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2017 ASBC Annual Meeting

HS-SPME-FID driven beer profiling targeting aroma active monocarboxylic acids

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2017 ASBC Annual Meeting
June 4–7, 2017
Sanibel Harbour Marriott
Fort Myers, FL, U.S.A.

Abstract

Short chain monocarboxylic acids (fatty acids) are an important group of flavor active compounds in beer.

In pale lagers they primarily result from yeast metabolism, whereas in hoppy ales late and dry hopping represents a second significant source.

In order to track these compounds in beer a straightforward HS-SPME-FID method was developed.

So many abbreviations!

- Headspace (HS) technique → removal of analytes from the gas space in equilibrium
- Solid Phase Microextraction (SPME) → enrichment of analytes from Headspace
- analytes are separated by gaschromatography (GC) and detected via flame ionization detector (FID)

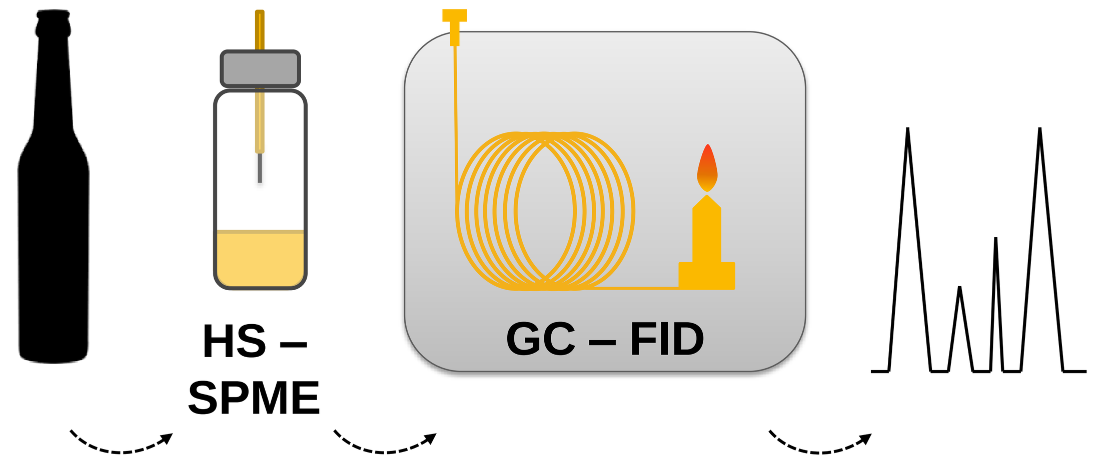

Figure 1: Schematic overview on method workflow

Method

System configuration:

GC	Shimadzu GC-2010
Column	FFAP 50m x 0.32mm (0.5µm)
Detector	flame ionization detector
Carrier gas	nitrogen
Temp. Inj./Det.	200 °C (Split 1:2) / 250 °C
Fiber	DVB/CAR/PDMS
Incub./Extract.	15/15 min; 50 °C; 500 rpm
Desorption	1 min

Table 1: GC temperature program

Rate	Temperature [°C]	Hold Time [min]
—	60	1
17	150	0
8	220	11
10	240	2

Sample preparation:

- 2 ml of a degassed sample are transferred into a 10 ml Headspace vial
- 4-Methylpentanoic acid (ISTD) is added and the vial is sealed with a screw cap

Calibration:

Range: 0.05 ppm – 4.00 ppm

Results

- Table 2 presents the results for C4 – C12 monocarboxylic acids of common and special beer types, concentrations of fatty acids depend on fermentation technology and hopping regime
- 2 + 3 Methylbutanoic acid with the same retention time are not separable in this presented method
- high variation of results between the beer styles → remarkable increase in C4 – C8 fatty acids in IPA, double IPA & Rye Pale Ale compared with Pils and Wheat beer
- chromatograms of late / dry-hopped beers show several unidentified peaks, that are absent in lager or pilsner styles (Fig. 2)

