



# Hallertau Mittelfrüh, Citra, and Topaz hops and their impact on the aroma properties of three single hopped beers using whirlpool hopping

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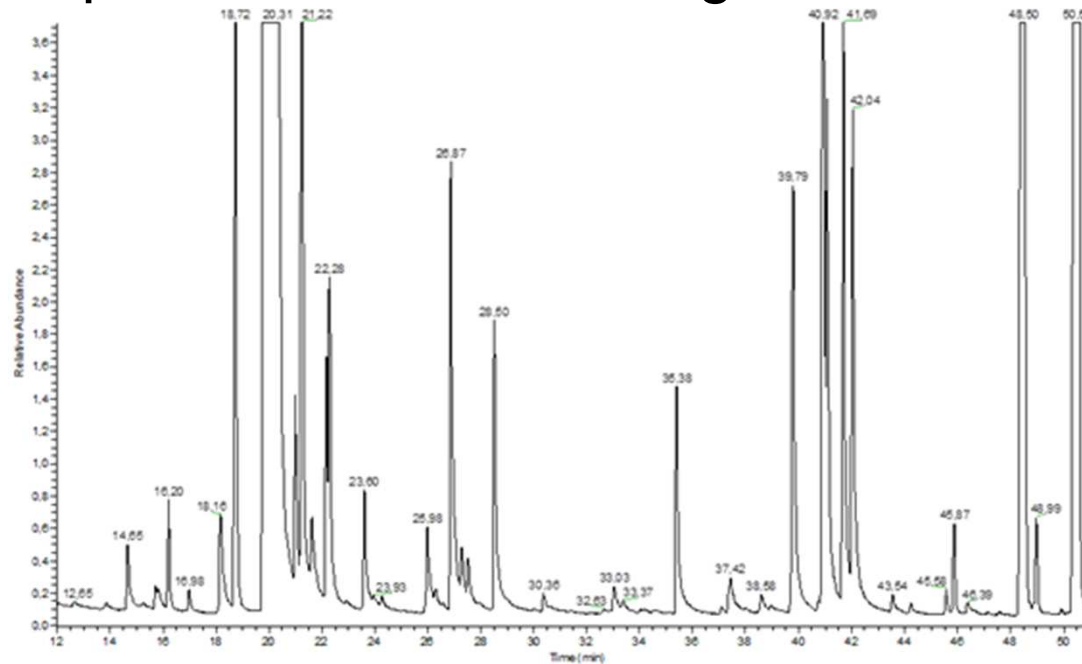
(1) Barth Innovations, Nuremberg, Germany

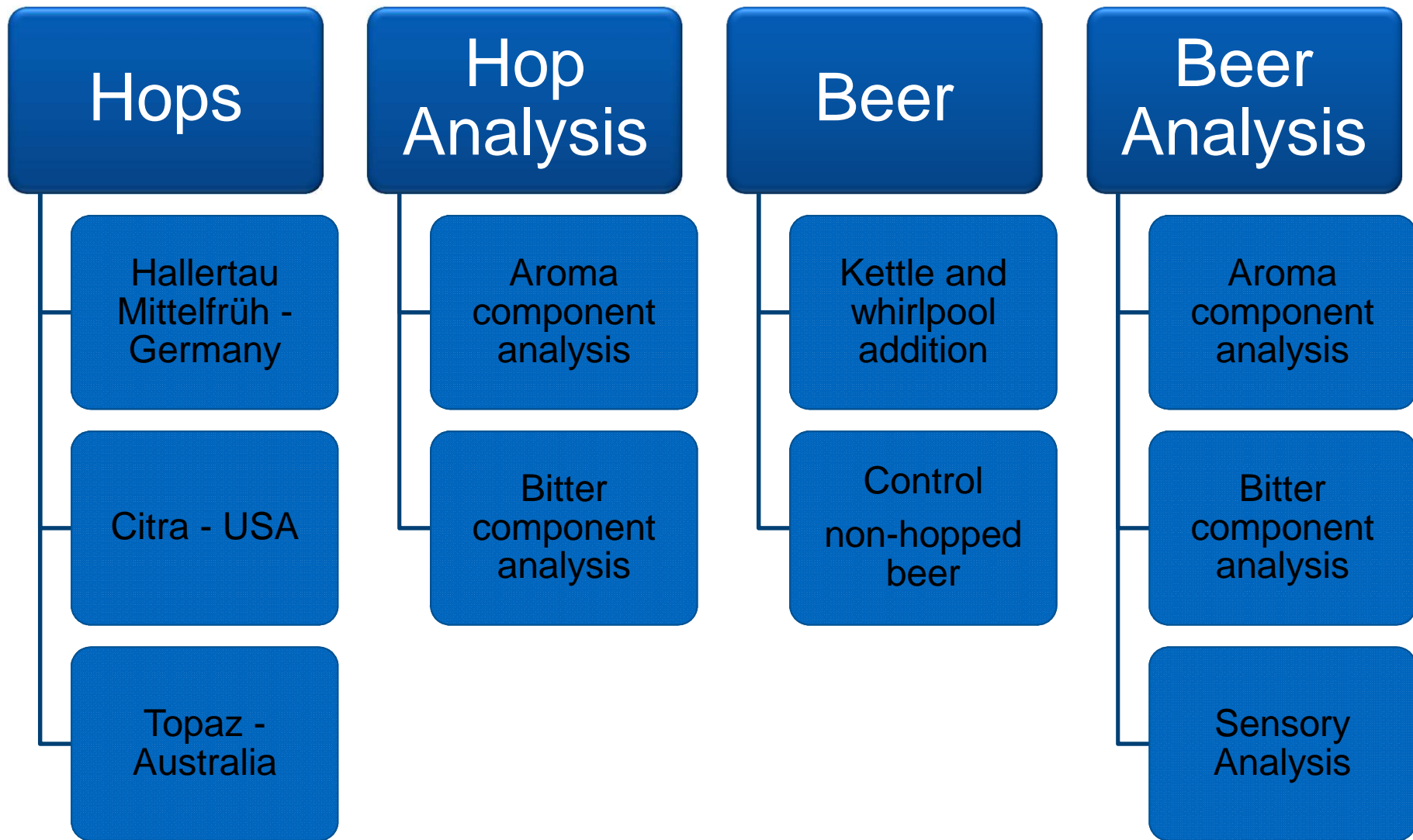
(2) Technische Universität München – Weihenstephan – Freising, Germany

