Elemental Non-targeted Profiling of 78 Whiskies Using ICP-MS and MPP

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Overview

- 78 whiskies were profiled for their elemental composition to reveal possible marker elements for geographical origin
- Inductively coupled plasma mass spectrometry (ICP-MS) was used to monitor different elements in a m/z range from 6 – 239.

Introduction

The Authenticity and the origin of foods and beverages are of high interest for consumers

- Especially, for high-value products such as whiskies or wines the determination of geographical origin is of high interest
- Profiling the inorganic, elemental composition could reveal geographical differences among whiskies due to raw materials, the distillation process and ageing conditions
- Whiskies are distilled from different types of raw grain or malted grain (barley, corn, rye, …)(Russell, 2003)

In previous studies on whiskies and other distillates elemental differences were found:

- Scotch whiskies showed varying amounts of Zn, Fe, Ni, Mg, Ca, Na, Cu and Pb (Adam et al., 2002)
- Sugar cane spirits from different Brazilian distilleries varied in Cd, Mg, Pb, Fe, Mn and Cu (Penteado and Masini, 2009)
- 12 elements successfully differentiate tequila and mezcal spirits (Al, Ba, Ca, Cu, Fe, Mg, Mn, K, Na, Sr, Zn, S) (Ceballos-Magana et al., 2009)

In this study we profiled 78 whiskies, differing in origin, style and age, for their elemental composition.

We were interested if we could identify unique elemental patterns for the different whiskey styles.

Experimental

Samples

78 different whiskies

- 34 Scotches (3 – 27 yrs.)
- 22 Bourbons (up to 12 yrs.)
- 8 Canadian whiskies 3 – 12 yrs.)
- 4 Irish whiskies (3 – 12 yrs.)
- 4 Rye whiskies
- 3 Tennessee whiskies
- 3 American whiskies

Instrumentation

An analytical method was developed based on (Woods, 2012).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrument</td>
<td>Agilent 7700x ICP-MS</td>
</tr>
<tr>
<td>Forward power</td>
<td>1550 W</td>
</tr>
<tr>
<td>Carrier gas flow</td>
<td>1.02 L/min</td>
</tr>
<tr>
<td>Spray chamber temperature</td>
<td>2°C</td>
</tr>
<tr>
<td>Sampling Depth</td>
<td>10 mm</td>
</tr>
<tr>
<td>ORS helium flow rate</td>
<td>4.3 mL/min</td>
</tr>
<tr>
<td>Internal standard elements</td>
<td>Li(^6), Sc(^45), Ge(^72), Y(^89), In(^115), Tb(^159), Bi(^209)</td>
</tr>
</tbody>
</table>

Data Analysis

- Calibration between 0.1 – 500 pbb for 24 Elements
- R (v3.0) for significance testing of sample, replicate and type effects (P ≤ 0.05).
- Mass Profiler Professional (MPP, v12.1) for
  - Graphical representation of differences using Principal Component Analysis (scaled to unit variance)
Results and Discussion

Method evaluation

A valid, accurate and precise method for the elemental profiling of whiskies was developed

- Calibration curves with excellent $R^2$ of 0.9990 or above for all calibrated elements from 0.1 to 500 ppb
- Limits of detection (LOD) for all monitored elements were below 0.1 ppb (Tab. 2), except for Al, Ca, K, Mg and Na.

Statistical Analyses

- A significant effect for whiskey type was found ($P \leq 0.05$), due to 24 elements that differed significantly among the whiskies. These 24 elements were used in the PCA (Fig. 1).

Tab. 2. Monitored elements with their limits of detection (LOD) and the concentration ranges found in the studied whiskies ($n=3$) (LOD = 3.14*SD, $n=7$).

