Analytical methods for quality control of beer mix beverages

H. Klein, C. Forster
Overview

- General aspects of quality control of beer mixes beverages
- Challenge to the analytics
- Critical remarks and additional information of analytical parameters
- Example of troubleshooting and performance of modern analytical systems
Quality control and investigation performed for

• Specification of base beer
• Specification of raw materials (multi-juice syrup with compound, sugar or syrup...)
• Evaluation of mixing process
• Specification of finished product
• Product stability (sedimentation, BBD...)
• Verifying the autenticity of raw materials
• Troubleshooting
Beer mix production process

- **Raw materials**
  - Multi Juice Compound
  - Syrup
- **Mixing process**
  - Radler Lemonade
- **Base beer**
  - Filtered beer from filter or BBT
- **Final product**
  - BBT <4°C
  - Radler to packaging
Two different mixing parts

**Base Beer**
- Lager beer
- Wheat beer
- Non-alcoholic beer

**Juice, Lemonade, Aroma**
- Lemon
- Lime
- Orange
- Grapefruit
- Apple
- Tea
- Lemon grass
- Cranberry
- Herbs
- Elderberry
- ......

Ingredients of non-beer part influence classical beer analyses
- Different or additional sugars
- Different or additional organic acids
- Sweeteners
- Cloudifiers
- Stabilizers
- ......
Concentration range of main analytical parameters

**Base beer:**
- Small ranges

**Beer mix beverage:**
- Large ranges

*Matrix effect*
Analytical reference methods

- Beer: EBC, MEBAK, ASBC
- Juices: IFU (International Federation of Fruit Juice Producers)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Beer</th>
<th>Juice</th>
<th>Beer Mix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brix</td>
<td>✗</td>
<td>✓</td>
<td>✗</td>
</tr>
<tr>
<td>Density</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
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<tr>
<td>Original Gravity</td>
<td>✓</td>
<td>✗</td>
<td>✓</td>
</tr>
<tr>
<td>Alcohol</td>
<td>✓</td>
<td>✗</td>
<td>✓</td>
</tr>
<tr>
<td>pH</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Bitterness</td>
<td>✓</td>
<td>✗</td>
<td>✓</td>
</tr>
<tr>
<td>CO₂</td>
<td>✓</td>
<td>✗</td>
<td>✓</td>
</tr>
<tr>
<td>Foam stability</td>
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<td>✗</td>
<td>✓</td>
</tr>
<tr>
<td>Turbidity</td>
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<td>✗</td>
<td>✓</td>
</tr>
<tr>
<td>Total acid</td>
<td>✗</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Organic acids</td>
<td>✗</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Sweeteners</td>
<td>✗</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Sugars</td>
<td>✗</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>
Challenge for the analytics of beer mix beverages

- Beer mix matrix is significantly different to beer matrix and more complex
- Specific (published) methods are missing for beer mix beverages
- Ring analyses provided for beer, lemonade, juice – not for beer mix beverage!

→ no precise statistical details about
  - accuracy
  - repeatability
  - comparability
## Common analytical methods and systems

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method</th>
<th>System</th>
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</thead>
<tbody>
<tr>
<td>Brix</td>
<td>refractometric (density)</td>
<td></td>
</tr>
<tr>
<td>Original gravity</td>
<td>density+alkolyzer</td>
<td>PBA</td>
</tr>
<tr>
<td>Alcohol</td>
<td>density+alkolyzer</td>
<td>PBA</td>
</tr>
<tr>
<td>Colour</td>
<td>photometric VIS</td>
<td>PBA</td>
</tr>
<tr>
<td>CO₂</td>
<td>volume expansion</td>
<td>PBA</td>
</tr>
<tr>
<td>pH</td>
<td>potentiometric</td>
<td>PBA</td>
</tr>
<tr>
<td>Turbidity</td>
<td>nephelometric</td>
<td>PBA</td>
</tr>
<tr>
<td>Bitterness</td>
<td>photometric UV</td>
<td>Photometer</td>
</tr>
<tr>
<td>Foam</td>
<td>foam collapse</td>
<td>Nibem</td>
</tr>
<tr>
<td>Total acid</td>
<td>potentiometric (end point)</td>
<td>Titrator</td>
</tr>
<tr>
<td>Organic acids</td>
<td>HPLC (enzym.)</td>
<td>HPLC</td>
</tr>
<tr>
<td>Sweeteners</td>
<td>HPLC</td>
<td>HPLC</td>
</tr>
<tr>
<td>Sugars</td>
<td>HPLC (enzym.)</td>
<td>HPLC</td>
</tr>
<tr>
<td>Aroma compounds</td>
<td>GC</td>
<td>GC</td>
</tr>
</tbody>
</table>