(3) KU Leuven - KAHO Sint-Lieven, Gent, Belgium

# Background

- Hop Flavor Database (ASBC Methods of Analysis)
- Analyze aromas in hops using gas chromatography mass spectrometer (GC-MS)
- Brew single hopped beers with whirlpool addition
- Analyze hop aromas in beer using GC-MS





# Hop Flavor Database – ASBC MOA

Chemical Name	Synonyms	Struture	Molecular Weight (g/mol)	Flavor Descriptors
<b>Myrcene</b>	β-Myrcene, 7-Methyl-3-methylene-1,6-octadiene	C10H16	136,23	herbs, metallic, resinous, spicy, balsamic, geranium-like, green, peppery, terpene, balsam, plastic, sweet carrot, slight piney, celery, lemon, woody



Conc. Minimum (mg/l)	Conc. Maximum (mg/l)	Conc. Mean (mg/l)	TH 1 (mg/l)	TH 2 (mg/l)	TH 3 (mg/l)	TH Water (mg/l)
0,0001	1	0,5	0,009	0,01	0,03	0,013-0,042



Formation/Description	Compound Classification	References	CAS Number
• biosynthetic product during hop growth that degrades to geraniol and linalool	Monoterpene	[4], [5], [9], [13], [17], [29], [43], [44], [59]	123-35-3

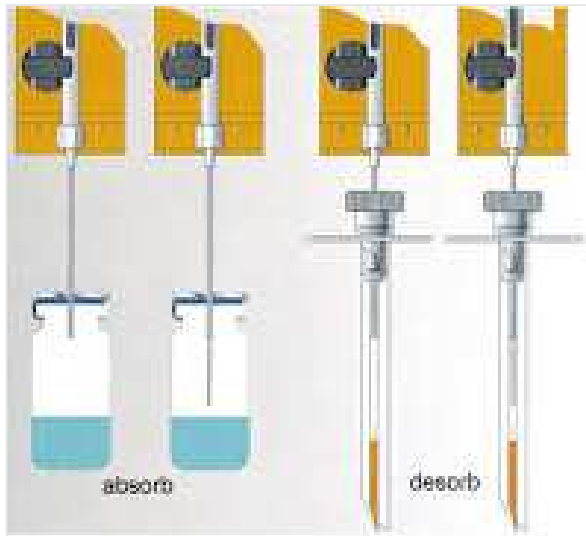


# Hops

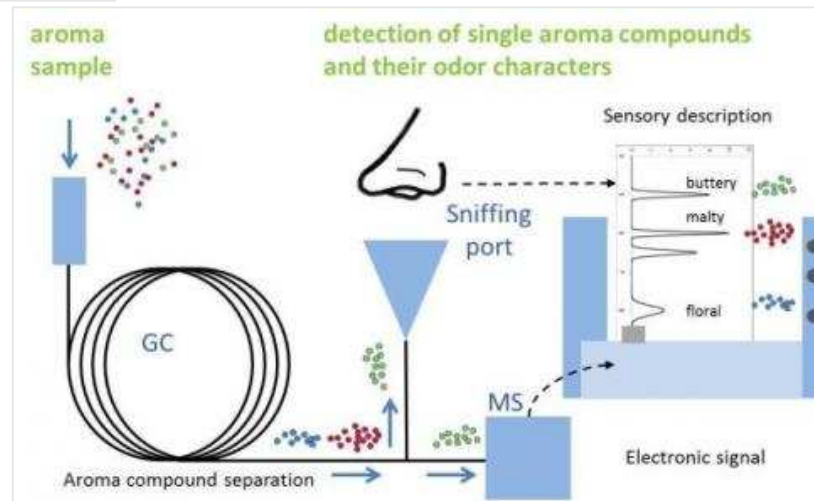
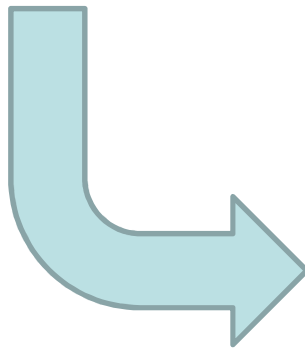
- Pellets (T90) from the 2012 harvest
- Analysis completed just prior to brewing trials

