Figure 1:
Three channel "Off-Flavor" Beer analyzer.

Application Note # CA-1818792

Analysis of volatiles in Beer, Malt and Wort using the Bruker three channel "Off-Flavor" Beer analyzer

Introduction

For breweries, quality control of their product is very complex. The quality of expected taste and smell of beer is at the end determined by people's tongue and nose. Disadvantage of these highly selective and sensitive sensors is the capability for quantitation. This is required to ensure a constant quality of the product independent on the production time in the year and production location. In order to maintain a constant quality, analytical equipment like Gas Chromatography (GC) is used to identify and quantify key-flavors. A number of components need to be present with a maximum and minimum concentration to guarantee the typical flavor of the beer. Other components may not exceed a concentration level to avoid an "off–flavor". Therefore a batch-to batch product conformance test is applied using a reference beer to validate the beer quality. Besides their contribution to the flavor, the information on component level of "off-flavors" is also highly valuable in order to identify the cause of an exceeding concentration, like a too high dimethyl sulfide (DMS) content, indicating among others the possible presence of a bacterial infection. Flavors and Off-flavors include a wide range of different chemical groups including alcohols, esters, acids, vicinal diketones and sulfides. This application note describes the headspace analysis of flavors and Off-Flavors in beer using a three channel 456-GC based analyzer.

Method set up

Due to human sensitivity to flavors, the components' threshold concentration is at the ppm down to the sub ppm range[1]. For GC analysis this means that sensitive and selective detectors are used to meet the required detection limits.

The detectors include:

- The Flame Ionization Detector (FID) highly selective to hydrocarbons including oxygenated hydrocarbons (oxygenates) like alcohols and esters
- The Electron Capture Detector (ECD) highly selective to halogens and ketones
- The Pulsed Flame Photometric Detector (PFPD) highly selective to sulfur containing components like dimethylsulfide (DMS)

Since the matrix of beer contains besides the flavors, a high amount of water and non-volatiles (polypeptides, carbohydrates and salts), the use of a headspace injection is the preferred sampling method.

Instrumentation

Technique	The Bruker Off-Flavor Beer analyzer is configured using three independent GC channels
Channel 1	
Injection:	S/SL, Split/Splitless Injector
Column:	BR-Swax 60m x 0.32mm, df=1µm
Detection:	Flame Ionization Detector (FID)
Channel 2	
Injection:	S/SL, Split/Splitless Injector
Column:	BR-5 50m x 0.53mm, df=1µm
Detection:	Electron Capture detector (ECD)
Channel 3	
Injection:	S/SL, Split/Splitless Injector
Column:	BR-SWax 30m x 0.32mm, df=1µm
Detection:	Pulsed Flame Photometric Detector (PFPD)
Sampler:	PAL COMBI-xt headspace injection system with sample tray cooling
Software:	CompassCDS Chromatography Software ChromSync plug-in software

Conditions

Settings	Chan. 1	Chan. 2	Chan. 3
Carrier gas	Hydrogen	Hydrogen	Hydrogen
Flow rate (mL/min)	3.5	4.5	5.0
injector	S/SL	S/SL	S/SL
Inj. Temp.	155°C	155°C	155°C
Split ratio	1:7	1:10	1:10
Detector	FID	ECD	PFPD
Gate delay	-	-	6 ms
Gate width	-	-	10 ms

Table 1: Method parameters

Results and Discussion

The analysis of beer shows a perfect detection of oxygenates using the FID shown in figure 2 and low level ketones using the ECD in figure 3[2].

ChromSync is used for batch-to-batch conformance testing by matching the results of a beer sample against a reference beer. The test includes pre-determined peak area windows resulting in degree-of-match performance values of the analyzed beer. See figure 6.

