Workshop: August 15th, 3:30 pm-4:45 pm

- 3:30 – Intro
- 3:35 – Methods of Analysis – Phil Chou
- 3:50 – Hop Storage Index – Mark Zunkel
- 4:05 – Basics of Sensory – Jeff Dailey
- 4:20 – Sensory
- 4:40 – Final words

Methods of Analysis: Alpha, Beta, Oil, HSI, & Advanced Methods for Oil Composition

Phillip Chou
John I. Haas, Inc.

Outline

- Challenge
- Hop Chemistry
- Methods of Analysis
- Leaf Hops
- Pellets
- Extracts
- Oils

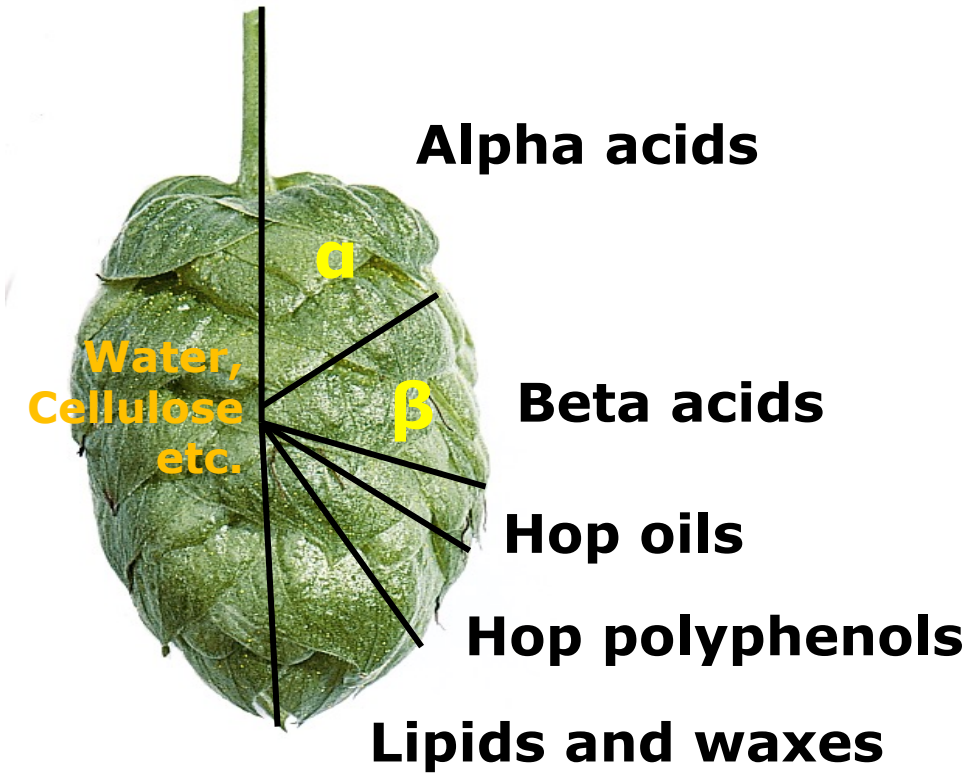
Sensory Evaluation

- Organoleptic & physical analysis delivers a general picture of:
  - ✓ Appearance/Color
  - ✓ Seed Content
  - ✓ Mixture of Different Varieties
  - ✓ Leaf Material
  - ✓ Foreign Matter
  - ✓ Aroma
  - ✓ Pests & Diseases

Bitterness Potential?
Aroma Chemistry?
Storage Stability?

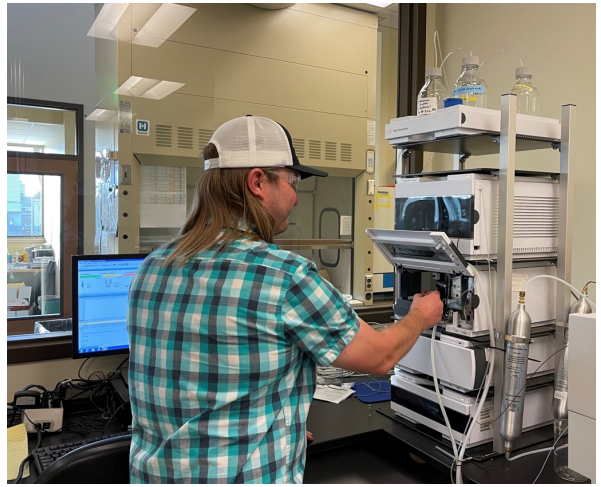
Hop Chemical Content

	% w/w
Alpha acids	2 - 18
Beta acids	1 - 10
Hop oils	0.5 - 3
Polyphenols	2 - 5
Waxes and Steroids	tr - 5
Proteins	15
Cellulose	40 - 50
Moisture	6 - 10
Monosaccharides	2
Pectins	2
Minerals (Ash)	10

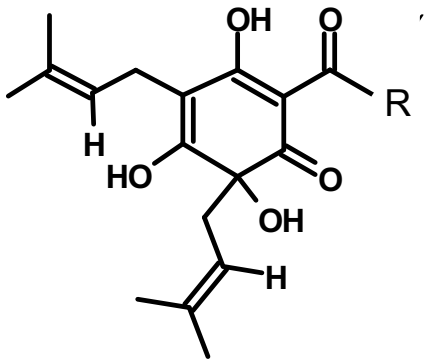


- Bitterness
- Hop Aroma
- Microbiological Stability
- Foam Enhancement
- Contribution to body & mouthfeel of a beer
- Improvement of haze and flavour stability
- Differentiation of beer types and brands

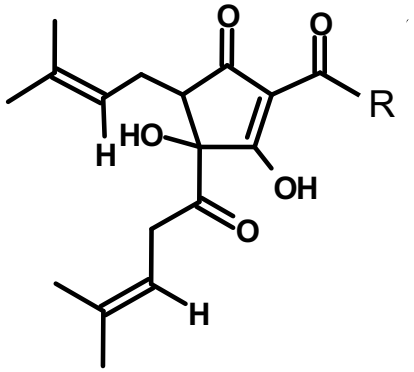
Hop Quality Control



Alpha & Isoalpha Acids



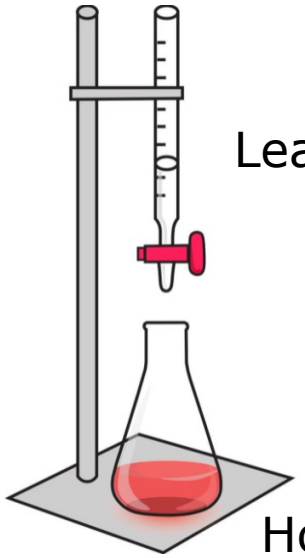
Hop Processing



Alpha Acids	***R***	***Isoalpha Acids***
Humulone	$-CH_2CH(CH_3)_2$	Isohumulone
Cohumulone	$-CH(CH_3)_2$	Isocohumulone
Adhumulone	$-CH(CH_3)CH_2CH_3$	Isoadhumulone

Lead Conductance

- Electromagnetic Method
  - ✓ Relatively "inexpensive"
  - ✓ Lead Acetate Titration + Conductance or Resistance measurements



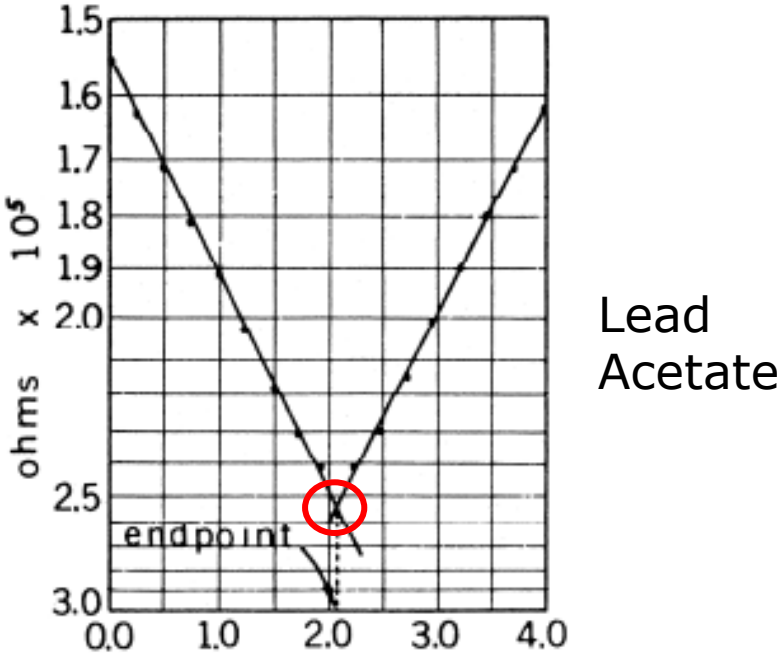
Lead Acetate

Titration

Hop Extract

α Acids + Lead Ions

Precipitate



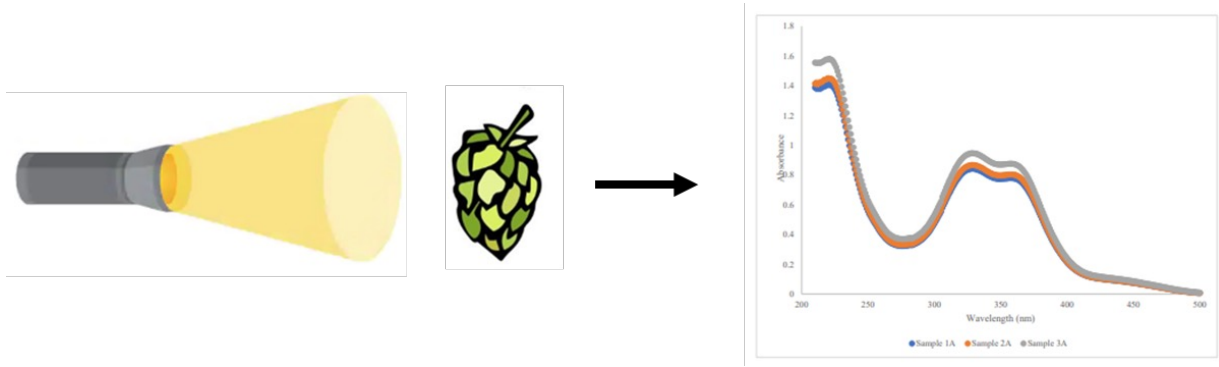
Lead Acetate

https://quizizz.com/admin/quiz/5ebf843e4d27c8001bd3a28c/titration-method

American Society of Brewing Chemists, Hops 6 Method

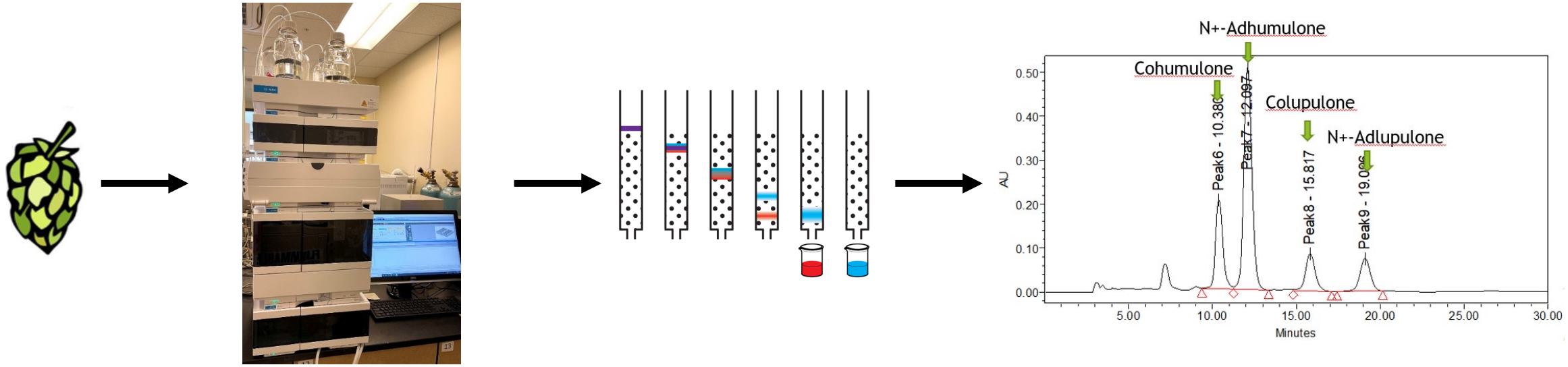
Ultraviolet-Visible (UV-Vis) Spectroscopy