	Hallertau Mittelfrüh (HHA)	Citra (CIT)	Topaz (TOP)
Alpha acids [% w/w]	3,8	11,8	11,9
Oil [ml/100g]	0,95	1,95	0,90
Hop Storage Index (HSI)	0,380	0,316	0,376

# Solid phase microextraction (SPME) and solvent assisted flavor extraction (SAFE) + sniffing

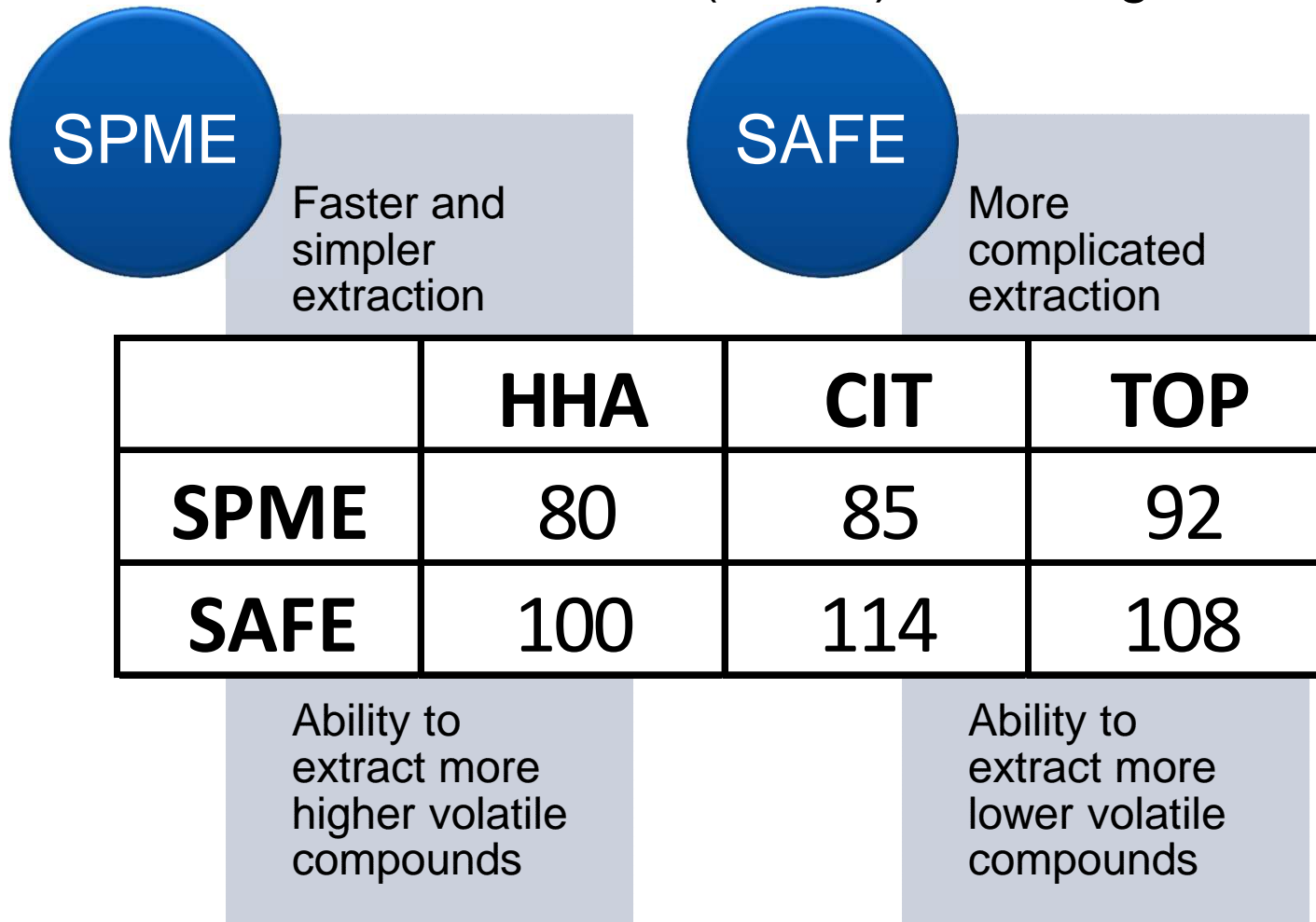


and



# Hop Analysis - Weihenstephan

- Comparison of hop aroma extraction techniques
  - Solid phase microextraction (SPME) and solvent assisted flavor extraction (SAFE) + sniffing



