ADVANCED BEER AROMA ANALYSIS

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Beer Analysis - Overview

- Production of Beer
- Sample Preparation and Analysis
- Relevance of Aroma Fingerprinting
- Comprehensive GCxGC-MS
- Targeted Analysis of Flavor and Off Flavour Compounds-Enhancing Selectivity and Sensitivity
Production of Beer and Aroma Influencing Steps

Maillard reaction products

~ 30 odor active compounds contribute to the aroma

Massive influence due to yeast activity
Mainly formation of alcohols and esters…

Ageing flavours (light, temperature, oxygen…)

L.C. Verhagen, Beer Flavour https://doi.org/10.1016/B978-008045382-8.00087-3
Aroma Compounds in Beer

So far several hundred volatiles from different chemical classes are identified in beer.

<table>
<thead>
<tr>
<th>Compound Class</th>
<th>Substance</th>
<th>Sensory Threshold [µg/L]</th>
<th>Odor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic acids</td>
<td>Butanoic acid</td>
<td>1000</td>
<td>Sweat, rotten milk</td>
</tr>
<tr>
<td>Ester</td>
<td>Isoamylacetate</td>
<td>510</td>
<td>Banana</td>
</tr>
<tr>
<td>Higher alcohols</td>
<td>2-Methylbutanol</td>
<td>320</td>
<td>Fusel alcohol</td>
</tr>
<tr>
<td>Vicinal diketones</td>
<td>Diacetyl</td>
<td>17</td>
<td>fermented milk</td>
</tr>
<tr>
<td>Guaiacols</td>
<td>Guaiacol</td>
<td>2.5</td>
<td>medicinal, smoky</td>
</tr>
<tr>
<td>Terpenes</td>
<td>(R)-Linalool</td>
<td>0.14</td>
<td>Earl Grey Tea, citrus</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>E-2-Nonenal</td>
<td>0.03</td>
<td>Cardboard</td>
</tr>
<tr>
<td>Sulfur compounds</td>
<td>Dimethyltrisulfide</td>
<td>0.03</td>
<td>Onion, rotten veggies</td>
</tr>
</tbody>
</table>

D. Saison et al. / Food Chemistry 114 (2009) 1206–1215 1209
Sensory Changes during Beer Ageing

B. Vanderhaegen et al. / Food Chemistry 95 (2006) 357–381
Sample Preparation based on SPME

NO solvent, NO waste
NO non volatiles
NO cross contamination from the solvent
Fast and simple
High throughput using autosampler
Typical sample size 0.1-2 mL
SENSITIVE ~ 1µg/L in full scan
Bottom fermented Pils lager beer brewed by Prof. Pavel Dostalek from the University of Chemistry and Technology, Prague especially for RAFA
Automated Retention Index Calculation and Identification

Automated RI calculation

MS Database search

<table>
<thead>
<tr>
<th>ID#</th>
<th>Name</th>
<th>Ret. Time</th>
<th>Ret. Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>47</td>
<td>2-Nonanol, acetate</td>
<td>23.950</td>
<td>1233</td>
</tr>
<tr>
<td>48</td>
<td>Acetic acid, 2-pheny</td>
<td>24.625</td>
<td>1269</td>
</tr>
<tr>
<td>49</td>
<td>1-Decanol</td>
<td>24.715</td>
<td>1274</td>
</tr>
<tr>
<td>50</td>
<td>3-Nonenolic acid, et</td>
<td>24.915</td>
<td>1284</td>
</tr>
<tr>
<td>51</td>
<td>Nonanoate &lt;ethyl&gt;</td>
<td>25.105</td>
<td>1294</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hit</th>
<th>Simil</th>
<th>Ret.</th>
<th>Compound Name</th>
<th>Mol Wt</th>
<th>Formula</th>
<th>Library</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>93</td>
<td>1258</td>
<td>1-Decanol $\text{Decyl alcohol}$$\text{n-Decan-1-ol}$</td>
<td>158</td>
<td>C10H22O</td>
<td>NIST14s.lib</td>
</tr>
<tr>
<td>2</td>
<td>92</td>
<td>1278</td>
<td>Decyl alcohol $\text{Decyl alcohol}$$\text{1-Decanol}$</td>
<td>158</td>
<td>C10H22O</td>
<td>FFNSC 3.lib</td>
</tr>
<tr>
<td>3</td>
<td>91</td>
<td>1258</td>
<td>1-Decanol $\text{Decyl alcohol}$$\text{n-Decan-1-ol}$</td>
<td>158</td>
<td>C10H22O</td>
<td>NIST14s.lib</td>
</tr>
</tbody>
</table>
Statistical Analysis can be helpful in the differentiation of different beer varieties.
Comprehensive GCxGC-MS

Shimadzu QP2010 plus
Column 1 ZB-1 HT 30*0.25*0.25
Column 2 BPX-50 2*0.15*0.15
35° C (1 min) @3° C/min to 240° C
ZOEX modulator 280° C (350 ms)
Modulation frequency 5 s
35-300 amu (50 scans/s)

~500 volatiles
Targeted Analysis of Flavor and Off Flavour Compounds-Enhancing Selectivity and Sensitivity
Enhancing Separation-MD GC

- Sniffing Port
- Heated Transfer Line
- INJ 2
- INJ 1
- FID
- DEAN Switch
- MS EI, PCI, NCI
- GC 2 polar
- GC 1 non polar

Switching Program:

<table>
<thead>
<tr>
<th></th>
<th>From</th>
<th>To</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.03</td>
<td>7.25</td>
</tr>
<tr>
<td>2</td>
<td>8.85</td>
<td>9.09</td>
</tr>
<tr>
<td>3</td>
<td>10.64</td>
<td>10.89</td>
</tr>
</tbody>
</table>
MDGC Determination of Dimethyltrisulfide (DMTS)

Preview mode (FID)
GC 1: 30 m DB 5 MS 0.25*0.25
35° C(1 min)@5° C/min to 230° C

Cut mode (MS)
GC 2: 30 m MN Wax 0.25*0.25
70° C(1 min)@6° C/min to 220° C

H₃C-S-S-S-CH₃

126 m/z
(E)-β-damascenone belongs to a class of carotenoid-derived carbonyl compounds. It is formed by degradation of neoxanthin, which is present in the basic ingredients of beer.

Sensory threshold 0.02-0.09 µg/L

Odor descriptor: fruity, cooked apples, coconut, tobacco, red fruit.

Sample size 2 mL
Interferences with coeluting compound

Scan 35-300 amu
5 scans/s
RXi5MS 30 m*0.25*1 µm
-10° C (1 min) @ 8° C/min to 280° C

Sample size 0.1 mL
No interferences

Transitions 121>105 CE 10
121>77 CE 25
5 scans/s
ZB5MS 30 m*0.25*0.25 µm
40° C (1 min) @ 10° C/min to 100° C
@ 4° C/min to 160° C
@ 25° C/min to 280° C
Thank you for your attention… and enjoy the special Shimadzu RAFA beer