- Spectroscopic Method
  - ✓ Rapid
  - ✓ Requires spectrophotometer purchase



High Performance Liquid Chromatography (HPLC)

- Chromatographic Method
  - ✓ Identify & quantify important hop compounds
  - ✓ Accurate
  - ✓ Expensive instrumentation

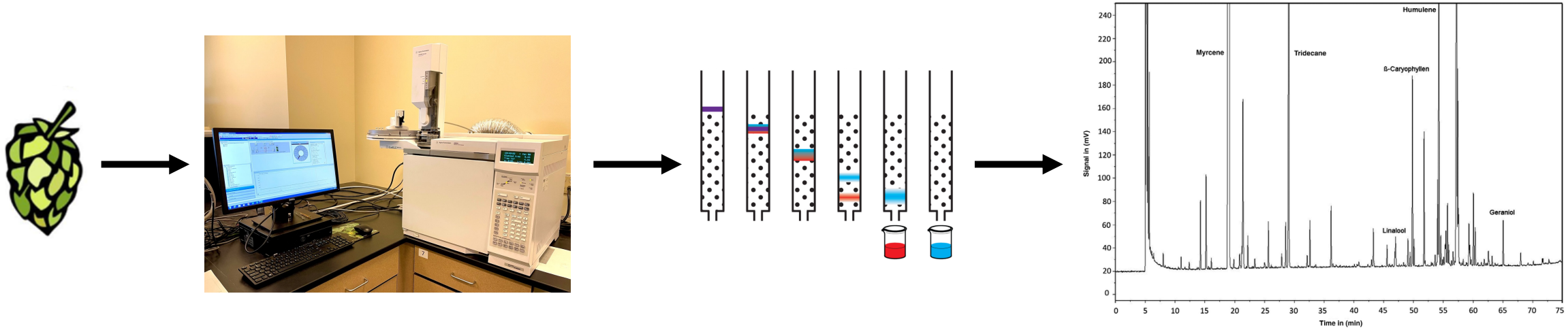


https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Analytical_Chemistry_2.1_(Harvey)/12_Chromatographic_and_Electrophoretic_Methods/12.2%3A_General_Theory_of_Column_Chromatography

https://www.uaex.uada.edu/farm-ranch/crops-commercial-horticulture/horticulture/ar-fruit-veg-nut-update-blog/posts/hops-drying-november-18-2019.aspx

Gas Chromatography (GC)

- Chromatographic Method
  - ✓ Identify & quantify hop aroma compounds
  - ✓ Accurate
  - ✓ Expensive instrumentation



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S. Raut et al. *J. Sci Food Agric.* **2020**, *101*, 2247.

Hop Analysis: Hop Storage Index (HSI)

ASBC Hops 12
EBC 7.13

$$HSI = \frac{\text{Absorbance}_{275}}{\text{Absorbance}_{325}}$$

Oxidized α & β Acids

α & β Acids

HSI	
0.250	Typical of fresh hops
0.300	10% oxidized
0.400	25% oxidized
0.500	33% oxidized
0.700	50% oxidized

Hop Analysis: Hop Storage Index (HSI)

ASBC Hops 12
EBC 7.13

Oxidized α & β Acids

$$HSI = \frac{Absorbance_{275}}{Absorbance_{325}}$$

α & β Acids

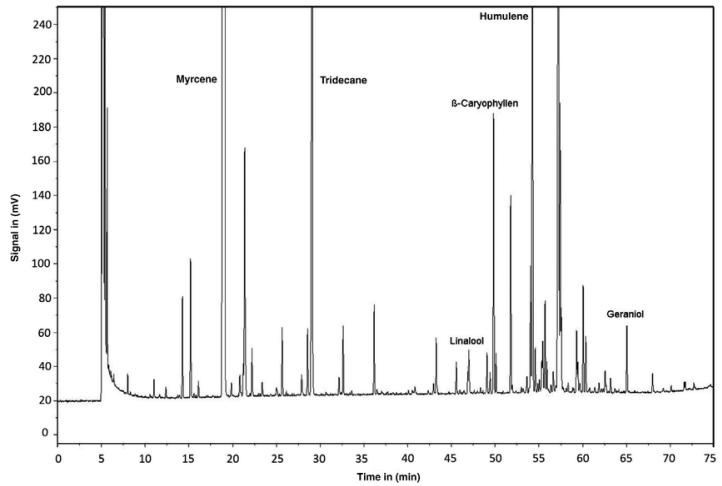
HSI	
0.250	Typical of fresh hops
0.300	10% oxidized
0.400	25% oxidized
0.500	33% oxidized
0.700	50% oxidized

Hop Analysis: Aroma

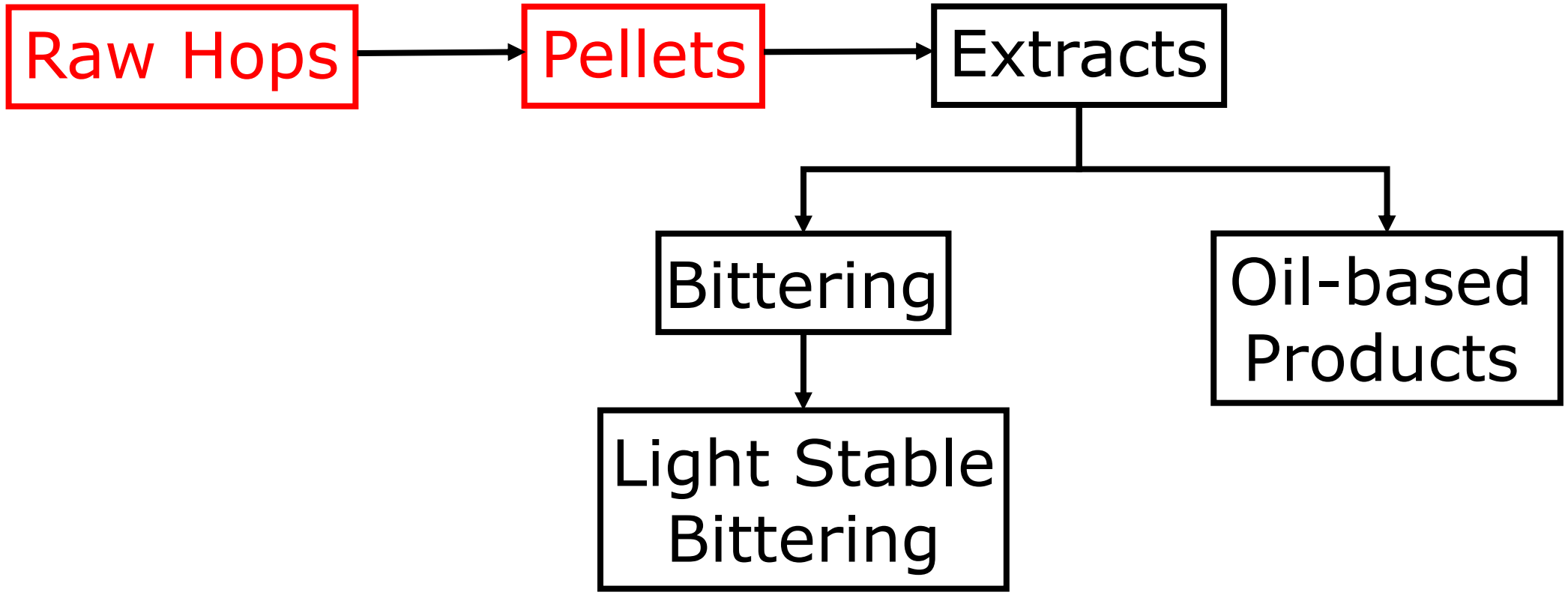
Extract

- Steam Distillation (ASBC Hops 13, EBC 7.10)
  - ✓ Total Oils (ml/100 g)

- Gas Chromatography (ASBC Hops 17, EBC 7.12)
  - ✓ Abundant Aroma Compounds
    - ➢ Myrcene
    - ➢ Caryophyllene
    - ➢ Linalool
    - ➢ Humulene
    - ➢ Geraniol
    - ➢ Farnesene



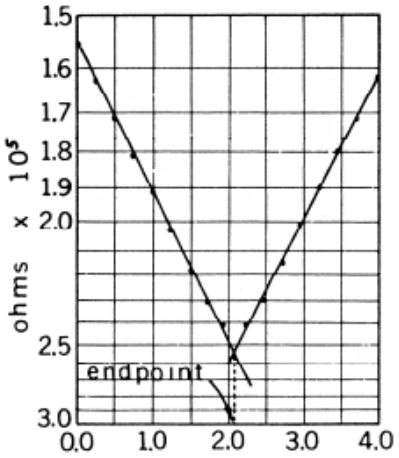
Hop Quality Control

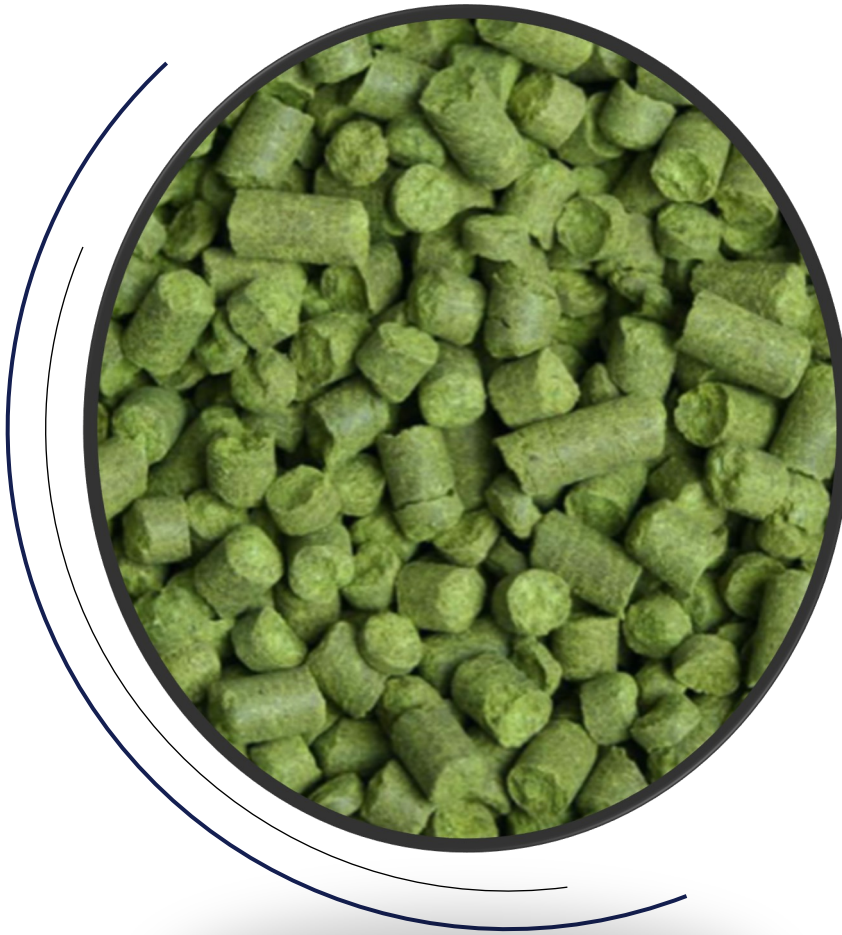


Hop Analysis: α- & β-Acids

Cones & Pellets

- Lead Conductance
  - ✓EBC 7.4/7.5, ASBC Hops 6
    - ➢Lead Conductance Value % ~ α-Acids