# Solid phase microextraction (SPME) - sniffing

Compound	SPME		
	Hallertau	Topaz	Citra
2-Methylpropanoic acid	plastic	x	x
3-Methylbutanoic acid	sweaty, musty	sweaty, musty	sweaty
2-Methylbutanoic acid	pineapple, tropical fruit	pineapple, tropical fruit	tropical fruit
S-Methyl 3-methylbutanethioate			sulfury
alpha-Pinene	x	slight glue	x
Methyl 5-methylhexanoate	flowery	x	x
6-Methyl 5-hepten-2-one			
Myrcene	flowery, green, fresh hops	flowery	fresh hops, green
Linalool	sweet, tropical fruit	fresh, sweet	sweet
Geraniol	flowery	apple-like	fresh fruit
alpha-Humulene	flowery	x	x

x = found in chromatogram but not smelled

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# Solvent assisted flavor evaporation (SAFE) – sniffing

Compound	SAFE		
	Hallertau	Citra	Topaz
Ethyl -butanoate	x	flowery	
3-Methylbutanoic acid	musty, rancid	old socks, rancid	rancid, sweat
2-Methylbutanoic acid	pineapple	sweaty, trop. fruit	trop. fruit
S-Methyl 3-methylbutanethioate	x	sweat, sulfury	sweat, sulfury
Myrcene	fresh, hoppy	resinous, fresh, hoppy	flowery, hoppy
Linalool	fresh fruit, citrus	citrus	citrus
(E,Z)-1,3,5-Undecatriene		solventy	
Borneol		slighty spicy	
Geraniol	fruity-flowery	lemon, solventy	sl. lemon
Methyl-4-decenoate	x	slighty solventy	x
Methyl-4,8-decadienoate	x	sweat, sulfury	x

x = found in chromatogram but not smelled

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# Single hopped beers with kettle and whirlpool additions

