Determination of carbonyl compounds in spirits and spirit products

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Introduction

• Alcoholic fermentation driven in industrial conditions receives outside ethyl alcohol also by-products,

• One of the fraction, which grants to spirits often unpleasant smell and taste are carbonyl compounds,

• Analytic works of different authors proved, that in spirits occur at least seventeen of different carbonyl compounds.
Carbonyl compounds present in alcoholic spirits:

- formaldehyde,
- acetaldehyde,
- acrolein,
- acetone,
- propionaldehyde,
- isobutyraldehyde,
- crotonaldehyde,
- valeraldehyde,
- isovaleraldehyde,
- capronaldehyde,
- 2-methylbutyraldehyde,
- butan-2-on,
- furfural,
- diacetyl,
- acetacetone,
- glioksal,
Influence of carbonyl compounds on organoleptic properties of spirits

• C1 – C4 carbonyl compounds (formaldehyde, acetaldehyde, acetone, propionaldehyde, isobuteraldehyde and crotonaldehyde) have high threshold limit of sensibility, considerably higher than concentration in practise present in rectified spirits.

• Acrolein, valeraldehyde, isovaleraldehyde and capronaldehyde have very negative influence on taste and smell of spirits in concentration in practise presented in rectified spirits.
Difficulties of determination of carbonyl compounds in spirits and spirits products.

- Determination of sum of carbonyl compounds according to standards doesn’t give full picture of influence of these group of contaminants for organoleptic properties of spirits.

- Quantity of C$_1$ - C$_4$ aldehydes in rectified spirit exceeds four time standard requirements doesn't disqualify such sample by organoleptic properties.

- Quantity of such aldehydes as valeraldehyde, isovaleraldehyde, capronaldehyde, acrolein, according to standards in range from 1 to 5 mg/dm$^3$ can preclude consumption utilizing of spirits.

- Gas chromatography analysis with direct injection of sample to chromatographic column without any preparation determines only contaminants presented at high concentrations, which have not important influence on organoleptic properties of final product.
From few years new analytical procedures for determination of individual carbonyl compounds in spirits and spirit products are being elaborated in Analytical Chemistry Department of Chemical Faculty at Gdańsk University of Technology.

The head of investigation team is

Waldemar Wardencki, PhD, DSc, associate professor of TUG.
Quality of raw material

• Quality of final product on all stage of production,

• Raw materials should fulfil high qualitative requirements,

• Acetaldehyde and acrolein react with sodium bisulfite and form 1-hydroxy-1-sulfonic acids sodium salts.

• Derivatives can be separated and determined by ITP.

• Method for determination of aldehydes in spirits using capillary isotachophoresis (ITP) was worked out.
Instrumentation

ITP was performed with isotachophoreograph model ItaChrom EA 101 from Villa Labeco s.r.o, Spisska Nova Ves, Slovakia. The instrument was equipped with Teflon preseparation column (internal diameter 0,8mm, 90 mm long) and Teflon analytical column (i.d. 0,3 mm, 160 mm long) both with conductivity detection.
Optimisation of derivatization

As optimised derivatization conditions were taken the following parameters: 2 cm$^3$ of sodium metabisulfite water solution (2 g/cm$^3$); 5,5 cm$^3$ of raw spirit sample, and water to 11 cm$^3$, added into vial with screw cap, 30 minutes of derivatization at 50$^\circ$C and 16 minutes of cooling and stabilizing at room temperature. Samples prepared in that way are stable for 6 hours, so they can be analysed during that time.
Optimisation of separation

Composition of electrolytes:
Leading electrolyte 1 (LE1): 10 mM HisCl + 10 mM His + 0.1% MHEC
Leading electrolyte 2 (LE2): 0.5 mM HisCl + 12.89 mM His + 0.1% MHEC
Termination electrolyte (TE): 4.97 mM glutamic acid + 2.58 mM His + 50% EtOH

Figure 1. Isotachophoregram of standard mixture of aldehydes obtained on preseparation column. 1-acrolein, 2-formaldehyde, 3-acetaldehyde, 4-propionaldehyde, 5-butyraldehyde, 6-valeraldehyde, 7-isovaleraldehyde.
Analytical procedure

Figure 2. Schematic diagram of the analytical procedure.
## Validation of the method