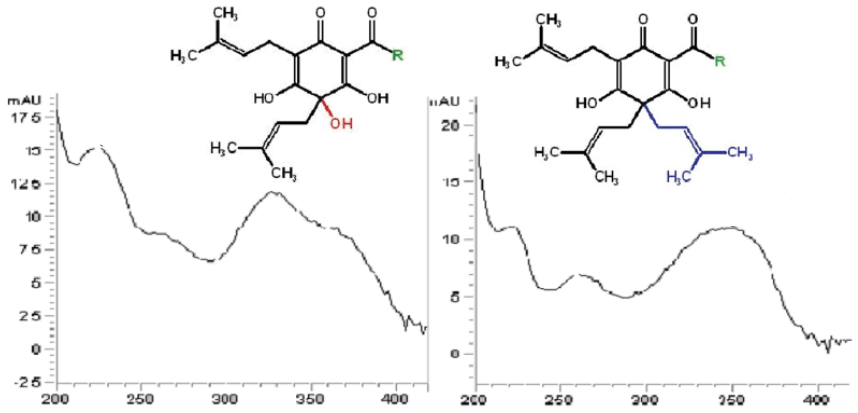


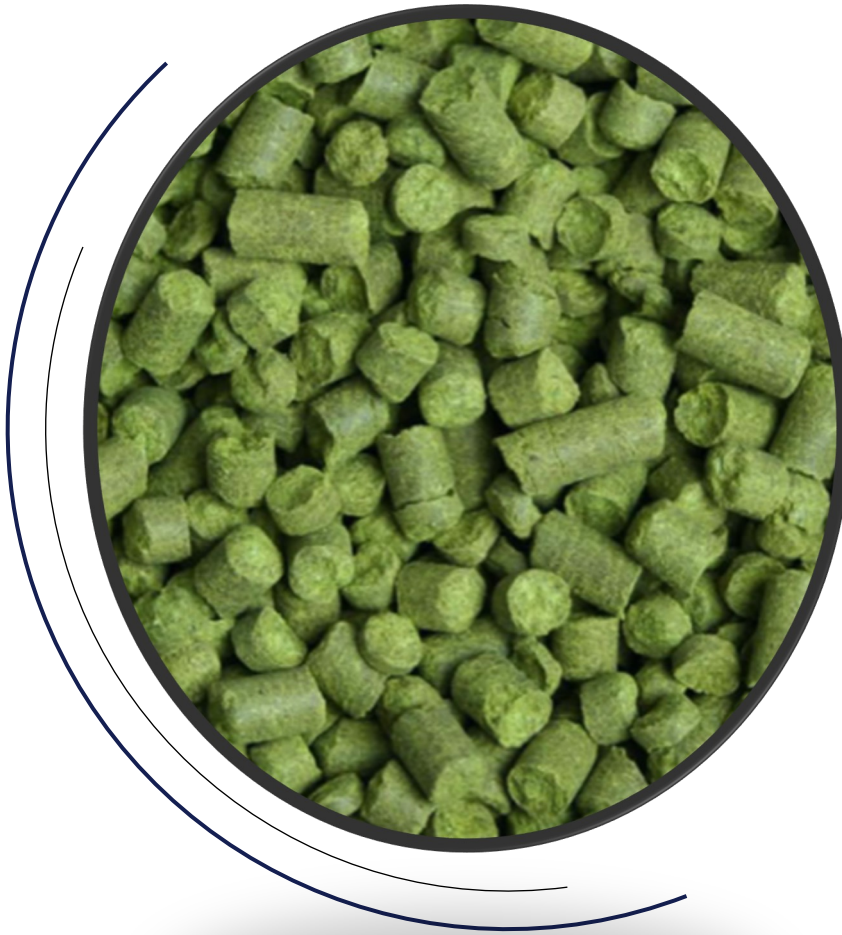


Hop Analysis: α- & β-Acids

Cones & Pellets

- UV-Vis
  - ✓ ASBC Hops-6 (355, 325, 275 nm)
    - ➢ % α-Acids
    - ➢ % β-Acids



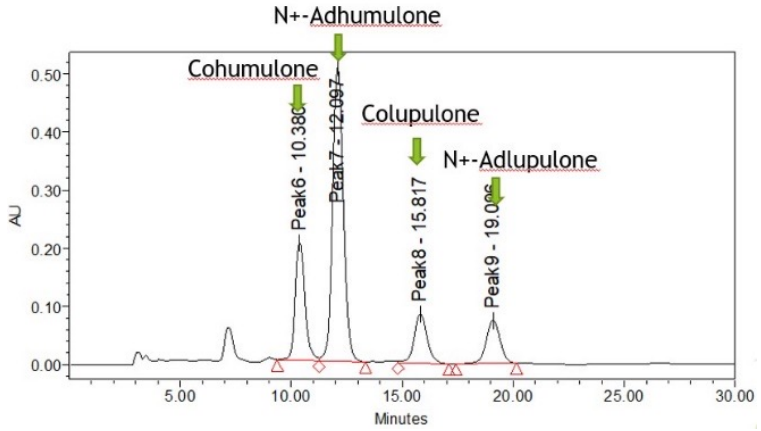


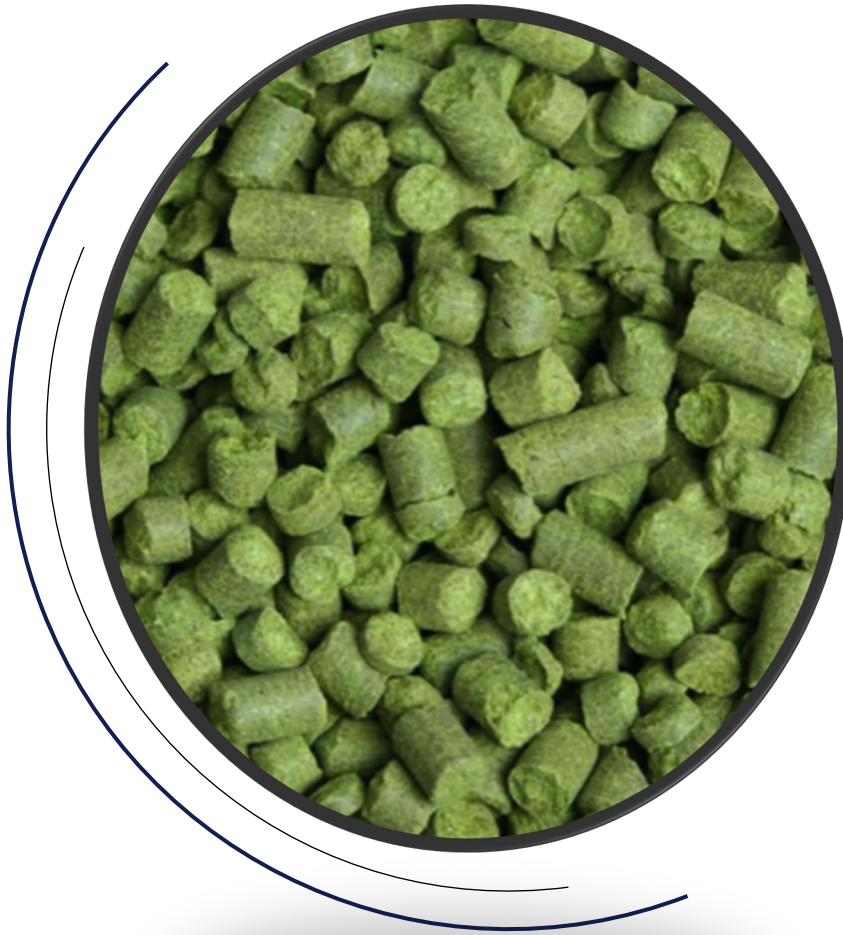
O. Kornysovaet al. *Adv. Med. Sci.* **2009**, *54*, 41.

Hop Analysis: α- & β-Acids

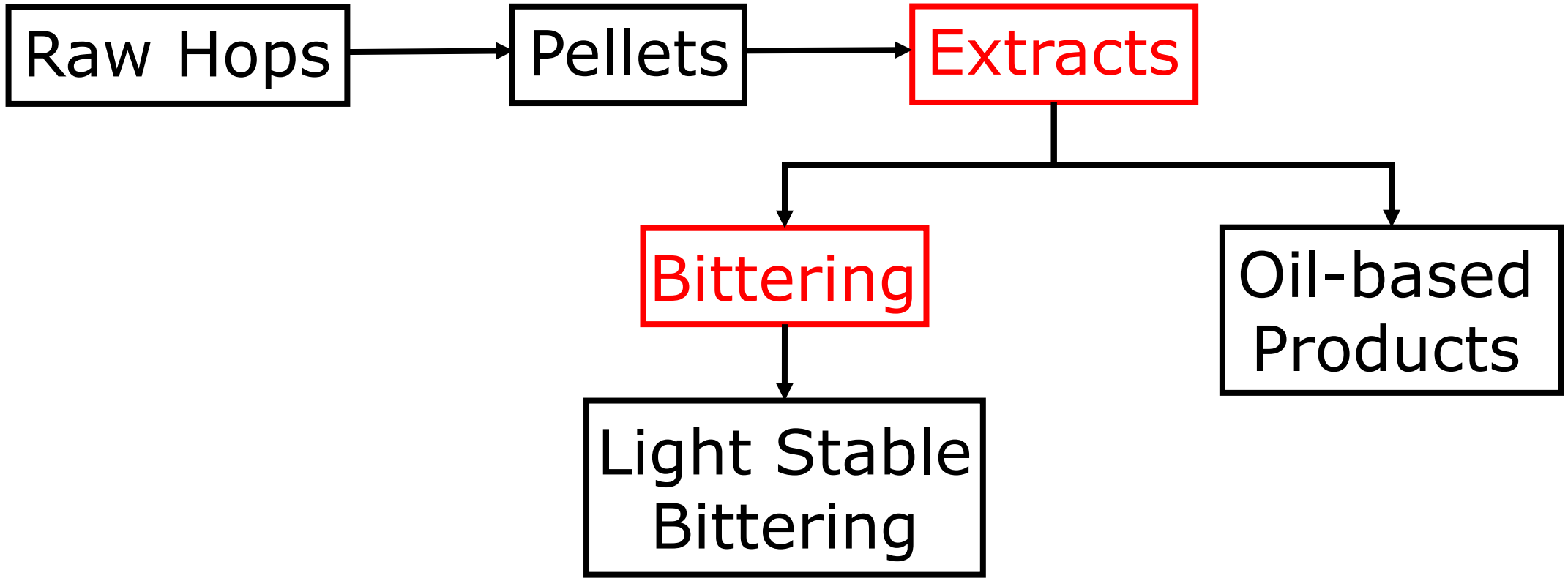
Cones & Pellets

- HPLC
  - ✓ ASBC Hops-14 (314 nm), EBC 7.7 (314 nm)
    - ➢ Humulone
    - ➢ Cohumulone
    - ➢ Adhumulone
    - ➢ β-Acids





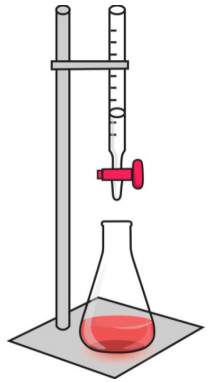
Hop Quality Control



Hop Analysis: α-Acids

Unisomerized Extract

- Lead Conductance
  - ✓ ASBC Hops 8, EBC 7.6
    - ➢ Lead Conductance Value % ~ α-Acids %