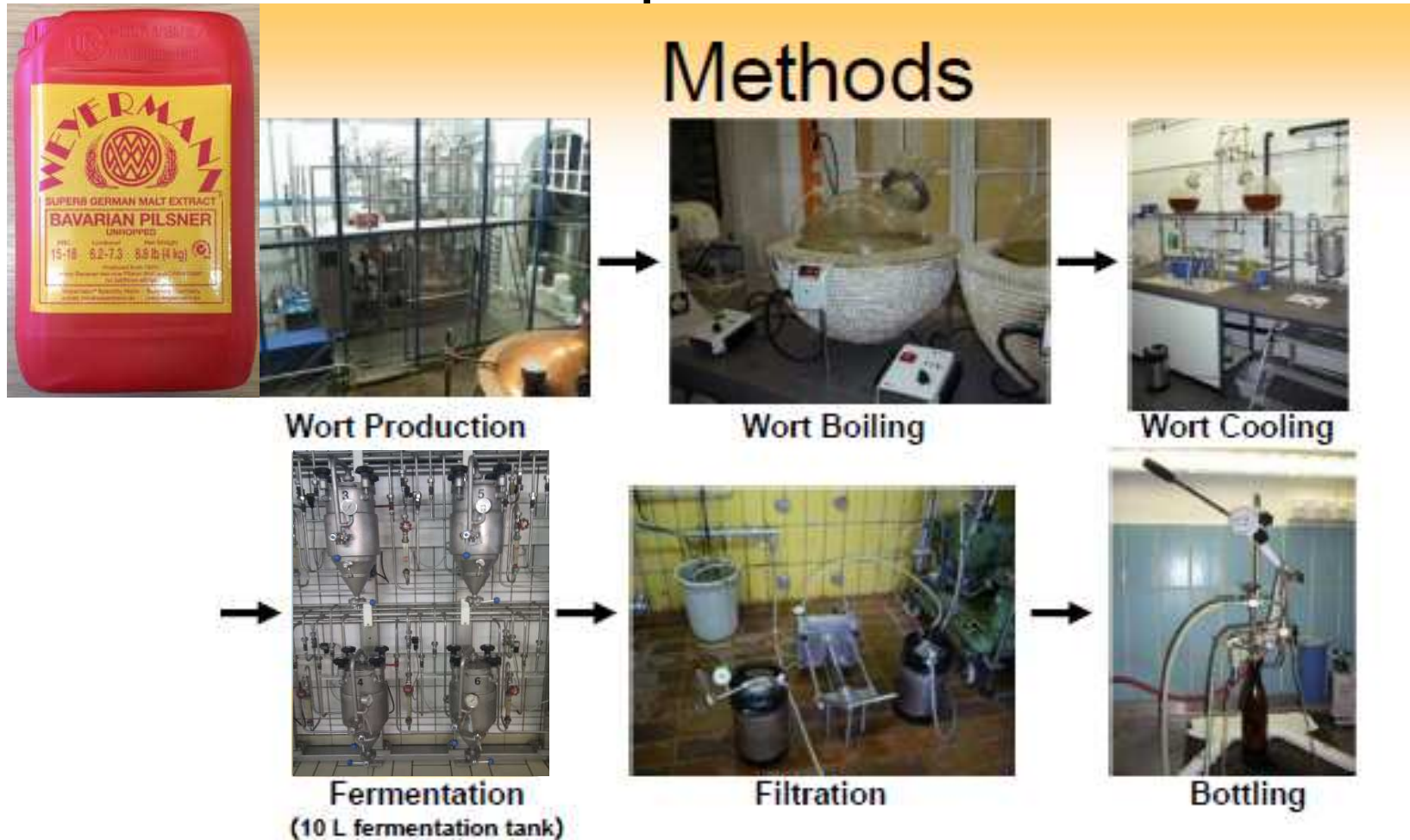


Fig.1 : Cited from Technische Universität München, Chair of Brewing and Beverage Technology

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# Beer

- Whirlpool dosage according to ml oil in pellets
- Added directly after boil
- 15 minute rest at  $> 90^{\circ}\text{C}$ , then cooled
- Pitching of lager yeast at  $10^{\circ}\text{C}$  at a rate of 10 g/l thick yeast slurry
- 7 days fermentation + maturation at  $8^{\circ}\text{C}$
- 7 days lagering at  $1^{\circ}\text{C}$

	$^{\circ}\text{P}$	Alc. [%vol]	Dosage kettle [g]	Dosage whirlpool [g]	Dosage whirlpool based on ml oil	pH beer
Hallertau	12,8	5,40	20	53	5,3	5,29
Citra	12,7	5,36	5,0	26	5,4	5,23
Topaz	12,6	5,27	0,0	56	5,4	5,15

# Hop Aroma Compounds – Belgium

Aroma Compounds	Hallertau (µg/l)	Citra (µg/l)	Topaz (µg/l)
Isobutyl isobutyrate	0,08	0,10	0,52
Myrcene	0,22	0,44	0,42
3-Methylbutyl 2-methylpropanoate	0,19	1,1	3,9
2-Methylbutyl 2-methylpropanoate	0,25	0,23	0,52
beta-Limonene	0,70	0,47	0,58
2-Nonanone	0,08	0,08	0,11
Linalool	245	215	158
beta-citronellol	0,81	2,1	4,2
Geraniol	-	39,0	47,0
2-Undecanone	0,23	0,92	0,65
2-Undecanol	1,2	3,7	2,9
Methyl geranate	1,5	29,4	4,8
Citronellol acetate	0,16	1,2	1,1
Geranyl acetate	0,28	0,54	1,8
beta-damascenone	0,14	0,09	0,10
alpha-Humulene	0,47	0,7	0,55
T-Cadinol	1,6	2,6	2,0

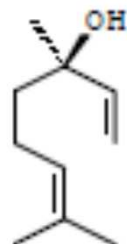
-All compounds are semi-quantitative data, except for Linalool and Geraniol, which are quantitative

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# (R/S)-Linalool in beer

- R-Linalool regarded as key hop aroma indicator substance in beer
- Amount of (R/S)-Linalool is similar to a dry hopped dosage (> 150 µg/l)

	Hallertau	Citra	Topaz	Threshold Beer
R-Linalool [µg/l]	229	201	145	2,2
S-Linalool [µg/l]	16,0	14,0	13,0	180
(R/S)-Linalool [µg/l]	245	215	158	8-80
R-Linalool [%]	93%	93%	92%	-
S-Linalool [%]	7%	7%	8%	-

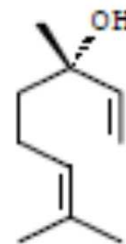


**(R)-linalool**

Odour threshold values:

2.2 µg/L (beer)

0.036 ng/L (air)



**(S)-linalool**

Odour threshold values:

180 µg/L (beer)

