Water Chemistry and Beer Flavor

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Water and Ions

• Water is a critical component of beer and life
  • ~85 – 90% of beer is water
• Ions are charged atoms or groups of atoms
• Most salts consist of pairs of ions in water
  • Cations – positively charged ions
  • Anions – negatively charged ions
• NaCl (table salt), dissolves to give Na\(^+\), Cl\(^-\)
• Ions in brewing frequently measured in ppm, (mg/L)
Mineral Content Effect on Beer

• Pure water (Distilled or RO) is poor for brewing
• Dissolved ions play several key roles in brewing
  • Allow for proper enzyme function in mash
  • Vital for yeast activity
    • Many trace metals play a role
• Ions in finished beer affect flavor
pH

• Water spontaneously breaks into small numbers of ions
  \[ \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- \]
  
• pH is a measure of the amount of H\(^+\) in solution

<table>
<thead>
<tr>
<th>pH Value</th>
<th>Characteristic</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;7</td>
<td>Acidic, more H(^+)</td>
</tr>
<tr>
<td>7</td>
<td>Neutral, even</td>
</tr>
<tr>
<td>&gt;7</td>
<td>Alkaline, more OH(^-)</td>
</tr>
</tbody>
</table>

• pH important at several steps in brewing process
  • Mash pH for enzyme activity
  • Final pH of beer
Alkalinity

• Measure of the capacity of solution to neutralize acid
• Mainly due to the presence of bicarbonate ($\text{HCO}_3^-$)

$$\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{CO}_2$$

• Higher alkalinity resists change in pH – “buffer”
• >100 ppm $\text{HCO}_3^-$ is considered alkaline

• Alkalinity is more important than the absolute pH
• High alkalinity makes it more difficult to achieve proper mash pH (5.2-5.7)
Hardness

- Hardness is a measure of the amount of Ca$^{2+}$ and Mg$^{2+}$

- Alkalinity can be removed by boiling
  \[ \text{Ca}^{2+} + 2\text{HCO}_3^- \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \]
- CO$_2$ is driven out of solution by boiling
- Boiled water racked off of precipitated CaCO$_3$
- Reduces the mineral content of Ca$^{2+}$
  - Reduction of Ca$^{2+}$ is *temporary hardness*
  - Remaining Ca$^{2+}$ and Mg$^{2+}$ *permanent hardness*

- Easiest to think of all ions in terms of absolute amounts!
Reduction of Alkalinity

- Boiling to remove $\text{CO}_2$, precipitate $\text{CaCO}_3$
- Dilute with distilled water
- Addition of acid to the water
  - Hydrochloric acid, $\text{HCl}$
  - Phosphoric acid, $\text{H}_3\text{PO}_4$
  - Lactic acid
Municipal Water Treatment

- Water in the US is disinfected with chlorine source
  - $\text{Cl}_2$, free chlorine
  - Chloramine, $\text{NH}_2\text{Cl}$
- Chlorine sources in brewing react to form chlorophenols
  - A medicinal ("band-aid") off flavor
  - Can also form with residual bleach
- Removal of chlorine sources
  - Boiling – can remove $\text{Cl}_2$
  - Carbon Filtration – Removes $\text{Cl}_2$ and Chloramine
  - Campden tablet (Potassium metabisulfite)
## Water Report - Example

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.0</td>
</tr>
<tr>
<td>Total Dissolved Solids (TDS) Est</td>
<td>416</td>
</tr>
<tr>
<td>Electrical Conductivity, mmho/cm</td>
<td>0.69</td>
</tr>
<tr>
<td>Cations / Anions, me/L</td>
<td>7.2 / 7.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium, Na</td>
<td>24</td>
</tr>
<tr>
<td>Potassium, K</td>
<td>1</td>
</tr>
<tr>
<td>Calcium, Ca</td>
<td>66</td>
</tr>
<tr>
<td>Magnesium, Mg</td>
<td>34</td>
</tr>
<tr>
<td>Total Hardness, CaCO₃</td>
<td>307</td>
</tr>
<tr>
<td>Nitrate, NO₃-N</td>
<td>0.9 (SAFE)</td>
</tr>
<tr>
<td>Sulfate, SO₄-S</td>
<td>12</td>
</tr>
<tr>
<td>Chloride, Cl</td>
<td>82</td>
</tr>
<tr>
<td>Carbonate, CO₃</td>
<td>6</td>
</tr>
<tr>
<td>Bicarbonate, HCO₃</td>
<td>234</td>
</tr>
<tr>
<td>Total Alkalinity, CaCO₃</td>
<td>201</td>
</tr>
</tbody>
</table>
Ions in Brewing – Calcium, Ca$^{2+}$

- Calcium is the most important ion in brewing
  - Reduces mash pH
    - Reacts with phosphates in the malt
  - Improves hot and cold break
  - Improves mash enzyme activity, stability
  - Gelatinizes starches, helps lautering
  - Provides nutrients for the yeast
  - Improves clarity in the finished beer
- Typical levels: 5-200 ppm (50-100 best)
Ions in Brewing – Magnesium, Mg$^{2+}$

- Magnesium is closely related to calcium
- Second ion of permanent hardness
- Not as effective as calcium in reducing mash pH
- Important yeast nutrient
- Typical levels: 2-50 ppm (10-30 best)
- High levels have negative consequences
  - >50 ppm gives astringent bitterness
  - >125 ppm acts as a diuretic
Ions in Brewing – Sodium, Na⁺

- Low levels can accentuate sweetness
  - Add a “roundness” or “fullness” to palate
- Typical levels: 2-100 ppm (<50 ppm best)
- Elevated levels affect fermentation and taste
  - High levels can be sour or salty
  - High levels also inhibit yeast performance
Ions in Brewing – Iron, Fe^{2+/3+}