Hop Analysis: α-Acids

Unisomerized Extract

- UV-Vis
  - ✓ ASBC Hops-8 (355, 325, 275 nm)
    - ➢ % α-Acids

Hop Analysis: α- & β-Acids

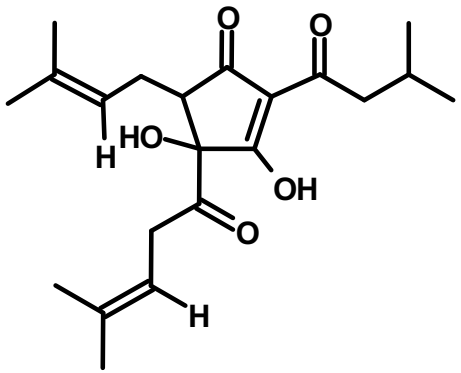
Unisomerized Extract

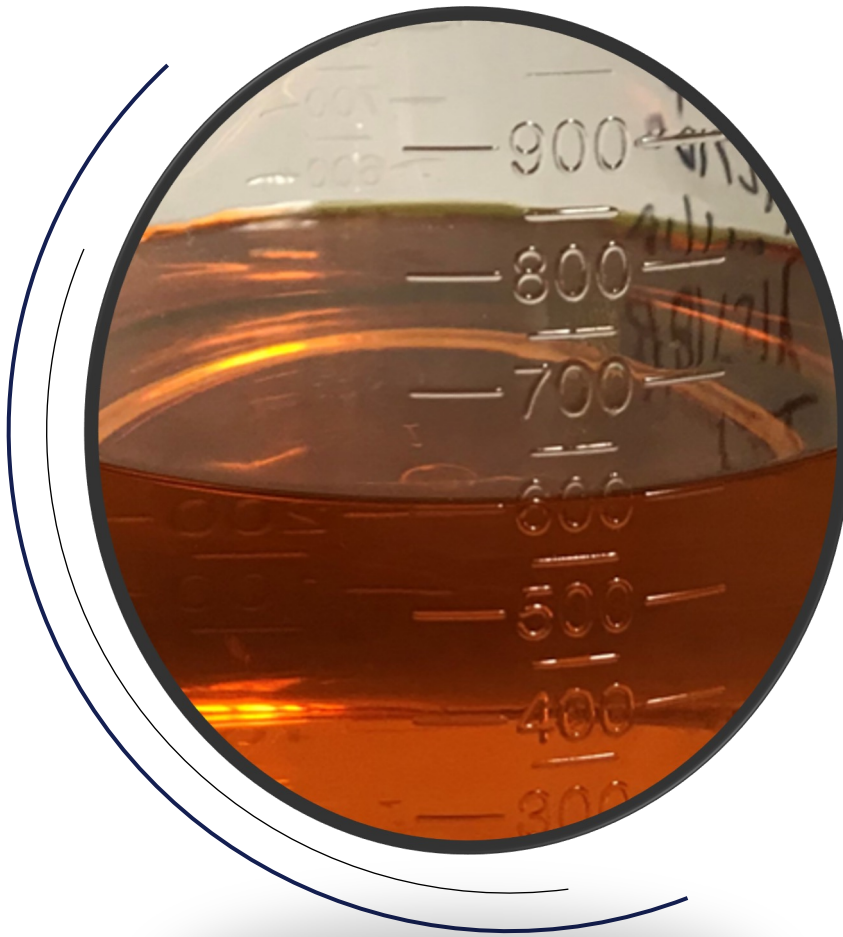
- HPLC
  - ✓ ASBC Hops-14 (314 nm), EBC 7.7 (314 nm)
    - ➢ Humulone
    - ➢ Cohumulone
    - ➢ Adhumulone
    - ➢ β-Acids

Hop Analysis: Isoalpha Acids

Isomerized Extract

- UV-Vis
  - ✓Maye, J. P., et al. *J. Am. Soc. Brew. Chem.* **2002**, *60*, 98.
    - ➢ Isoalpha Acids (255 nm)

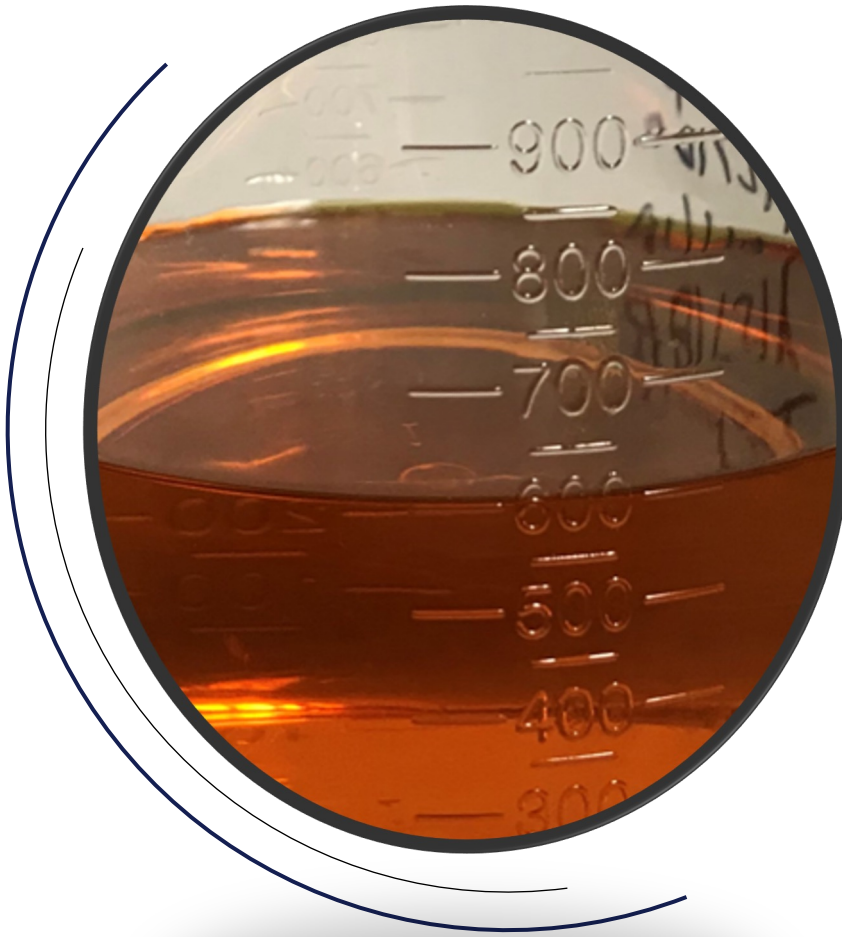




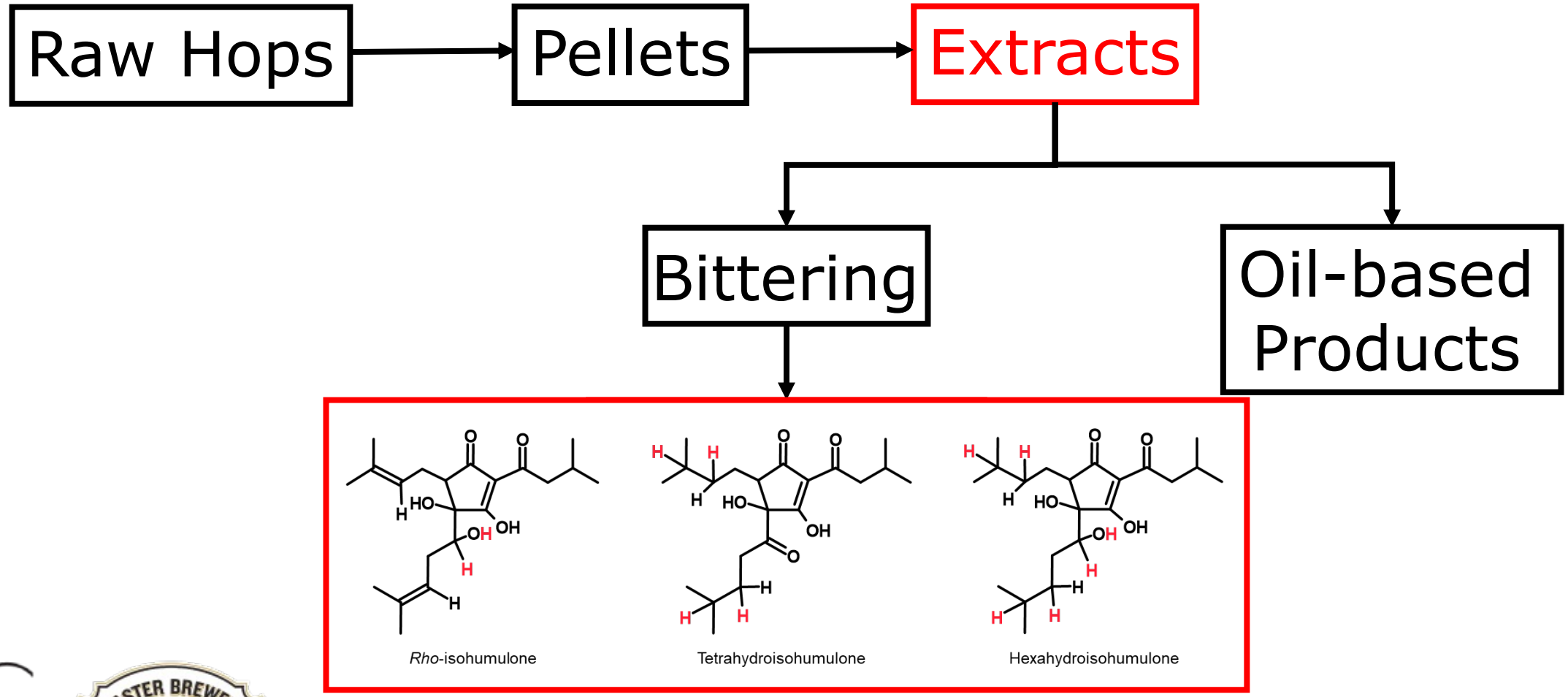
Hop Analysis: Isoalpha Acids

Isomerized Extract

- HPLC
  - ✓ ASBC Hops-9 (280 nm), EBC 7.9 (270 nm)
    - ➢ Isohumulone
    - ➢ Isocohumulone
    - ➢ Isoadhumulone
  - ✓ ASBC Hops-16, EBC 7.8 (314 & 280 nm)
    - ➢ Isohumulone
    - ➢ Isocohumulone
    - ➢ Isoadhumulone
    - ➢ Alpha Acids
    - ➢ Beta Acids



Hop Quality Control



Hop Analysis: Reduced Isoalpha Acids

Isomerized Light Stable Extract

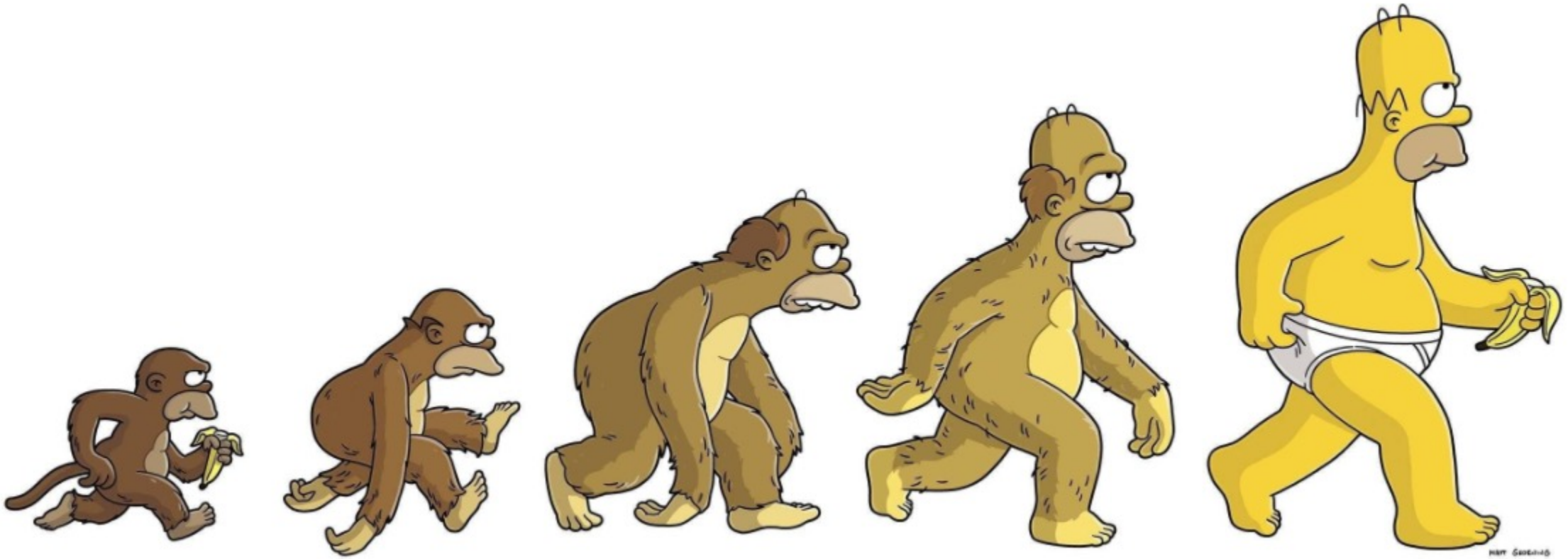
- UV-Vis
  - ✓ Maye, J. P., et al. *J. Am. Soc. Brew. Chem.* **2002**, *60*, 98.
    - ➢ *Rho*-isoalpha Acids (253 nm)
    - ➢ Tetrahydroisoalpha Acids (253 nm)
    - ➢ Hexahydroisoalpha Acids (253 nm)
  - ✓ ASBC Hops-18 (253 nm)
    - ➢ Tetrahydroisoalpha Acids