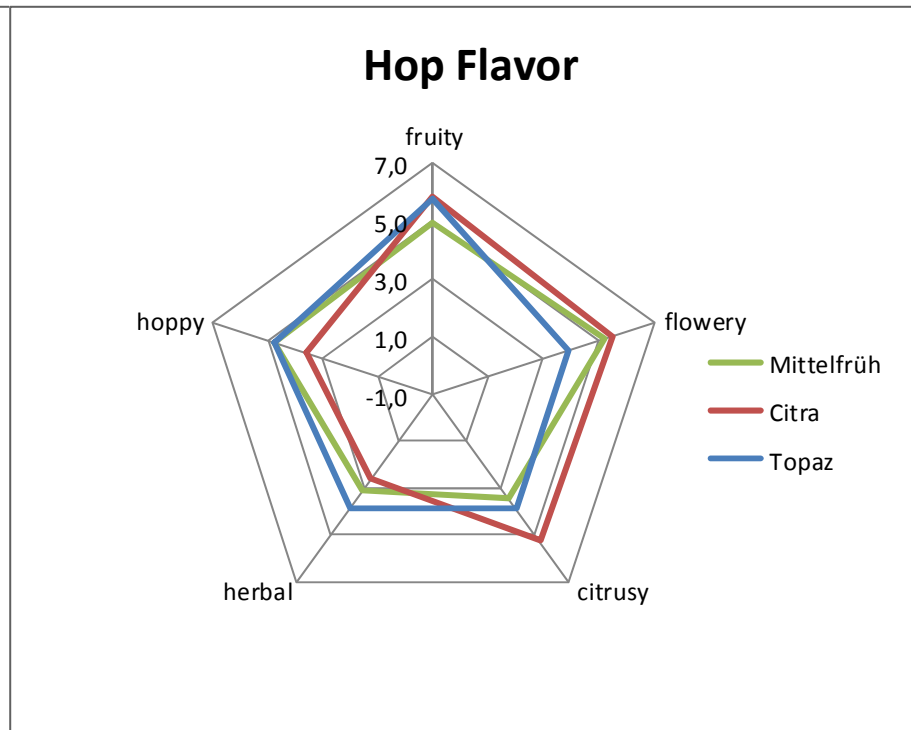
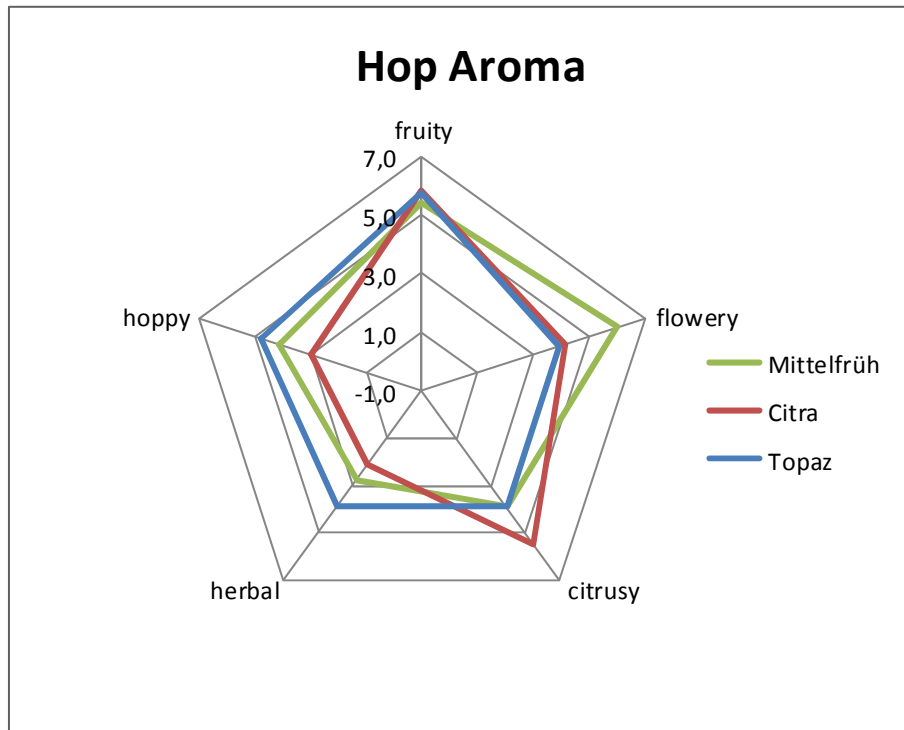
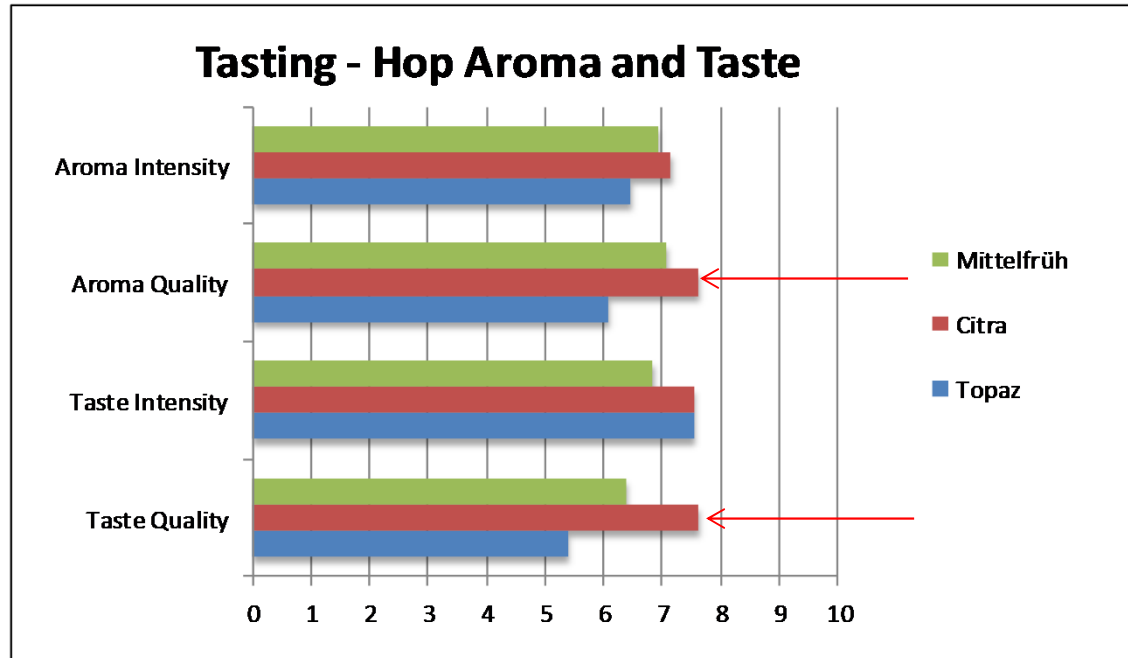
2.9 ng/L (air)