Table I. The analytical parameters of developed method.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Equation of calibration plot</th>
<th>$R^2$</th>
<th>Limit of Detection (LOD) [mg/dm³ 100% EtOH]</th>
<th>Limit of Quantification (LOQ) [mg/dm³ 100% EtOH]</th>
<th>Precision (RSD) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetaldehyde</td>
<td>$y = 0.2399x + 0.7894$</td>
<td>0.999</td>
<td>0.54</td>
<td>1.08</td>
<td>6.19</td>
</tr>
<tr>
<td>Acrolein</td>
<td>$y = 3.7104x + 0.9877$</td>
<td>0.998</td>
<td>0.03</td>
<td>0.06</td>
<td>10.99</td>
</tr>
</tbody>
</table>
# Real sample analysis

Table II. Results of analysis of exemplary samples.

<table>
<thead>
<tr>
<th>Raw spirits samples (EtOH concentration [%])</th>
<th>Compound concentration [mg/dm³ 100% EtOH ± SD]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>acrolein</td>
</tr>
<tr>
<td>Sample 1 (91,0%)</td>
<td>1,544 ± 0,049</td>
</tr>
<tr>
<td>Sample 2 (90,7%)</td>
<td>1,093 ± 0,031</td>
</tr>
<tr>
<td>Sample 3 (91,6%)</td>
<td>0,8961 ± 0078</td>
</tr>
<tr>
<td>Sample 4 (90,2%)</td>
<td>0,342 ± 0,041</td>
</tr>
<tr>
<td>Sample 5 (90,2%)</td>
<td>0,990 ± 0,014</td>
</tr>
<tr>
<td>Sample 6 (91,5%)</td>
<td>1,766 ± 0,016</td>
</tr>
<tr>
<td>Sample 7 (91,1%)</td>
<td>0,733 ± 0,016</td>
</tr>
<tr>
<td>Sample 8 (91,6%)</td>
<td>2,500 ± 0,031</td>
</tr>
</tbody>
</table>
Conclusions

• The parameters of the derivatization and the isotachophoretic separation were established.

• The developed ITP method enables the separation and quantitative determination of acrolein and acetaldehyde.

• Detection limits are: 0,03 mg/dm³ 100% EtOH for acrolein and 0,54 mg/dm³ 100% EtOH for acetaldehyde.

• Capillary isotachophoresis seems to be a good alternative to chromatographic methods.

• It is simple to use, low costs and give good results.
**Final product quality**

- Determination of carbonyl compounds is not so easy.
- Direct chromatographic analysis doesn’t allow the determination of carbonyl compounds on this level of concentration.
- Sample preparation is needed

In this work, the possibility of using a photoionization detector (PID) for analysis of aldehydes and ketones in alcoholic matrices after their derivatization with TCPH reagent has been studied. The formed hydrazones have been extracted from headspace of alcoholic solutions using solid-phase microextraction (SPME), a simple, solvent-free, inexpensive, reliable and easily automated technique.
Instrumentation

• GC 8000 made by Carlo Erba Instruments,
• Photoionization detector with 9,6 eV UV lamp,
• Capillary column RTX 5 (30 m, 0,25 mm i.d., 0,25 um df),
• Splitless injector.
• SPME set from Supelco,
• Magnetic stirrer,
• Home made thermostat.

Optimized chromatographic conditions:
• Oven program: 70 °C [3 min], 70-150 °C [30 °C/min], 150 °C [4 min], 150-230 °C [5 °C/min], 230-250 °C [20 °C/min], 250 °C [2 min].
• Injector temperature: 240 °C
• Detector temperature: 325 °C
• Carrier gas: H₂ (105 kPa), make up: N₂ (40 kPa), purge: N₂ (10 kPa).
Fig. 3. Chromatogram of the standard mixture of aldehydes. Numbered peaks are: 1- TCPH; 2 – formaldehyde; 3, 3’ – acetaldehyde; 4 – acetone; 5, 5’ – propionaldehyde; 6 – acrolein; 7, 7’ – isobutyraldehyde; 8, 8’ – butyraldehyde; 9 – isovaleraldehyde; 10 – crotonaldehyde; 11 – valeraldehyde; 12, 12’ – capronaldehyde; 13 – furfural.
Optimisation of derivatization

The following parameters were examined:
• Concentration of derivatizing reagent,
• Time and temperature of the reaction.
• Ethanol concentration
• pH of sample

For the analysis of rectified spirits and “pure” vodkas, the needed quantity of TCPH was established as 1 mg per one sample. On the basis of the literature data a 70 °C was chosen as a temperature of derivatization. Because, the derivatization reaction is relatively fast, this step was performed together with microextraction.
Optimisation of Solid Phase Micro Extraction

Following coatings were investigated:
• PDMS 100 µm,
• PDMS 7 µm,
• CAR/PDMS 75 µm,
• PDMS/DVB 65 µm,
• PA 85 µm.