Hop Analysis: Reduced Isoalpha Acids

Isomerized Light Stable Extract

- HPLC
  - ✓ EBC 7.9 (270 nm)
    - ➢ Isoalpha Acids
    - ➢ Rho-isoalpha Acids
    - ➢ Tetrahydroisoalpha Acids
    - ➢ Hexahydroisoalpha Acids

Methods Evolution

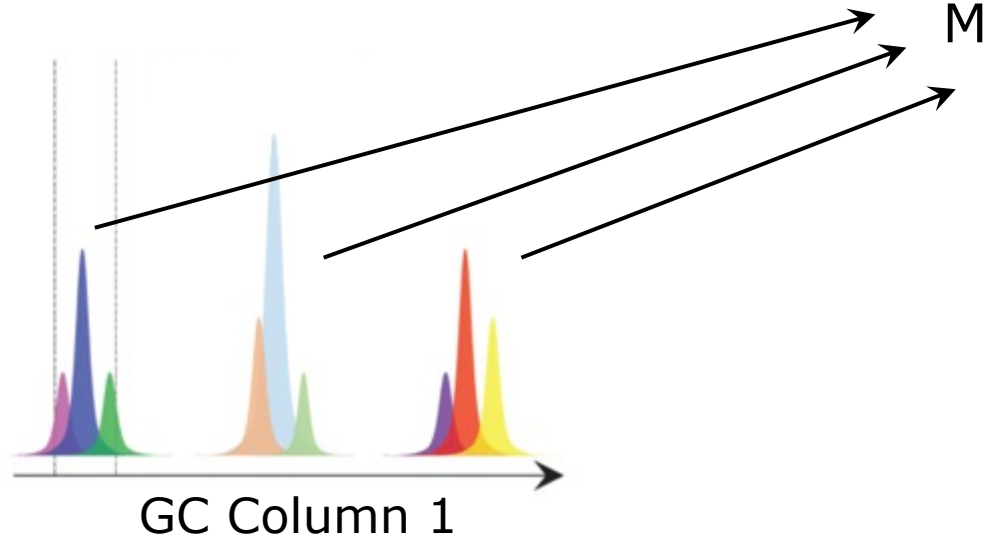


Hop Analysis: Aroma

GC-GC-Mass Spectrometry-Olfactometry (GC-GC-MS-O)

Hop Analysis: Aroma

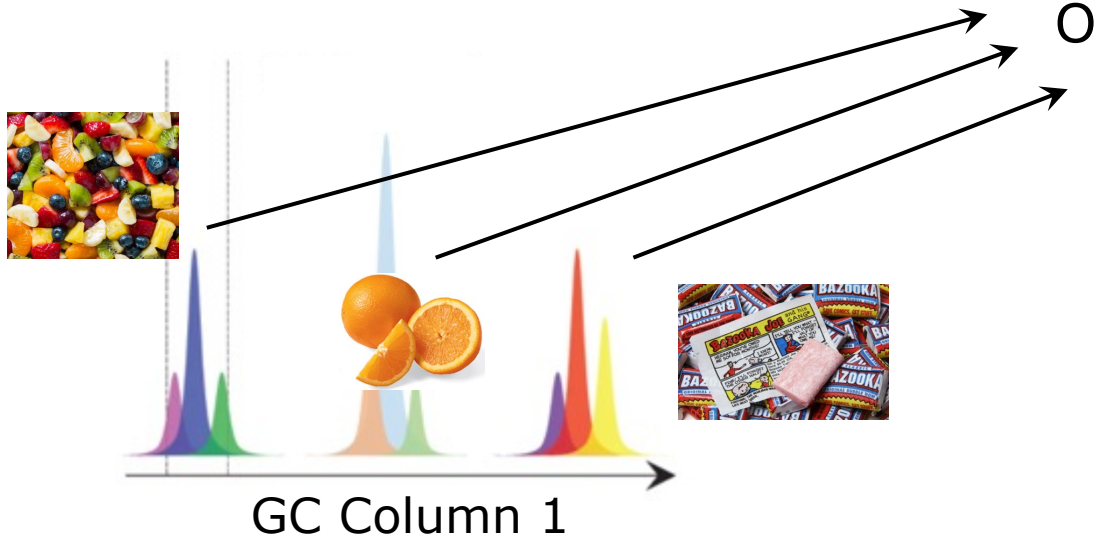
GC-Olfactometry (GC-O)



https://www.chromatographyonline.com/authors/dwight-r-stoll

Hop Analysis: Aroma

GC-Olfactometry (GC-O)

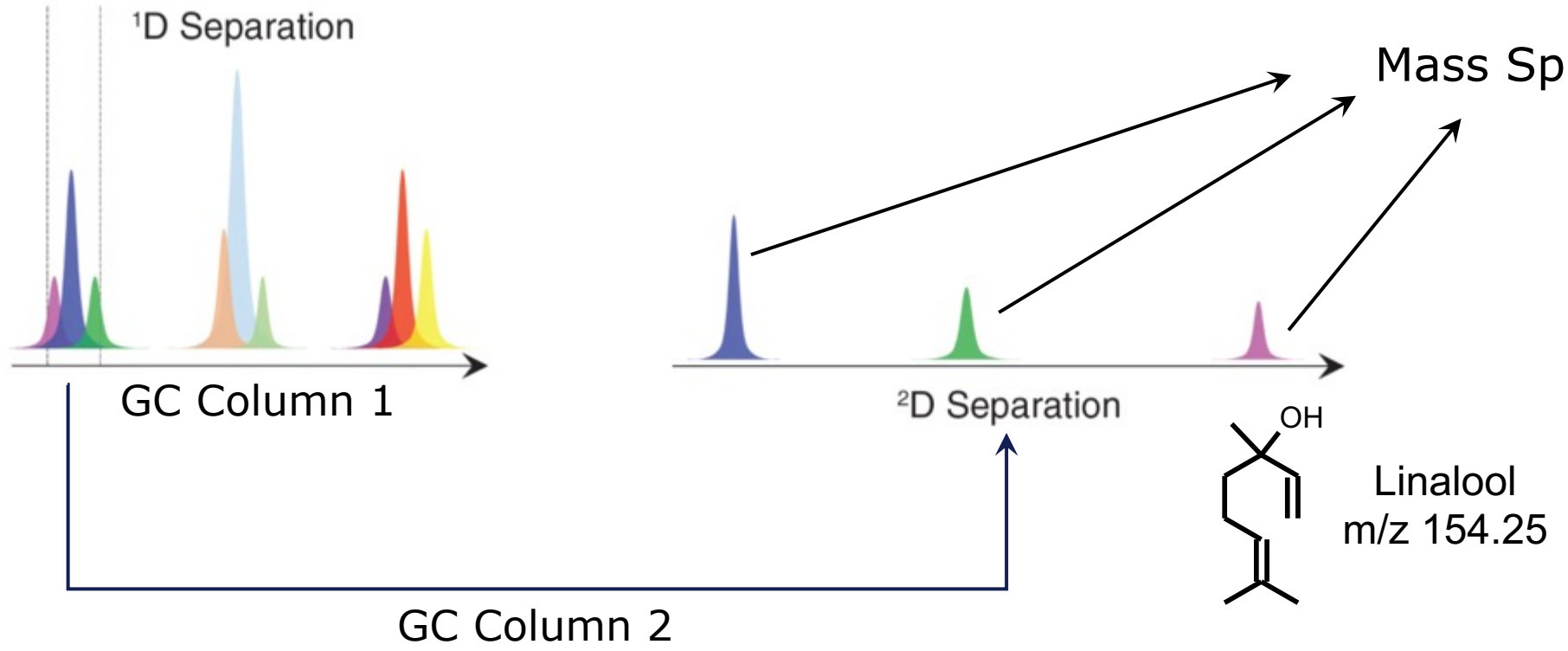


https://www.chromatographyonline.com/authors/dwight-r-stoll

Hop Analysis: Aroma

GC-GC-Mass Spectrometry-Olfactometry (GC-GC-MS-O)

- 2 Dimensional GC



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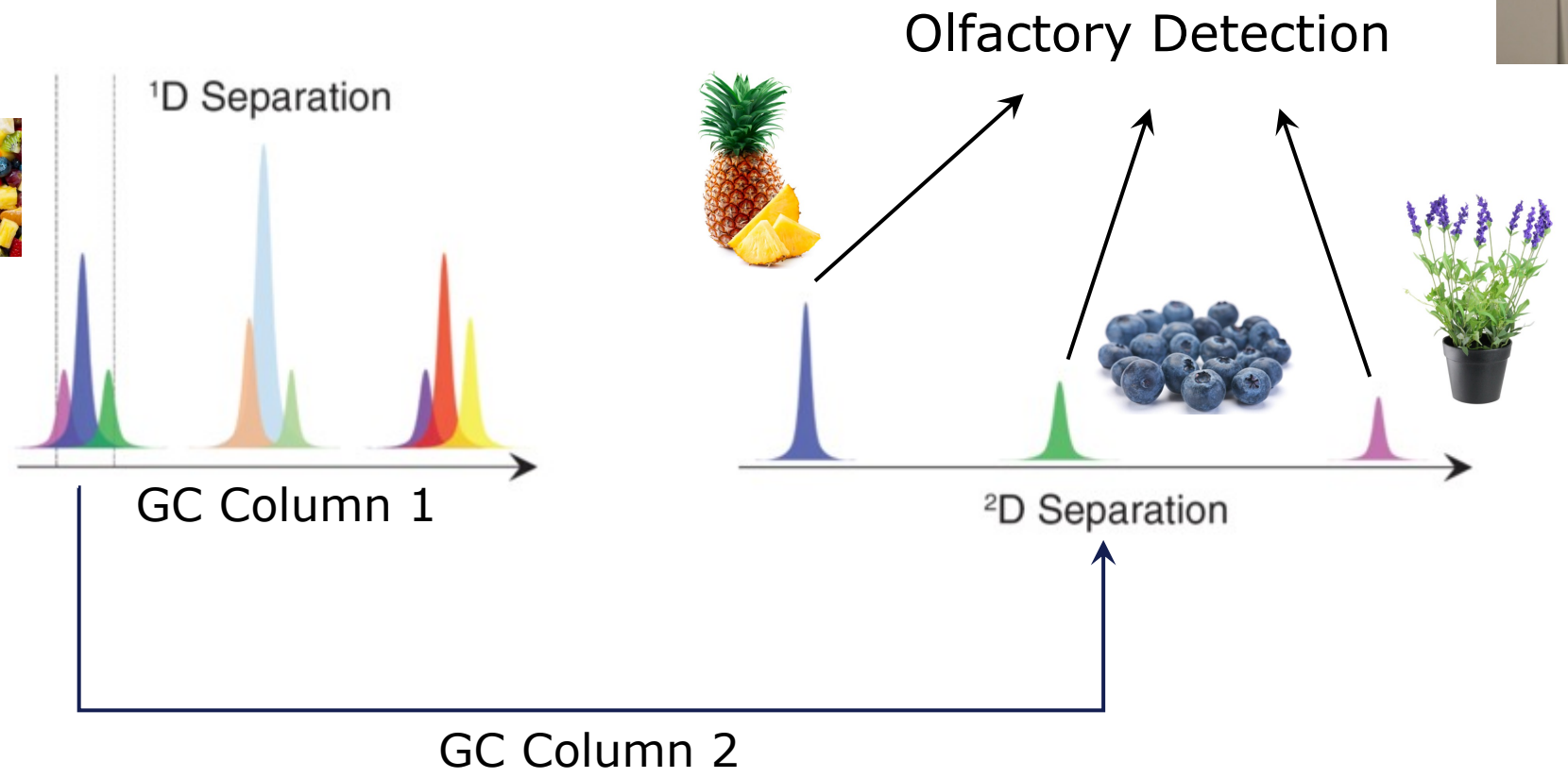
Hop Analysis: Aroma