# Sensory A

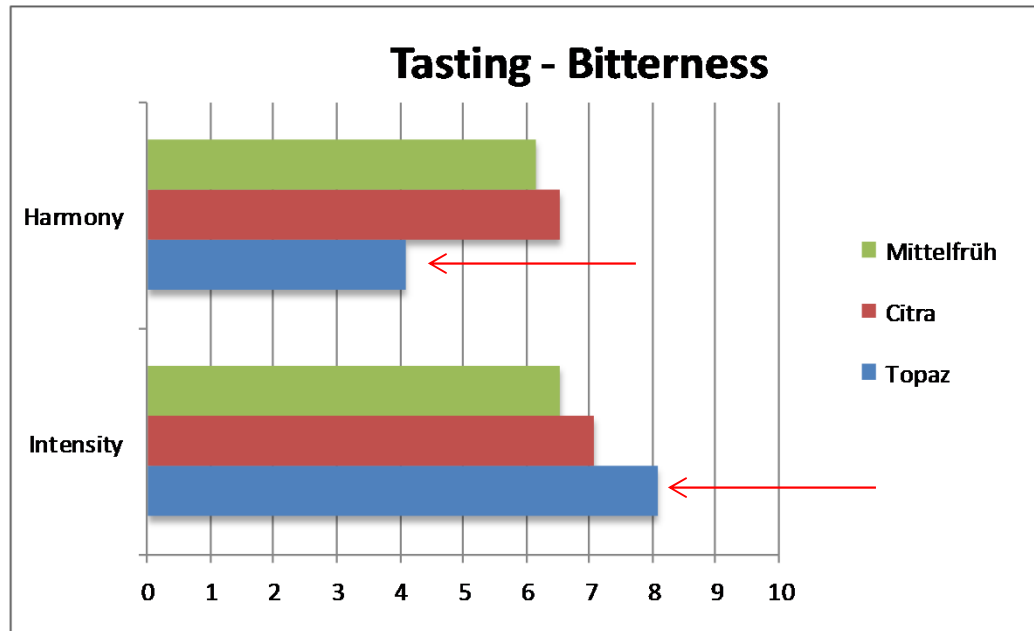
- Tasting was completed with a trained tasting panel at TUM – Weihenstephan composed of 13 panelists
- Two forms were used:
  - Tasting sheet for hop aroma and flavor
  - Modified tasting sheet from research brewery in St. Johann, Germany