Among tested SPME fibers only the fiber coated with 100 µm PDMS ensures high efficiency of microextraction and good selectivity.

The generated SPME absorption-time profiles for tested carbonyl compounds on PDMS 100 µm fiber at 70 °C showed that an extraction time of 50 min yielded the sufficient extraction and acceptable precision.
Figure 4. Schematic diagram of the analytical procedure.
Validation of the method

Table III. The analytical parameters of developed method.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Slope (*10^-6) [area counts /mg/dm³]</th>
<th>R²</th>
<th>Limit of Detection (LOD) [mg/dm³ 100% EtOH]</th>
<th>Limit of Quantification (LOQ) [mg/dm³ 100% EtOH]</th>
<th>Precision (RSD) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde</td>
<td>1.267</td>
<td>0.9866</td>
<td>0.18</td>
<td>0.37</td>
<td>8.33</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>1.468</td>
<td>0.9931</td>
<td>0.36</td>
<td>0.72</td>
<td>3.08</td>
</tr>
<tr>
<td>Acetone</td>
<td>2.438</td>
<td>0.9977</td>
<td>0.028</td>
<td>0.056</td>
<td>6.77</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>1.416</td>
<td>0.9997</td>
<td>0.0053</td>
<td>0.011</td>
<td>4.94</td>
</tr>
<tr>
<td>Acrolein</td>
<td>8.295</td>
<td>0.9708</td>
<td>0.20</td>
<td>0.41</td>
<td>12.93</td>
</tr>
<tr>
<td>Isobutyraldehyde</td>
<td>0.785</td>
<td>0.9993</td>
<td>0.0016</td>
<td>0.0033</td>
<td>5.47</td>
</tr>
<tr>
<td>Butyaldehyde</td>
<td>1.006</td>
<td>0.9996</td>
<td>0.0077</td>
<td>0.015</td>
<td>8.89</td>
</tr>
<tr>
<td>Isovaleraldehyde</td>
<td>1.077</td>
<td>0.9997</td>
<td>0.0021</td>
<td>0.0043</td>
<td>4.25</td>
</tr>
<tr>
<td>Crotonaldehyde</td>
<td>0.594</td>
<td>0.9975</td>
<td>0.0054</td>
<td>0.011</td>
<td>2.54</td>
</tr>
<tr>
<td>Valeraldehyde</td>
<td>7.264</td>
<td>0.9997</td>
<td>0.011</td>
<td>0.022</td>
<td>8.23</td>
</tr>
<tr>
<td>Capronaldehyde</td>
<td>2.937</td>
<td>0.9974</td>
<td>0.070</td>
<td>0.14</td>
<td>10.23</td>
</tr>
<tr>
<td>Furfural</td>
<td>0.723</td>
<td>0.9987</td>
<td>0.0019</td>
<td>0.0038</td>
<td>5.50</td>
</tr>
</tbody>
</table>
## Real sample analysis

Table IV. Results of analysis of real samples.

