spray chamber at 2°C
  - 1550 W RF power, 1.8 V RF matching voltage, 10 mm sampling depth, mm annular gap
  - He flow (4.3 mL/min), high energy He (10 mL/min for As), O2: (0.5 mL/min for Se)
- 4200/4210 MP-AES (Agilent)
  - Concentric microelectrode, double pass cyclonic spray chamber at RT
  - 2000 mL/L ionization buffer mixed with sample

Acknowledgments and References

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References