GC-GC-Olfactometry (GC-GC-O)



https://www.chromatographyonline.com/authors/dwight-r-stoll

Summary

- Hops have rich chemical profiles
- Different ways to approach bitter and flavor compound analyses.
- Technology is continuing to evolve

Hop Storage Index (HSI): Influencing Factors

Mark Zunkel
BarthHaas

Outline

- Hop Storage Index (HSI)
- Background and analysis
- Variety Dependance
- Storage – bales and pellets
- Outliers
- Final words

Method to Analyse Hop Ageing

HSI is important to brewers as a quality indicator of hop harvesting, processing, handling, packaging and storage

- Spectrophotometric method (UV):
  - ASBC Hops 12 (6A)
  - EBC 7.13
  - MEBAK R-300.12.110
- α and β-acids → Max. 325 nm
- Degradation/oxidation of α and β-acids → Max. 275 nm

$$HSI = \frac{A_{275\,nm}}{A_{325\,nm}}$$

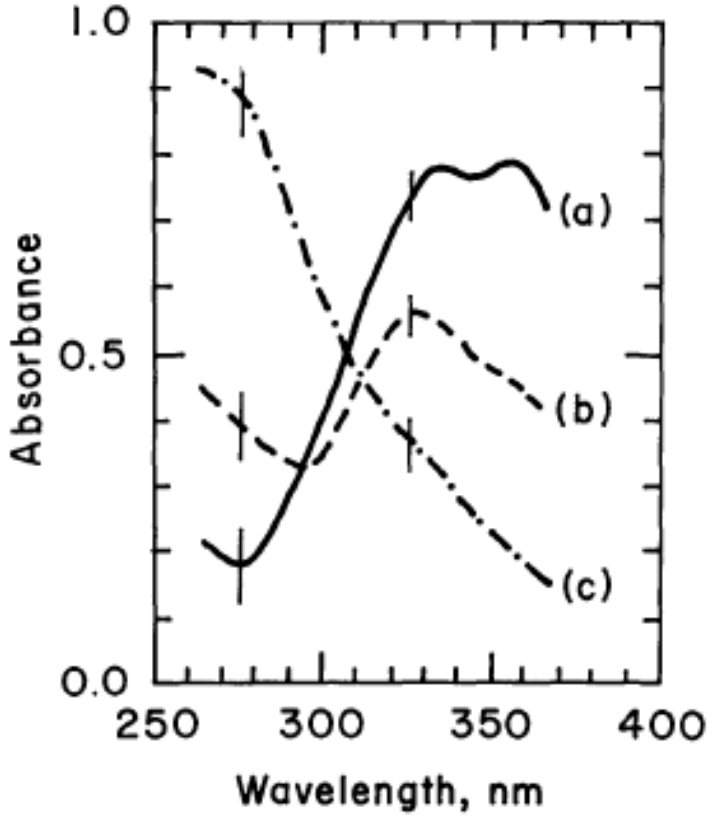


Fig. 1. Alkaline methanol spectra of α-acids and β-acids from lupulin: a, HSI = 0.25; b, HSI = 0.69, c, HSI = 2.44.

HSI Classification

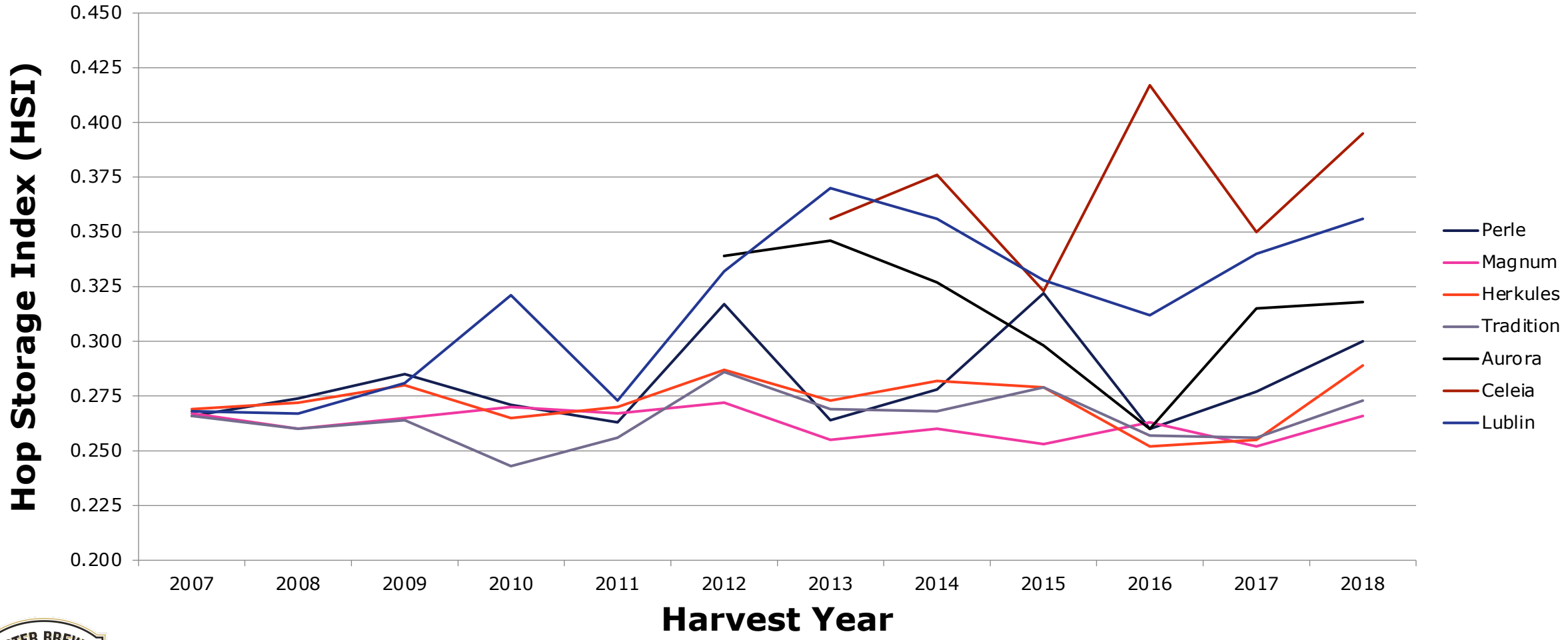
HSI	Transformation	Aging Degree
≤0.250	0	Very fresh
≤0.310	≤10%	Freshly picked
0.310-0.400	10-21%	Hops of normal storage and processing
0.400-0.500	21-31%	Old Hops
0.500-0.600	31-39%	Very old Hops
>0.600	>39%	Expired hops

Growing/harvesting conditions

Processing from whole cones to pellets

Storage until addition to brewing process

Harvest Year and Hop Variety Dependent



Hop Variety Dependent

Average, minimum and maximum of eleven hop varieties grown in the United States from 2009-2019.

	Ave.	Min.	Max
Cascade	0.239	0.188	0.363
Cenntenial	0.239	0.188	0.363
Chinook	0.263	0.213	0.412
Citra	0.271	0.224	0.351
Mosaic	0.266	0.236	0.316
Willamette	0.279	0.210	0.370
Zeus	0.269	0.226	0.406
Nugget	0.264	0.236	0.304
Summit	0.276	0.240	0.385
Columbus	0.269	0.223	0.374
Sabro	0.261	0.235	0.297

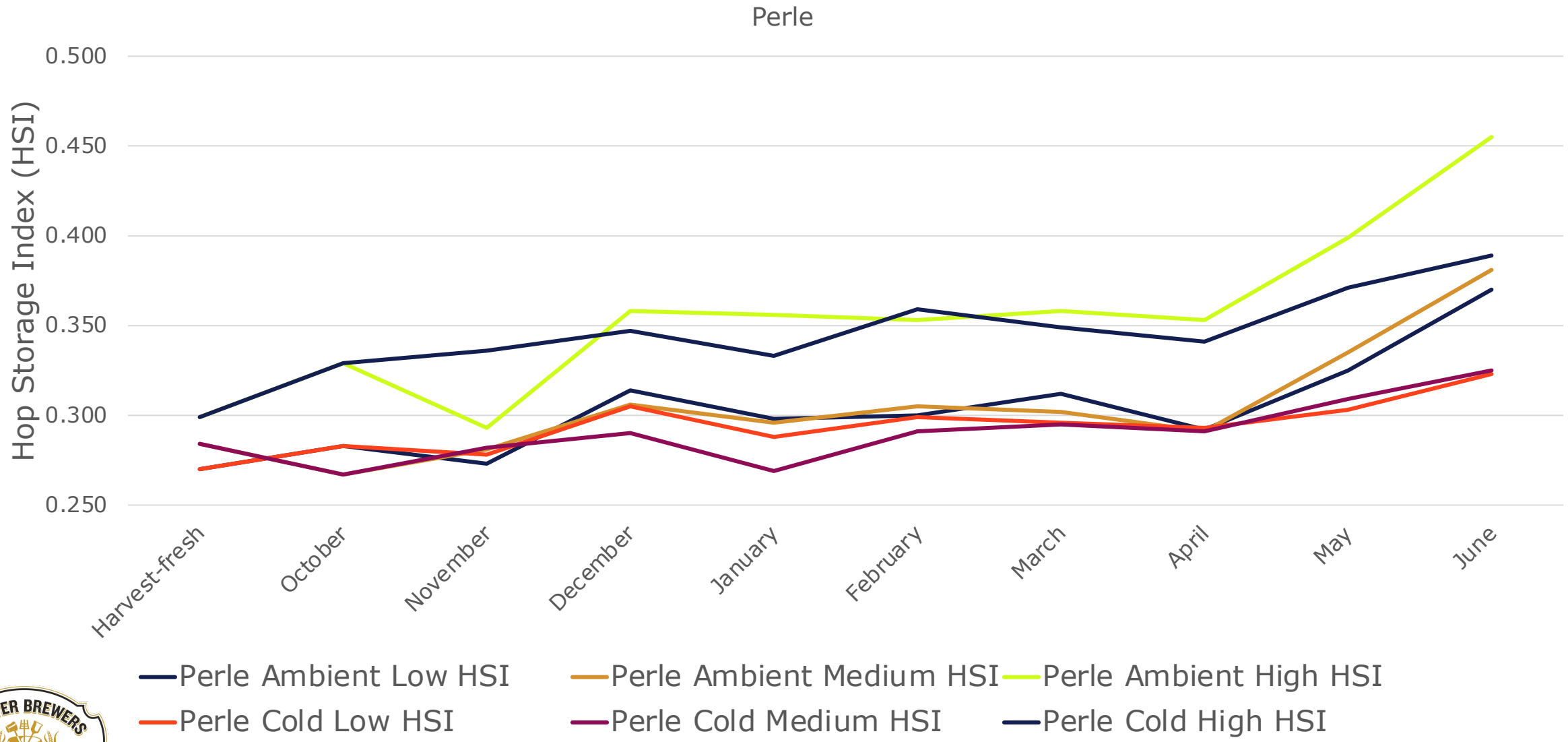
Average, minimum and maximum of sixteen European hop varieties from 2009-2019.

