In Summary

An improved version of the beer analyzer has been developed and validated. This robust, accurate and efficient set-up for the determination of volatile esters and alcohols in beer analyzes samples fully autonomously from the moment the vials are filled to the brim with beer and placed on the autosampler. The most important asset of this analyzer version compared to the previous is the option to automatically process beers with deviating alcohol percentages, which requires additional steps of either diluting with water or spiking with ethanol depending on the actual alcohol percentage of the beer. This option has been successfully implemented and the analyzer does not have to process beers with low and high alcohol content in a particular order as the lead time always remains below the incubation time of 12 min and is therefore able to analyze high and low alcohol containing beers next to each other. And opposed to the initial manual procedure, the GC method is optimized by using a parallel inlet leading to an FID and ECD detector instead of the traditional 2-channel set-up. This has a major advantage as the sample is analyzed via one single injection, which allows further optimization of the oven program as there is no delay due to a second injection, and this on its turn leads to improved separation in the chromatogram.

- Chromatography not impacted
- No Manual operations
- Linearity, Reproducibility & Repeatability comparable with traditional method
- Robust
- Accurate
- Cycle time less than 35 min

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Application Note

SampleQ

Automated determination of volatile esters and alcohols in beer.

Keywords: GC-FID/ECD, headspace, sampleprep, automation, beer, VDK

Introduction

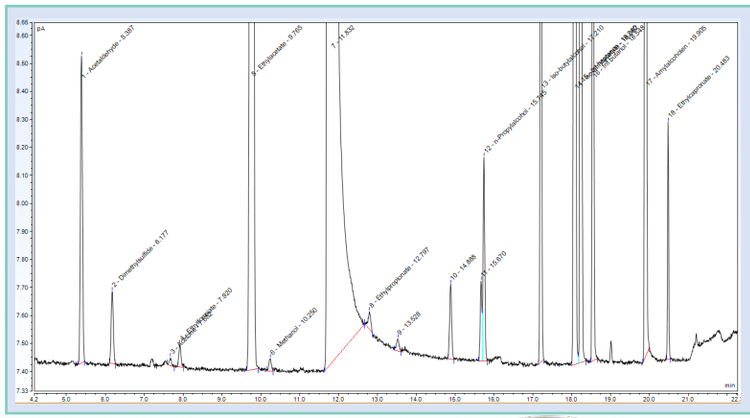
Today, the brewing process is well understood, predominantly because of the detailed insights that are provided by the myriad of analyses that are applied on raw materials, end product as well as brewing intermediates. Obviously, the alcohol content is one of the most important parameters to monitor. Therefore, brewing masters apply GC-FID technology in which the beer is introduced directly and effectively separated in its elementary constituents. Other parameters that are routinely tested include the analysis of vicinal diketones (VDK) such as diacetyl (2,3-butanedione) and 2,3-pentanedione. VDK are naturally occurring volatile substances characterized by a substantial organoleptic signature. But in lager beers, for example, they are considered off-flavors resulting from incomplete fermentation. Consequently, monitoring VDKs in breweries is an essential quality control parameter to verify whether complete fermentation has occurred. Additional off-notes include esters such as ethyl acetate and isoamyl acetate, and aldehydes such as acetaldehyde. Similarly, to the alcohol content, these components too are determined by means of GC though instead of injecting the beer directly, they are measured by means of headspace GC using either ECD detection (VDK) or FID (esters and aldehydes).

Therefore, SampleQ has developed a fully automated and affordable set-up, which only requires the analyst to place the vial on the autosampler. This robust set-up can simplify the analyses significantly and consequently is a valuable asset in quality labs of breweries.

The **repeatability** was determined by filling a series of vials with beer from the same bottle (n=20, 10 per GC). Each sample was processed with the sampler and analyzed on both GCs within 24 h after preparation. The results clearly show that the repeatability of this analyzer compared to the first version has improved in nearly all areas, this is mainly attributed to a more efficient sample processing which increases the speed and as such reduces the time the beer samples are exposed to air.