<table>
<thead>
<tr>
<th>element</th>
<th>m/z</th>
<th>LOD [ppb]</th>
<th>range [ppb]</th>
<th>element</th>
<th>m/z</th>
<th>LOD [ppb]</th>
<th>range [ppb]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>.&quot;</td>
<td>636.8</td>
<td>0 - 9464.7</td>
<td>Se</td>
<td>78</td>
<td>0.05</td>
<td>0 - 0.62</td>
</tr>
<tr>
<td>K</td>
<td>.&quot;</td>
<td>1671.8</td>
<td>1844.1 - 40582.1</td>
<td>Rb</td>
<td>85</td>
<td>0.05</td>
<td>0 - 46.39</td>
</tr>
<tr>
<td>Mg</td>
<td>.&quot;</td>
<td>397.9</td>
<td>0 - 3324.2</td>
<td>Zr</td>
<td>90</td>
<td>0.1</td>
<td>0 - 15.54</td>
</tr>
<tr>
<td>Na</td>
<td>23</td>
<td>5.77</td>
<td>0 - 36379.44</td>
<td>Nb</td>
<td>93</td>
<td>0.16</td>
<td>0 - 11.57</td>
</tr>
<tr>
<td>Al</td>
<td>27</td>
<td>1.59</td>
<td>0 - 613.94</td>
<td>Mo</td>
<td>95</td>
<td>0.02</td>
<td>0 - 6.82</td>
</tr>
<tr>
<td>V</td>
<td>51</td>
<td>0.04</td>
<td>0 - 23.66</td>
<td>Sn</td>
<td>118</td>
<td>0.03</td>
<td>0 - 29.81</td>
</tr>
<tr>
<td>Mn</td>
<td>55</td>
<td>0.02</td>
<td>0 - 142.91</td>
<td>Sb</td>
<td>121</td>
<td>0.01</td>
<td>0 - 4.39</td>
</tr>
<tr>
<td>Fe</td>
<td>56</td>
<td>0.12</td>
<td>0 - 518.77</td>
<td>Te</td>
<td>125</td>
<td>0.02</td>
<td>0 - 0.14</td>
</tr>
<tr>
<td>Co</td>
<td>59</td>
<td>0.01</td>
<td>0 - 2.29</td>
<td>Ba</td>
<td>137</td>
<td>0.03</td>
<td>0 - 37.82</td>
</tr>
<tr>
<td>Cu</td>
<td>63</td>
<td>0.12</td>
<td>0 - 1716.43</td>
<td>Ta</td>
<td>181</td>
<td>0.09</td>
<td>0 - 0.95</td>
</tr>
<tr>
<td>Ga</td>
<td>69</td>
<td>0.04</td>
<td>0 - 10.57</td>
<td>W</td>
<td>182</td>
<td>0.15</td>
<td>0 - 5.48</td>
</tr>
<tr>
<td>As</td>
<td>75</td>
<td>0.01</td>
<td>0 - 9.69</td>
<td>Pt</td>
<td>195</td>
<td>0.1</td>
<td>0 - 0.18</td>
</tr>
</tbody>
</table>

* Concentrations were measured with an Agilent 730 axial ICP-OES at 396.847 nm (Ca), 769.897 nm (K), and 279.800 nm (Mg).

Fig. 1. 2D PCA plots using only the elements that differ significantly among the whiskey samples. (left) Product plot showing the different whiskey samples color coded according to type. (right) Loadings plot with significantly different elements (elements with a * were measured with an Agilent 770 ICP-OES due to their high concentration levels.)
Results and Discussion

Sample Discrimination based on the elemental profile

Samples clustered according to whiskey type (Fig. 2)

- Rye (in yellow) and Tennessee (in black) whiskies showed some overlap with the Bourbons (in blue), while American whiskies (in red) showed the largest variability.
- Canadian (in pink) and Irish (in light blue) whiskies were more similar based on their elemental profile
- Scotch (in green) showed less overlap with other whiskey types.

⇒ water used for cutting the alcohol after distillation and ageing (Ceballos-Magana, 2009)
⇒ ageing process (wood containers, previous use of wood barrels, ...)
⇒ distillation equipment (copper still, stainless steel, ...) and process (Adam et al., 2002)
⇒ raw materials (origin of grains, yeasts, fermentation, ...)

Fig. 2. 3D PCA product showing the different whiskey samples, color coded according to type from two different viewing angles.

Conclusions

- The elemental composition of 78 whiskies, differing in type was profiled with ICP-MS.
- A accurate and precise analytical method showed significant concentration differences in 24 elements over several magnitudes (sub-ppb to mid-ppm).
- Whiskies clustered according to type, with some overlap between whiskies from the US (Bourbon, TN, Rye).
- Observed differences are most likely the combination of water, processing and raw materials used.

References


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