Name		Verkostungsformblatt für Bier				
(klare Biere) Probenbezeichnung		Bier 1	Bier 2	Bier 3	Bier 4	
<b>Aussehen</b>	<b>Prüfkriterien</b>					
	1 deutlich zu hell	9	9	9	9	
	2 zu hell	8	8	8	8	
	3 etw as zu hell	7	7	7	7	
	4 Spur zu hell	6	6	6	6	
	5 typgerecht	5	5	5	5	
	4 Spur zu dunkel	4	4	4	4	
	3 etw as zu dunkel	3	3	3	3	
	2 zu dunkel	2	2	2	2	
	1 deutlich zu dunkel	1	1	1	1	
<b>Glanz / Trübung</b>	5 klar, leuchtend	5	5	5	5	
	4 klar	4	4	4	4	
	3 opalisierend	3	3	3	3	
	2 opal	2	2	2	2	
	1 trüb, Bodensatz	1	1	1	1	
	<b>Schaum</b>	5 durchgehend fein	5	5	5	5
		4 fein bis mittel	4	4	4	4
		3 mittel	3	3	3	3
		2 mittel bis grob	2	2	2	2
		1 grobe Blasen	1	1	1	1
<b>Haltvermögen</b>		5 sehr gut anhaftend	5	5	5	5
		4 gut anhaftend	4	4	4	4
		3 befriedigend anhaftend	3	3	3	3
		2 w enig anhaftend	2	2	2	2
		1 schlecht, kein Anhaften	1	1	1	1
<b>Geruch</b>	5 typisch, ausgeprägter Charakter	5,0	5,0	5,0	5,0	
	4 rein, noch typisch	4,5	4,5	4,5	4,5	
	3 leichte Fehler	3,5	3,5	3,5	3,5	
	2 deutliche Geruchsfehler	2,5	2,5	2,5	2,5	
	1 starke Fehler, ungenießbar	1,0	1,0	1,0	1,0	
<b>Geschmack</b>	5 typisch, ausgeprägter Charakter	5,0	5,0	5,0	5,0	
	4 rein, noch typisch	4,5	4,5	4,5	4,5	
	3 leichte Fehler	3,5	3,5	3,5	3,5	
	2 deutliche Geschmacksfehler	2,5	2,5	2,5	2,5	
	1 starke Fehler, ungenießbar	1,0	1,0	1,0	1,0	
<b>Trunk</b>	1 deutlich zu voll, mastig	9	9	9	9	
	2 zu voll	8	8	8	8	
	3 etw as zu voll	7	7	7	7	
	4 Spur zu voll	6	6	6	6	
	5 typgerecht	5	5	5	5	
	4 Spur zu leer	4	4	4	4	
	3 etw as zu leer	3	3	3	3	
	2 leer	2	2	2	2	
	1 deutlich zu leer, w ässrig	1	1	1	1	
	<b>Weichheit</b>	5 sehr w eich	5	5	5	5
4 w eich		4	4	4	4	
3 nicht ganz abgerundet		3	3	3	3	
2 unharmonisch		2	2	2	2	
1 hart		1	1	1	1	
<b>Rezenz</b>	1 adstringierend	9	9	9	9	
	2 zu rezent	8	8	8	8	
	3 etw as zu rezent	7	7	7	7	
	4 Spur zu rezent	6	6	6	6	
	5 angenehm rezent	5	5	5	5	
<b>Intensität</b>	4 genügend rezent	4	4	4	4	
	3 mäßig rezent	3	3	3	3	
	2 w enig rezent	2	2	2	2	
	1 schal, abgestanden	1	1	1	1	
	1 deutlich zu bitter	9	9	9	9	
	8,5	8,5	8,5	8,5		
	2 zu bitter	8	8	8	8	
	7,5	7,5	7,5	7,5		
	3 etw as zu bitter	7	7	7	7	
	6,5	6,5	6,5	6,5		
4 Spur zu bitter	6	6	6	6		
5,5	5,5	5,5	5,5			
5 typgerecht bitter	5	5	5	5		
4,5	4,5	4,5	4,5			
4	4	4	4			
4 Spur zu w enig bitter	3,5	3,5	3,5	3,5		
3 etw as zu w enig bitter	3	3	3	3		
2,5	2,5	2,5	2,5			
2 zu w enig bitter	2	2	2	2		
1,5	1,5	1,5	1,5			
1 deutlich zu w enig bitter	1	1	1	1		
<b>Qualität</b>	5 sehr fein	5	5	5	5	
	4,5	4,5	4,5	4,5		
	4 fein	4	4	4	4	
	3,5	3,5	3,5	3,5		
	3 etw as nachhängend	3	3	3	3	
2,5	2,5	2,5	2,5			
2 nachhängend/breit	2	2	2	2		
1,5	1,5	1,5	1,5			
1 deutlich nachhängend/breit	1	1	1	1		
<b>Präferenz / Reihenfolge (1=Bestes)</b>						
<b>geschätzte BE</b>						

# Sensory Results



# Ranking and Bitterness



Sample	Hallertau	Citra	Topaz
Ranking (😊 1-5)	2,10	1,80 😊	3,10
predicted sensory BU	24,9	27,7	32,7
measured IBU	36,5	38,5	68,5
iso-alpha-acids [mg/l]	22,1	25,4	29,7



# Descriptors

<b>Aroma</b>		
<b>Mittelfrüh</b>	<b>Citra</b>	<b>Topaz</b>
(red) berries	muscatel	resinous
gooseberries	grape juice	fruity
smoky	grapefruit	berries
grapefruit	tomatoes	green fruits
flowery	citrus	tomato leaves
woody	flowery	green-grassy
	musty	lychee

<b>Taste</b>		
<b>Mittelfrüh</b>	<b>Citra</b>	<b>Topaz</b>
resinous	fruity	resinous
geraniol	peach	biscuit
cider	grapefruit	grassy
solventy	lime	kiwi
	gooseberries	passion fruit
	lemon	herbal
		fruity

# Conclusions

- 2- und 3-methylbutyric acid, S-methyl 3-methylbutanethioate, myrcene, linalool and geraniol are important aroma compounds in hops
- Whirlpool hopping can contribute high levels of R-linalool and geraniol to beer
- Levels of 3-methylbutyl 2-methylpropanoate, beta-citronellol, methyl geranate and geranyl acetate varied widely dependent on hop variety
- When whirlpool hopping, large differences between sensory BU, measured IBU and measured iso-alpha-acids can occur

# Acknowledgements

- Barth-Haas Group for the hop samples and Barth-Haas Grant
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- Christina Schönberger and Martina Gastl

Thank you for your kind attention

Questions?

**BARTH-HAAS GRANT**  
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