Table 2: Average values of monocarboxylic acids (C4 – C12) from duplicate determination in typical beer styles from different breweries [ppm]

beer style	Non alcoholic beer	Pils	Wheat beer	IPA #1	IPA #2	Double IPA	Rye Pale Ale
Butanoic acid (C4)	< 0.05	0.90	1.17	3.30	1.91	3.14	> 4.0
Isopentanoic acid (C5) (Σ 2 + 3 Methylbutanoic acid)	0.60	0.75	0.77	2.76	1.61	3.07	1.67
Pentanoic acid (C5)	0.07	0.07	0.09	1.01	0.26	0.34	0.20
Hexanoic acid (C6)	0.76	1.86	1.48	2.48	2.29	2.64	3.04
Octanoic acid (C8)	1.53	2.26	2.71	3.45	2.83	2.37	> 4.0
Decanoic acid (C10)	0.75	0.62	0.95	0.98	0.49	0.59	0.66
Dodecanoic acid (C12)	0.37	0.21	0.33	0.28	0.14	0.23	0.20

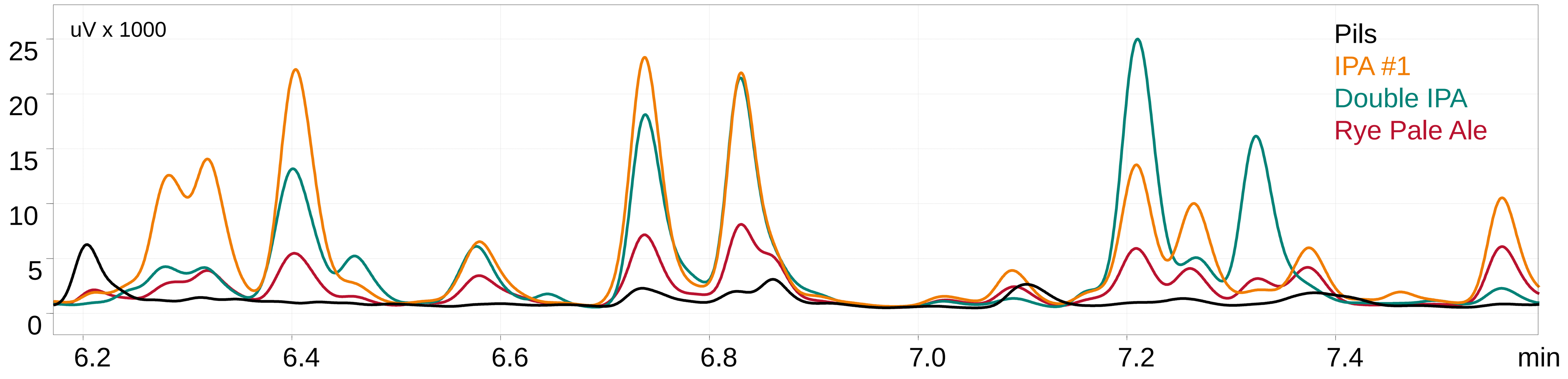

Figure 2: Comparison of different beer styles with respect on changes in using different hops and hopping technologies (Pils, IPA #1 (single hop variety, kettle + dry-hopping), Double IPA (6 varieties, kettle + dry-hopping), Rye Pale Ale)

Discussion

Strengths:

- short and medium chain fatty acid analysis in the range of 0.05 – 4 ppm
- no complex sample preparation
- GC-Method with appr. 21 minutes runtime
- robust quantification using an internal standard assay and GC-FID

Shortcomings:

- specific GC column needed
- identification of unknowns would require mass selective detection

Conclusion:

The method is an easy to use, fast and cost effective method to monitor monocarboxylic acids.

References

- Horák et al. "Analysis of Free Fatty Acids in Beer: Comparison of Solid-Phase Extraction, Solid-Phase Microextraction, and Stir Bar Sorptive Extraction“ Journal of Agricultural and Food Chemistry **2009** 57(23), 11081-11085

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