Peak Identification

1. Acetaldehyde
2. DMS
3. Acetone
4. Ethylformate
5. Ethylacetate
6. Methanol
7. Ethanol
8. Ethylpropionate
9. Propanol
10. Isobutylalcohol
11. Isoamylacetate
12. Isoamylalcohol
13. Amylalcohol
14. Ethylcapronate

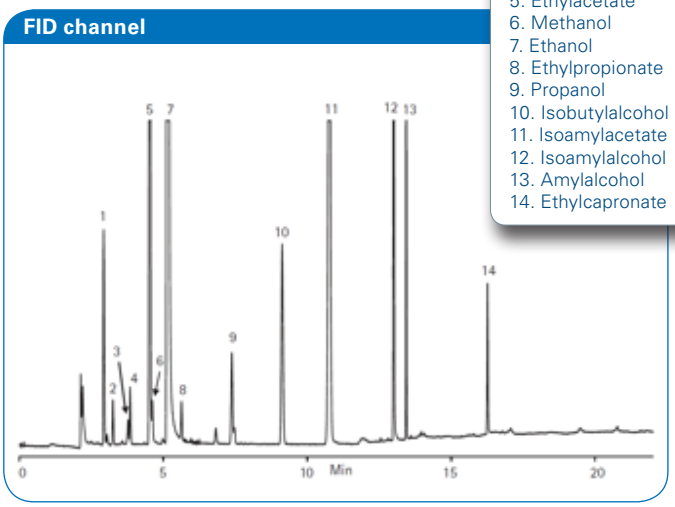

Figure 2: Beer analysis using FID detection

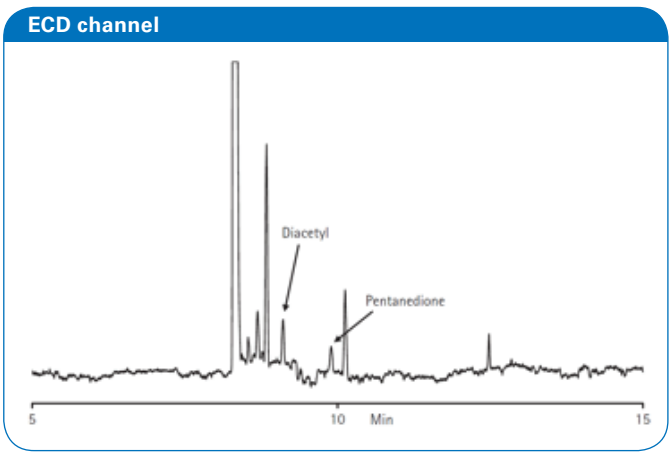

Figure 3: Beer analysis using ECD detection

The analysis of DMS analysis in wort is done using the PFPD channel as shown in figure 4. Although DMS is detected by the FID (peak 2 in figure 2), extra sensitivity is required to meet Limit of Quantitation (LOQ). Using a Sulfur containing internal standard, the analysis with the PFPD is free from any component interference as shown in figure 4. Even when the DMS concentration is low, quantitation is not interfered with other volatiles. Figure 5 shows the analysis of DMS in wort.

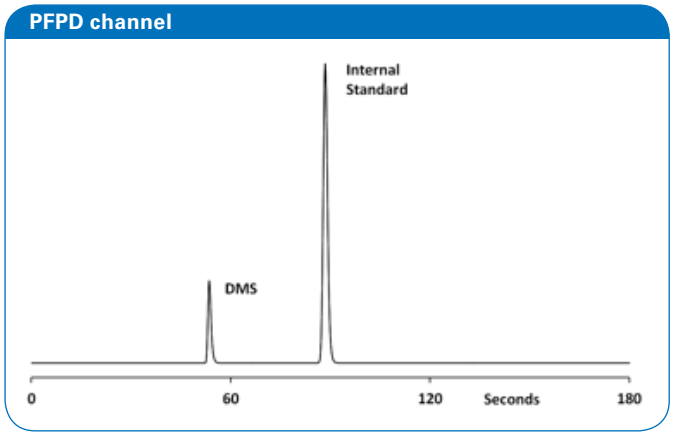

Figure 4: Test analysis using PFPD detection

ChromSync is used for batch-to-batch conformance testing by matching the results of a beer sample against a reference beer. The test includes pre-determined peak area windows resulting in degree-of-match performance values of the analyzed beer. See figure 5.