PBA = Packaged Beer Analyzer
Gravity and alcohol

Brix: [°Bx]
• Traditionally used in sugar, juice and honey manufacturing
• 1 degree Brix = 1 gramm sucrose in 100g solution → %-mass
• Measured by refractometer or density
• Standardized on sucrose table!

Original Gravity: [° Plato]
• Used by brewing industrie (comparable scale to Brix if alcohol is absent!)
• Calculated from density (oscillating U-tube) and alcohol measurement
• Standardized on sucrose table!

Alcohol content: [%vol]
• Current available technology using Alcolyzer Anton Paar (NIR technology)
Brix and original gravity

**Citric acid concentration range**

- **beer**
  
  0.15 – 0.25 g/l

- **beer mix beverage**
  
  0.7 - 3.1 g/l

Brix and OG strongly influenced by citric acid concentration - particularly in lemon-radlers!

2g citric acid/l equivalent to 0.15 %-mass higher OG in the product
Limitation

- Alcohol content > 0,1 %vol → accurate results
- Alcohol content < 0,1 %vol → incorrect results
Colour and bitterness

**Colour:** [EBC] VIS 430nm
- Sample must be clear
- Sometimes depending on amount/size of particle filtration difficult or impossible

Remark:
- $E_{700\text{nm}} > 0.020$ A additional preparation is necessary!
- Kieselguhr - membrane filtration - centrifugation - comparator
- Products presenting other colours than yellow must be measured at suitable wave length(s) or special equipment

**Bitterness:** [EBU] iso-octan extraction, UV 275nm
- Ingredients of non-beer part can influence the result
- e.g. coffein shows higher bitterness results
Foam

**Foam:** [s] Nibem foam meter
- Generally foam stability in beer mix beverage is lower than in beer because of influence of essential oil in non-beer part
- Effect is time dependant and strong directly after filling

**Remark:**
- not to be analysed directly after filling!

![Foam stability vs. time of analyses](image_url)
**Turbidity**

**Turbidity:** [EBC]

### Lagerbeer
- Turbidity 0,6 EBC
- Particles: 12.000 / 5 ml
- Main size < 1 µm

### Beer mix beverage (Lemon Typ)
- Turbidity 54 EBC
- Particles: 850.000 / 5 ml
- Main size 4 - 10 µm
Turbidity

- depends on average of particle diameter and particle count
- various types of product not comparable
- visual impression not always linear to measured result

Remark:

- Homogenisation necessary using bottle turner due to the sedimentation

- Expand calibration range up to 200 EBC

- Some instruments have a measuring limit at 100 EBC

(Dilution?)
pH and total acid

pH:
- in radler approx. 1 unit lower
- in case of the higher acid content beer: pH = 4,0 - 4,6
  radler: pH = 3,2 – 3,8

Remark:
- Not applicable for the determination of (total-)acid concentration (tricarbon acid / dicarbon acid)

Total acid (titratable): [g/l]
- Based on endpoint of main acid and prescribed calculation factors
- Result expressed as: e.g. total acid 2,3 g/l calculated as citric acid