<table>
<thead>
<tr>
<th>Carbonyl compound</th>
<th>Krakus</th>
<th>Zimowa</th>
<th>Lodowa</th>
<th>Absolwent</th>
<th>Bols</th>
<th>Peterburt</th>
<th>Smirnoff</th>
<th>Sprit</th>
<th>Home made spirit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formaldehyde</td>
<td>*</td>
<td>*</td>
<td>-</td>
<td>0,09349 ± 0,00064</td>
<td>0,118 ± 0,036</td>
<td>-</td>
<td>0,164 ± 0,053</td>
<td>-</td>
<td>1,99 ± 0,38</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>4,59 ± 0,19</td>
<td>4,14 ± 0,26</td>
<td>6,12 ± 0,33</td>
<td>5,65 ± 0,76</td>
<td>3,94 ± 0,25</td>
<td>4,29 ± 0,71</td>
<td>4,4 ± 0,31</td>
<td>4,94 ± 0,66</td>
<td>15,0 ± 2,5</td>
</tr>
<tr>
<td>Acetone</td>
<td>0,112 ± 0,012</td>
<td>0,15 ± 0,012</td>
<td>0,181 ± 0,017</td>
<td>0,243 ± 0,067</td>
<td>0,0993 ± 0,0057</td>
<td>0,1085 ± 0,0033</td>
<td>0,0836 ± 0,0090</td>
<td>0,097 ± 0,016</td>
<td>0,0249 ± 0,0097</td>
</tr>
<tr>
<td>Propionaldehyde</td>
<td>0,01496 ± 0,00097</td>
<td>0,01556 ± 0,00041</td>
<td>0,0143 ± 0,0013</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>0,00578 ± 0,00043</td>
<td>**</td>
<td>0,0096 ± 0,0021</td>
</tr>
<tr>
<td>Acrolein</td>
<td>**</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>Isobutyraldehyde</td>
<td>0,00504 ± 0,00031</td>
<td>0,01019 ± 0,00073</td>
<td>0,0057 ± 0,00049</td>
<td>-</td>
<td>**</td>
<td>0,00348 ± 0,00058</td>
<td>**</td>
<td>**</td>
<td>0,293 ± 0,084</td>
</tr>
<tr>
<td>Butyraldehyde</td>
<td>0,0376 ± 0,0072</td>
<td>0,0289 ± 0,0031</td>
<td>0,03149 ± 0,00048</td>
<td>0,0292 ± 0,0012</td>
<td>0,0365 ± 0,0035</td>
<td>0,0309 ± 0,0035</td>
<td>0,02509 ± 0,00065</td>
<td>0,0283 ± 0,0046</td>
<td>0,121 ± 0,051</td>
</tr>
<tr>
<td>Isovaleraldehyde</td>
<td>0,018 ± 0,0012</td>
<td>0,00601 ± 0,00038</td>
<td>0,0482 ± 0,0018</td>
<td>**</td>
<td>0,00563 ± 0,00034</td>
<td>0,00454 ± 0,00024</td>
<td>-</td>
<td>*</td>
<td>0,56 ± 0,12</td>
</tr>
<tr>
<td>Krotonaldehyde</td>
<td>0,0491 ± 0,0027</td>
<td>0,0354 ± 0,0011</td>
<td>0,06761 ± 0,00076</td>
<td>0,0218 ± 0,0031</td>
<td>*</td>
<td>0,01764 ± 0,00041</td>
<td>**</td>
<td>0,0305 ± 0,0011</td>
<td>**</td>
</tr>
<tr>
<td>Valeraldehyde</td>
<td>*</td>
<td>**</td>
<td>*</td>
<td>*</td>
<td>**</td>
<td>-</td>
<td>**</td>
<td>**</td>
<td>0,245 ± 0,028</td>
</tr>
<tr>
<td>Capronaldehyde</td>
<td>**</td>
<td>**</td>
<td>*</td>
<td>*</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>Furfural</td>
<td>0,0043 ± 0,0013</td>
<td>0,00431 ± 0,0003</td>
<td>0,02591 ± 0,00098</td>
<td>0,0164 ± 0,0019</td>
<td>**</td>
<td>0,0094 ± 0,0013</td>
<td>**</td>
<td>**</td>
<td>0,0617 ± 0,0021</td>
</tr>
</tbody>
</table>

* - detected under the limit of quantification
** - under the limit of detection
Conclusions

• The TCPH derivatization – headspace SPME-CGC-PID procedure produced acceptable precision data for quantitative analysis of carbonyl compounds in spirits and “pure” vodkas,

• The use of the photoionization detector (PID) enables to obtain reliably simple chromatograms,

• TCPH is at least 100 times cheaper than frequently used for such purposes o-(2,3,4,5,6-pentafluorobenzylohydroxyloamine) (PFBHA).

• The proposed method can be a useful tool to control the quality of vodkas and spirits during production. Also, it can be used to check the authenticity of alcoholic products.
Thank you for your attention