	Ave.	Min.	Max.
Hallertau Mittelfrüh	0.264	0.189	0.353
Hersbrucker	0.240	0.178	0.312
Tettnang Tettnanger	0.261	0.213	0.318
Spalter Select	0.273	0.192	0.348
Tradition	0.253	0.198	0.313
Saphir	0.291	0.219	0.366
Perle	0.275	0.227	0.350
Northern Brewer	0.288	0.239	0.361
Hallertau Magnum	0.259	0.232	0.324
Taurus	0.274	0.246	0.302
Herkules	0.267	0.238	0.309
Czech Saaz	0.286	0.208	0.391
Aurora	0.317	0.250	0.358
Celeia	0.374	0.272	0.575
Lubliner	0.319	0.215	0.413
Marynka	0.316	0.258	0.401

HSI during storage - Bales

- Packaged in woven polypropylene bales
- Oxygen permeable
- Storage at cold temperatures remain stable

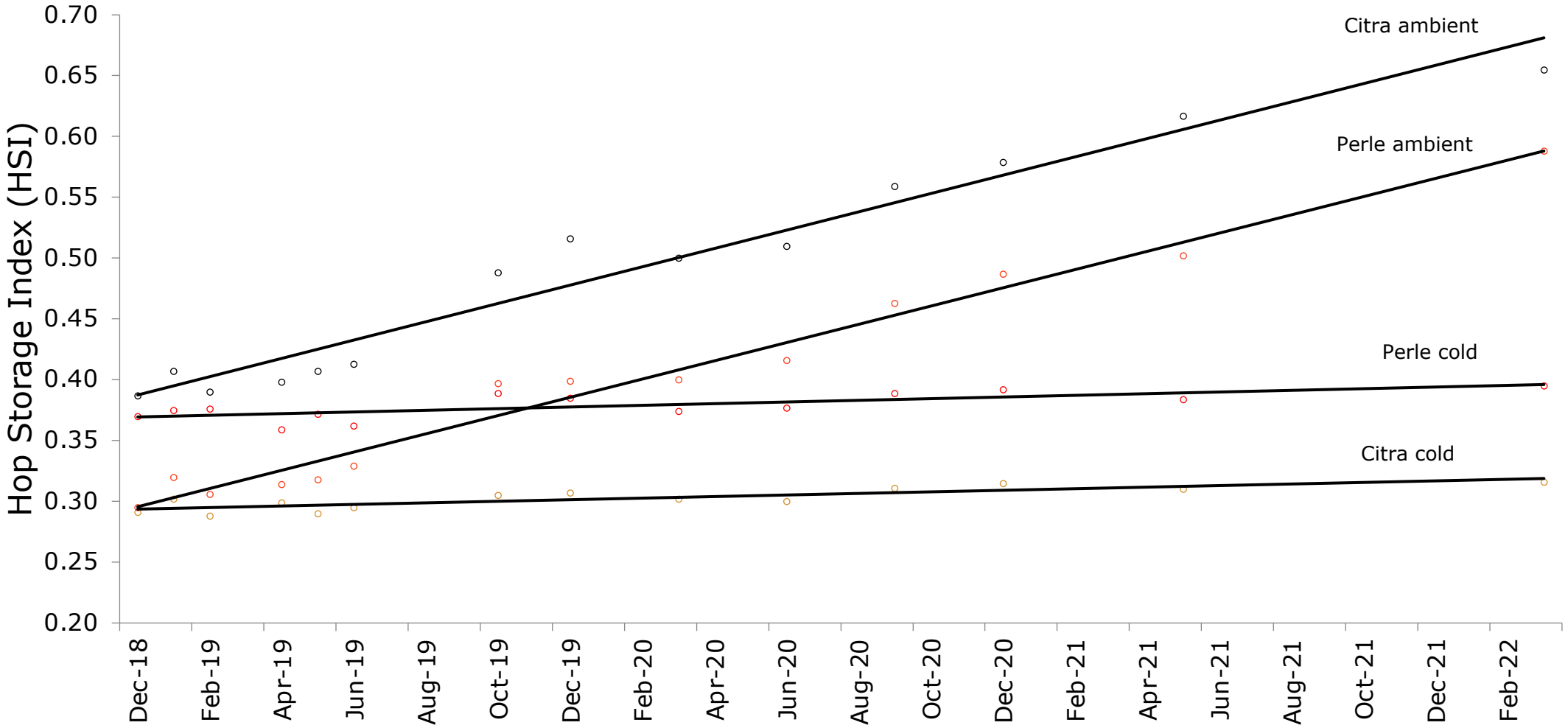
Storage of Bales



HSI of packaged pellets

- Storage in inert gas (CO_2 and/or N_2)
- Very low oxygen content (<2%) in soft packs
- Degradation of aroma and bitterness compounds
- Cold temperatures keep valuable components stable

Storage pellets over three years



Degradation over time

- Aged hops ≠ Poor HSI

Saaz	2008	2018
EBC 7.5	4.0%	3.7%
ASBC	3.6%	3.1%
HSI	0.340	0.380

7.5-14% alpha loss over 10 years

- Cold storage

Perle	1999	2016
EBC 7.5	10.0%	8.0%
ASBC	-	6.0%
HSI	-	0.525
Oil	-	1.45 ml/100 g

20% alpha loss over 17 years

Outlier – Celeia/Styrian Golding

	2013	2014	2015	2016	2017	2018	2019	2020
Average	0,356	0,376	0,308	0,424	0,385	0,425	0,348	0,327
Median		0,341	0,305	0,454	0,378	0,409	0,350	0,322
Minimum		0,330	0,272	0,299	0,310	0,311	0,320	0,295
Maximum		0,479	0,350	0,540	0,520	0,575	0,370	0,349
Number of samples	1	5	10	17	29	24	5	5
	Average 2013-2020						0,369	

How can we use HSI for hop quality?

- Traditional HSI classification not valid for all hop varieties
- Quality of a hop variety can not be determined based on one measurement
- Two measurements are necessary for determining the age of a hop

Green that's Gold

Basics of Sensory, Methods, and Strategies for Selection

ASBC

MASTER BREWERS ASSOCIATION OF THE AMERICAS EST 1887

Sensory Elements of Selection

- Preparation Ahead of Time
  - Training your selection team
  - Establishing your target profile
- The Actual Selection
  - Scheduling
  - What to look for
  - Strategy
  - Methods of Evaluation
- How we select at Haas with Sensory Plus (and how it applies to you)

I WANT YOU… TO PICK THE BEST HOPS

Preparation Ahead of Time

- Training is Key!
  - Raw material sensory ‘hits’ differently than beer sensory
    - Ex. Myrcene is 30-60% of hop oil in whole cone/pellets but <1% of the residual hop oil in beer (below sensory threshold)
    - Whole Pellet and Hop Grind (ASBC Sensory-16)
  - An agreed upon sensory lexicon is a must!
    - Does every decision-maker understand what “intensely fruity” means?
    - Is “fruity” sufficiently descriptive to differentiate between quality lots?

CHECK THE STANDARDS IN FRONT OF YOU!!

What is this even?!

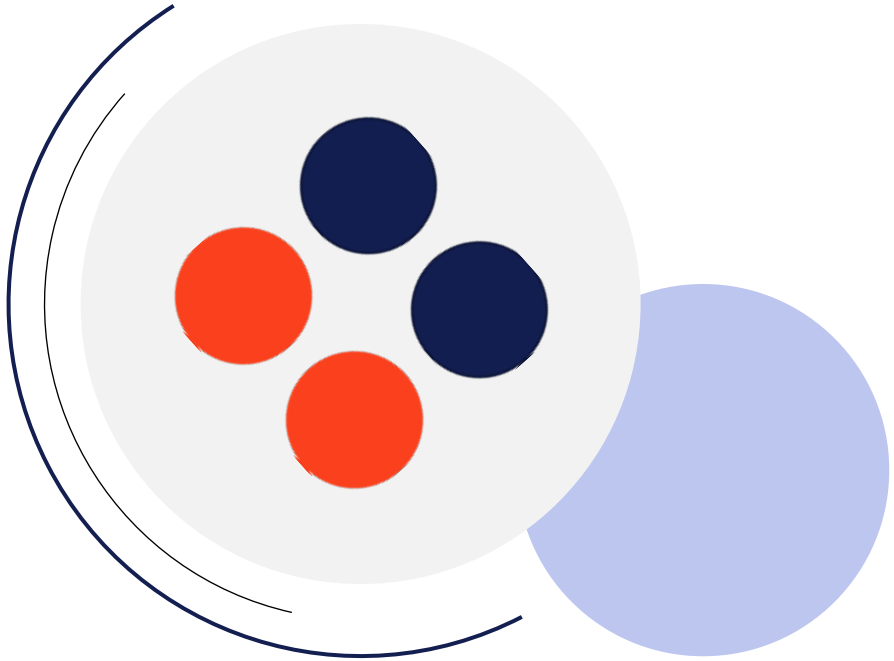
Training Your Selection Team

Make sure you're all speaking the same language!

- Do you know what your brewer means when they describe Citra as, "the best, new vinyl shower curtains"?
- Choose terms that are common enough to be accessible, but specific enough to not be redundant – or choose an existing lexicon like 'Hopsessed,' ASBC Sensory-12, or DraughtLab
- Train with standards – my 'floral' is not the same as yours!

This is a 'Dank'-Free zone

Validating Your Selection Team



Can your team discriminate and describe *consistently?*

- Cascade vs Sabro (easy)
- Cascade vs Mosaic (easy)
- Cascade vs Citra (easy)
- Cascade vs CTZ (easyish)
- Cascade vs Centennial (slightly harder)
- Centennial vs Citra
- CTZ vs Citra
- Citra vs Mosaic
- Citra lot 1 vs Citra lot 2 (etc…)

Setting a Target

- Know your brand and required volumes
- Define your expectations for quality ***objectively***
- How you use the hop impacts how narrowly selected lots must comply with the target

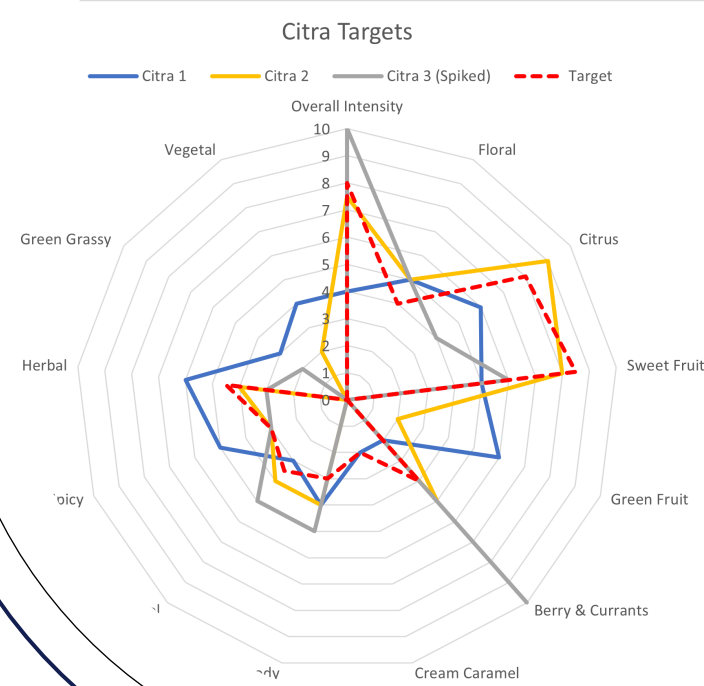
Kettle/Bittering ↑ Less Critical

Kettle/Whirlpool/Flavor Addition

Dry Hop ↓ More Critical

Types of Targets

Hop	Floral	Citrus	Sweet Fruit	Green Fruit	Berries & Currant	Woody Aromatics	Herbal	Green-Grassy	Vegetal
WHP Citra	6	4	2	3	3	4	4	5	2
DH Citra	4	6	7	0	4	4	0	3	5
Unacceptable Citra	3	9	5	0	5	3	6	0	9
WHP Mosaic	5	4	5	2	5	4	4	6	3
DH Mosaic	5	8	7	0	7	5	4	4	3
Unacceptable Mosaic	2	3	6	0	9	6	8	3	6
WHP Cluster	8	3	2	4	3	6	2	4	4
DH Cluster	4	3	8	2	6	6	4	4	5
Unacceptable Cluster	0	6	1	2	3	3	5	4	8