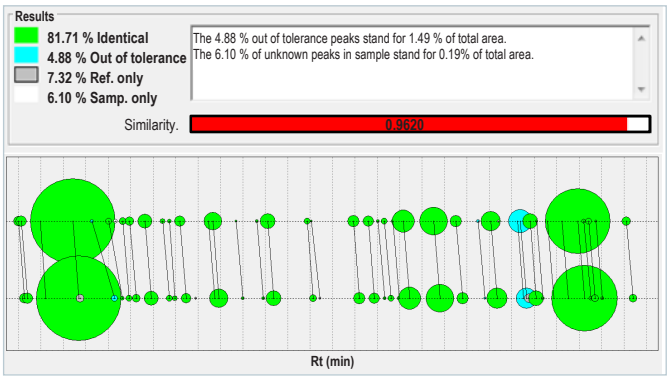

Figure 6: ChromSync compares a sample chromatogram (top) with the reference (bottom) generating a degree of similarity. Peak areas within tolerance limits (green), outside of tolerance limits (blue), peaks missing from the sample (white) and the reference peaks (grey) are shown as color coded disks with the size illustrating the peak area.

Keywords
Beer
Wort
Malt
Gas chromatography
Off flavor

Instrumentation & Software
Bruker three channel "Off-Flavor" Beer Analyzer
Bruker CompassCDS Chromatography Software
Bruker ChromSync plug-in Software

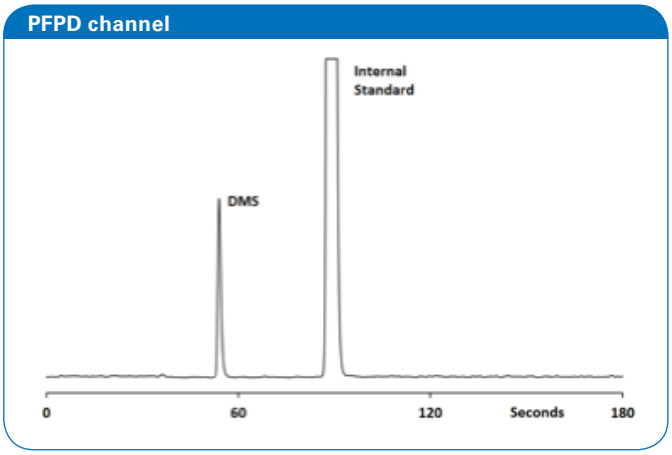

Figure 5: DMS analysis in wort with PFPD. The signal is shown 50 times amplified compared to figure 4.

Conclusion

The Bruker three channel "Off-Flavor" Beer analyzer is optimized for the analysis of volatiles in beer, malt and wort. Aldehydes, esters, alcohols, are analyzed on channel 1 using the FID detector. The vicinal diketones 2,3-butanedione (diacetyl) and 2,3-pentanedione are analyzed on channel 2 using the ECD detector. Dimethyl sulfide is either analyzed on channel 1 using the FID detector in case of beer analysis and on channel 3 using the PFPD detector for low DMS detection in beer and for DMS analysis in wort and malt. ChromSync herewith is an excellent tool for conformance testing of the beer quality.

Authors

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References

[1] Odor measurement review. Page 118-127: "Measurement of Odor Threshold by Triangle Odor Bag Method"
Office of Odor, Noise and Vibration Environmental Management, Bureau Ministry of the Environment, Government of Japan

[2] Bruker application note CA-1818791 Analysis of "Off-Flavors" in Beer using the Bruker two channel Off-Flavor Beer analyzer

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