Total acid = consumption caustic * factor

<table>
<thead>
<tr>
<th></th>
<th>pH</th>
<th>factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malic acid</td>
<td>8,1</td>
<td>0,67</td>
</tr>
<tr>
<td>Citric acid</td>
<td>8,1</td>
<td>0,64</td>
</tr>
<tr>
<td>Tartaric acid</td>
<td>7,0</td>
<td>0,75</td>
</tr>
</tbody>
</table>
Organic acids

**Organic acids**: HPLC or enzymatic

- Composition/ratio of different acids provide information about origin/authenticity of non-beer part
- Presence of specific/rare acids are typical for some fruits (e.g. salicylic acid in berries, sorbic acid in cranberry)

![Graph showing organic acids in different fruits and ratio of citric/malic acid](image)
Organic acids

- Ratio citric acid / i-citric acid is usually used in juice industrie for evaluation of authenticity of products
- Presence of i-citric acid is good indicator for origin from citric acid in lemon based mixed beverages
- Ratio citric acid / i-citric acid in beer is approx. 10-15
- Ratio citric acid / i-citric acid in lemon radler with natural citric acid from the fruit is approx. 30-60
- Ratio citric acid / i-citric acid in radler with added citric acid > 100 up to 300
Sugars

**Sugars:** [g/100ml] HPLC

- In beer nearly all fermentable sugars present in low concentration
- Spectrum of carbohydrates in beer mix beverage provide additional information:

*Is sugar or artificial sweetener or both used to sweeten the product and which type of sugar is used?*
Sugars

Fructose
• has highest sweetening power

Sucrose
• in case of low pH sucrose converts into glucose and fructose
  ratio 1:1 indicates usage of sucrose

Glucose
• ratio glucose/fructose much bigger

Oligosaccharides
• higher concentration of maltotetraose-pentose....
  indicates usage of glucose syrup

Sorbit
• occurs mainly in apple, pear and used as sweetener
Troubleshooting

Example: GC

- Contamination of beer with turbid lemon radler
- Positive sensory detection at concentration of about 0.4% Radler (4 ml/l) in beer
- Analytical detection possible due to differences in matrix of beer compared to radler e.g. turbidity, fructose, particle, aroma....

<table>
<thead>
<tr>
<th></th>
<th>Turbidity 25°</th>
<th>Particle</th>
<th>Fructose</th>
<th>Citric acid</th>
<th>GC head space</th>
<th>GC extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure beer</td>
<td>EBC</td>
<td>count</td>
<td>g/100ml</td>
<td>g/l</td>
<td>peak height</td>
<td>peak height</td>
</tr>
<tr>
<td>Beer + 0,2% radler</td>
<td>0,2</td>
<td>6.700</td>
<td>8</td>
<td>0,18</td>
<td>330</td>
<td>4.270</td>
</tr>
<tr>
<td>Beer + 1% radler</td>
<td>0,46</td>
<td>10.400</td>
<td>23</td>
<td>0,197</td>
<td>1.680</td>
<td>26.800</td>
</tr>
<tr>
<td>Beer + 3% radler</td>
<td>1,16</td>
<td>15.500</td>
<td>47</td>
<td>0,23</td>
<td>5.080</td>
<td>75.000</td>
</tr>
<tr>
<td>Detection limit</td>
<td>too low</td>
<td>too low</td>
<td>too low</td>
<td>too low</td>
<td>500 µl/l</td>
<td>100 µl/l</td>
</tr>
</tbody>
</table>

Using modern technologies such as GC-SPME-MS detection limit approx. of 2µl radler in 1l beer is possible!
Conclusion

• Matrix of beer mix beverages more complex compared to beer
• Additional quality parameters relevant for beer mix beverages
• Matrix of non-beer part influences classical beer analyses
• No validated (normed) analytical methods available for beer mix beverages
• Specific analytes provide information on origin and authenticity of raw materials and ingredients