- Iron is not a desirable ion in brewing beyond trace levels
- Not often a problem in city water
- More frequently found in well water
- At low levels can affect the flavor of beer (0.05 ppm)
  - Metallic, blood-like flavor
Ions in Brewing – Trace Metals

• These ions are all important at very low levels
  • Not something you need to add to beer
• Copper, Cu\(^{2+}\)
  • High levels can contribute to haze
• Manganese, Mn\(^{2+}\)
  • Similar to iron in unpleasant taste
• Zinc, Zn\(^{2+}\)
  • Critical for yeast performance
  • Advisable range 0.1-0.2 ppm
Ions in Brewing – Bicarbonate, $\text{HCO}_3^-$

- Primary contributor to alkalinity
- Directly related to carbonate ($\text{CO}_3^{2-}$)
- Many negative effects on beer
  - Reduce the lowering of mash pH
  - Inhibits cold break
  - Hurts starch gelatinization (accessibility)
  - Impedes yeast activity in fermentation
- Contributes harsh, bitter flavors in subtle pale beers
- Difficult to work with unless using dark malts
Ions in Brewing – Sulfate, $\text{SO}_4^{2-}$

- A very weakly basic anion, not alkaline
- Gives beer a dryer, fuller flavor
- Has a major effect on perception of bitterness
  - Can make the beer too dry, sharp
  - With more hopped beers, can give a clean bitterness
- In excessively high levels is strongly bitter, harsh
Ions in Brewing – Chloride, Cl⁻

• Another very weakly basic anion, not alkaline
• Increases stability, clarity of beer
• Enhances beer flavor and palate fullness
• Ratio of chloride to sulfate is an important consideration
  • Can change perception of bitterness
• High levels give a salty character
Common Minerals to Adjust Water

- Gypsum
  - Calcium Sulfate, CaSO$_4$•2H$_2$O
- Calcium Chloride
  - CaCl$_2$•2H$_2$O
- Calcium Carbonate
  - Chalk, CaCO$_3$
- Table Salt
  - Sodium Chloride, NaCl
- Epsom Salts
  - Magnesium Sulfate, MgSO$_4$•7H$_2$O
Water Adjustment in Extract Beer

- Water adjustment in extract beer is not often necessary
  - Mash is already completed
- Can be used to adjust flavor of final beer
- Difficult to know what original water profile was
  - Extract was already mashed and ions concentrated
- Can use pure water to dilute extract

- Significant salt additions can add too many ions to beer
## Famous Brewing Waters

<table>
<thead>
<tr>
<th>City</th>
<th>Calcium</th>
<th>Magnesium</th>
<th>Sodium</th>
<th>Sulfate</th>
<th>Bicarbonate</th>
<th>Chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plzen</td>
<td>7</td>
<td>2</td>
<td>2</td>
<td>5</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>Dortmund</td>
<td>225</td>
<td>40</td>
<td>60</td>
<td>120</td>
<td>180</td>
<td>60</td>
</tr>
<tr>
<td>Munich</td>
<td>75</td>
<td>18</td>
<td>2</td>
<td>10</td>
<td>150</td>
<td>2</td>
</tr>
<tr>
<td>Vienna</td>
<td>200</td>
<td>60</td>
<td>8</td>
<td>125</td>
<td>120</td>
<td>12</td>
</tr>
<tr>
<td>Burton</td>
<td>275</td>
<td>40</td>
<td>25</td>
<td>450</td>
<td>260</td>
<td>35</td>
</tr>
<tr>
<td>Dublin</td>
<td>120</td>
<td>5</td>
<td>12</td>
<td>55</td>
<td>125</td>
<td>20</td>
</tr>
<tr>
<td>Edinburgh</td>
<td>120</td>
<td>25</td>
<td>55</td>
<td>140</td>
<td>225</td>
<td>65</td>
</tr>
<tr>
<td>London</td>
<td>90</td>
<td>5</td>
<td>15</td>
<td>40</td>
<td>125</td>
<td>20</td>
</tr>
</tbody>
</table>
Brewing Water and Style Development

- Many beer styles originated because of water
- High carbonate water, low sulfate
  - London, Dublin, Munich
  - Dark grains help to reduce mash pH
- Very hard water
  - Dortmund, Burton-on-Trent
  - High sulfate accentuates dryness, smooths bitterness
- Low mineral content
  - Plzen
  - High hopping without a harsh bitterness
- These water levels may not be what they use today!
# Brewing Cities Associations

A list of styles commonly associated with particular cities

<table>
<thead>
<tr>
<th>City</th>
<th>Style</th>
<th>City</th>
<th>Style</th>
</tr>
</thead>
<tbody>
<tr>
<td>Düsseldorf</td>
<td>Düsseldorf Altbier</td>
<td>Burton-on-Trent</td>
<td>English Pale Ale</td>
</tr>
<tr>
<td>Berlin</td>
<td>Berliner Weisse</td>
<td>Newcastle</td>
<td>No. English Brown Ale</td>
</tr>
<tr>
<td>Einbeck</td>
<td>Traditional Bock</td>
<td>Senne Valley</td>
<td>Lambic</td>
</tr>
<tr>
<td>Köln (Cologne)</td>
<td>Kölsch</td>
<td>Dublin</td>
<td>Dry Stout</td>
</tr>
<tr>
<td>Edinburgh</td>
<td>Scottish 60/-</td>
<td>San Francisco</td>
<td>California Common</td>
</tr>
<tr>
<td>Bamberg</td>
<td>Classic Rauchbier</td>
<td>Vienna</td>
<td>Vienna Lager</td>
</tr>
</tbody>
</table>