Repeatability

Component	%RSD analyzer v1	% RSD analyzer v2
Acetaldehyde	0,9	0,50
Dimethyl sulfide	2,9	0,77
Acetone	14,6	4,98
Ethyl formate	11,7	4,80
Ethyl acetate	0,4	0,16
Methanol	7,4	5,33
Ethyl propionate	5,2	3,77
n-Propyl alcohol	2,0	0,34
iso-Butyl alcohol	0,4	0,20
iso-Amyl acetate	0,5	0,30
Amyl alcohols	0,3	0,21
Diacetyl	1,8	0,43
2,3-Pentaandion	1,1	0,41



The chromatogram of the **FID** channel shows that all components are separated with sufficient resolution. Only isoamyl acetate and heptanone are not baseline separated, but this poses no real issue. There is a large non-labeled ethanol peak at approximately 12 minutes visible in both chromatograms, as well as a smaller impurity at 15,5 min, which elutes right before isopropyl alcohol. From experience, it is known that this impurity has no influence on the results. Lastly, there is a slight baseline increase after the elution of ethyl caproate, which is caused by the higher oven temperature during the back-out phase, but this also has no negative impact.

Reproducibility

Component	%RSD Manual method	%Average
Acetaldehyde	2,8	2,2
Dimethyl sulfide	4,1	1,4
Ethyl acetate	2,1	1,8
n-Propyl alcohol	5,8	0,6
iso-Butyl alcohol	0,9	0,4
iso-Amyl acetate	2,1	2,0
Amyl alcohols	0,6	0,5
Diacetyl	7,1	3,8
2,3-Pentaandion	4,9	3,5

Linearity, Reproducibility and Repeatability in line with original method or even improved

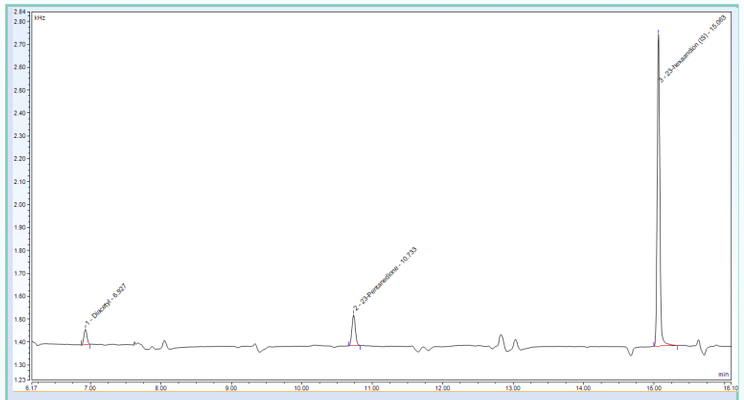
In order to check the **linearity** of the GC method, a series of 5 calibration standards were prepared, with all components of interest in a 5 vol% EtOH in water solution. The results show a coefficient of determination (R2) of 0,999 with a linear fit for all components.

Parallel inlet for FID/ECD detection in one single injection

For the **reproducibility** eight series of standard beer (for each series n=20, 10 per GC) were processed within 24 h after preparation and compared with the results of the manual method. For most components the reproducibility even has improved substantially in comparison to the manual method. The reproducibility for methyl sulfide and iso-butyl alcohol has improved with a factor of 2 to 3, for n-propyl alcohol this is even a factor of 9,7 times better. Acetates, on the other hand, exhibit a precision much closer to that of the manual method.

Fully automated sample preparation of beer samples with varying alcohol content

On one side, the **FID** channel is connected to the Wax-column because it is not compatible with ECD detection. And on the other side the **ECD** channel is connected to the Rtx-5 column.



The chromatogram of the **ECD** channel clearly shows that the separation of different components is ample sufficient and the peak shapes are Gaussians with a minor tailing for the ISTD.