Citra – ***Strong*** Lime, Orange; ***Strong-Moderate*** Stone Fruit, Mango; ***Moderate-Low*** Floral, Catty; ***Low*** Vegetal, Resin

1 THE SELECTION

Visual Quality

- Don’t judge a hop by its cover
- “Green is Gold” is too simplistic – many varieties like Ekuanot and Comet are yellow as are hops from Oregon
- Evaluate: Mold, mildew, windburn, and the color of the lupulin

Know what you're looking at…

Idaho Citra –

Oregon Citra –

Washington Citra –

Washington Citra –

Know what you're looking at…

Idaho Citra –
Sample Arrived Sept 15
Intensity: 9/10
Profile: Intense Black Currant (Catty), Strong Lime Zest, Grapefruit, Peach Fuzz and Flesh, Slight Grassy

Oregon Citra –
Sample Arrived Sept 12
Intensity: 10/10
Profile: Intense Lime Flesh, Subtle Grapefruit, Moderate Green Mango, Passion Fruit

Washington Citra –
Sample Arrived Sept 15
Intensity: 7/10
Profile: Strong Citrus Zest, Black Currant (Catty), Moderate Sweaty Tropical Fruits, Fresh Pine Needles

Washington Citra –
Sample Arrived Sept 18
Intensity: 8/10
Profile: Intense Sweet Fruit, Ripe Melon, Stone fruits, Moderate Lemon/Orange Zest, Slight Grassy

Sweet Caroliiiinnnee…. (ba ba ba)

- After looking, you do actually need to *reach out* and *touch* the cones.
- Use the whole sample cup!
- Gently press the cones into the table – they should be slightly springy
- But also, you need to rub the hops…

Physical Quality

- Listen too your hands
- Slowly grind a palm’s full of hops back-and-forth
- How spongy, hard, silky, or dusty do the hops feel?
- Rubbing more vigorously, do they turn to dust or do they roll up like wet rags?
- Hops should put up some resistance but *eventually* (after 4-5 rubs) yield and pull apart

Sensory Quality

- Look for what you need, not what you want
- Gentle sniffs on the whole and slightly ground cone gives a good evaluation for intensity and presence of macro defects
- A deeper evaluation of fully ground cones will reveal the nuances and overall character
- But! Hop and beer sensory are not equivalent

Beer – Hop Sensory Correlations

BEER

HOPS	OHAI	Floral	Citrus	Sweet Fruit	Green Fruit	Berry & Currant	Cream Caramel	Woody Aromatic	Menthol	Herbal	Spicy	Green-Grassy	Vegetal	Liking
OHAI	0.85	-0.25	0.71	0.78	-0.15	0.71	0.17	0.10	-0.02	-0.22	0.58	0.15	0.83	0.77
Floral		0.36	0.33	0.09	0.44	-0.35	0.02	-0.33	0.34	-0.13	-0.39	0.39	-0.53	0.22
Citrus			0.42	0.90	0.66	0.27	-0.19	0.29	-0.12	-0.02	0.42	0.26	0.62	0.73
Sweet Fruit				0.55	0.35	0.85	0.30	0.04	0.32	0.04	0.45	0.26	0.64	0.73
Green Fruit					0.50	0.26	0.07	-0.51	0.23	0.14	-0.26	0.20	-0.11	-0.11
Berry & Currant						0.77	0.32	0.19	0.34	0.25	0.55	0.04	0.80	0.45
Cream Caramel							0.55	0.57	0.58	0.52	0.14	0.72	0.33	0.44
Woody Aromatic								0.67	0.43	0.46	0.37	0.23	0.36	0.26
Menthol									0.45	0.71	0.32	0.48	0.14	0.35
Herbal										0.21	0.48	0.42	0.08	-0.09
Spicy											0.55	0.22	0.55	0.47
Green-Grassy												0.04	0.08	0.51
Vegetal													0.41	0.49
Liking														0.87

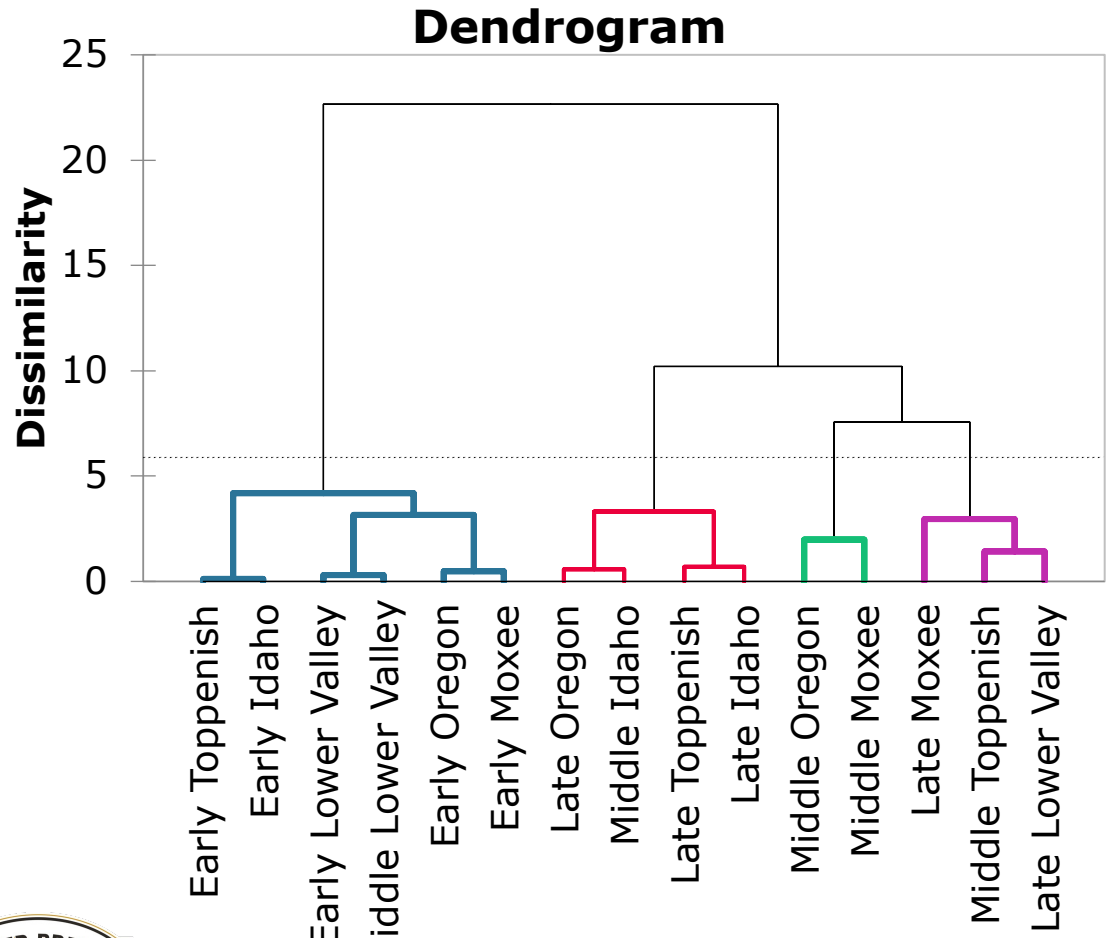
*For a competent discussion on this matter, come to Dr. Marshall Ligare's presentation tomorrow during Ingredients II

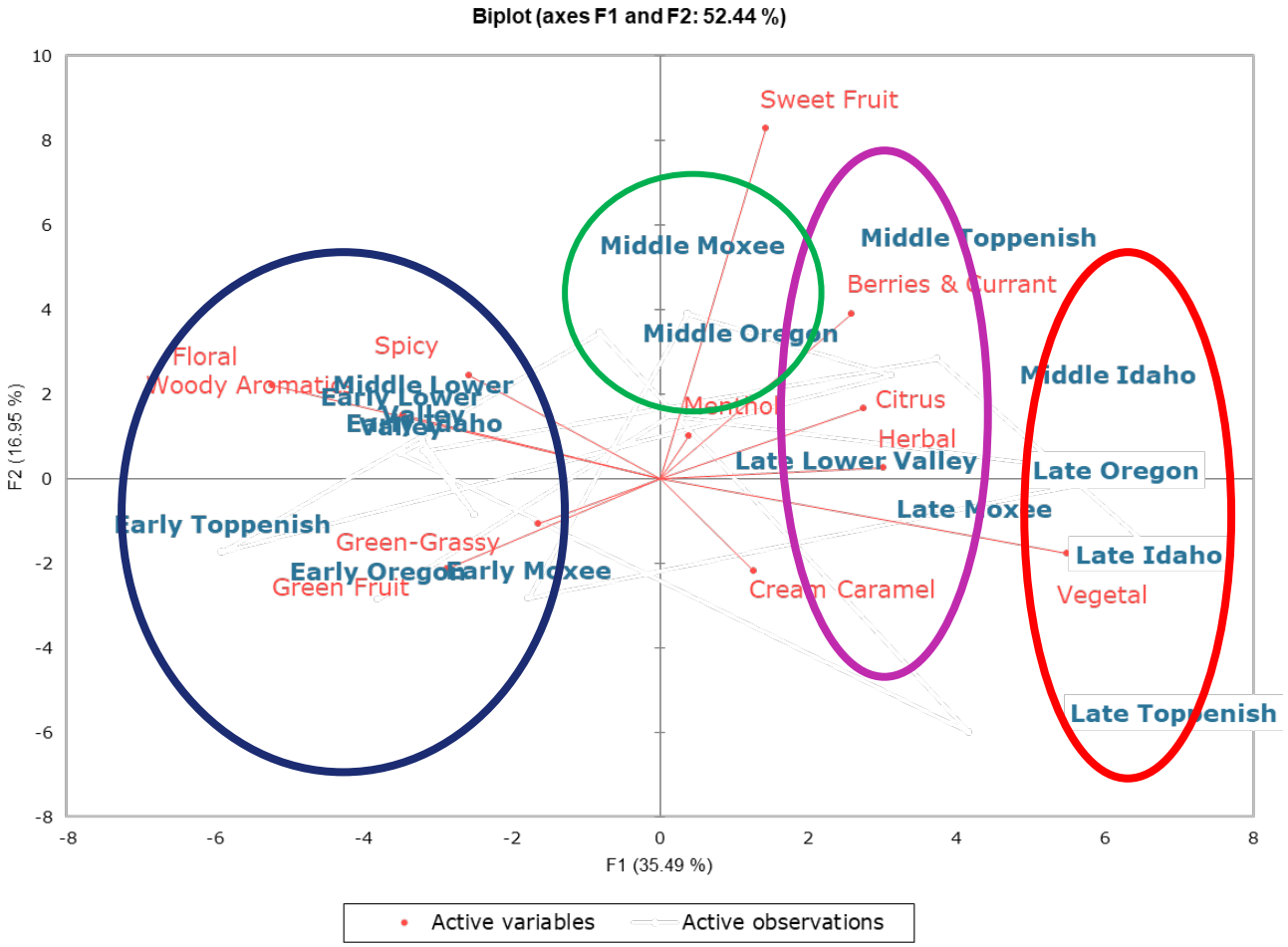
Collect Data!

- Choose a system and stick with it year-over-year
- As you evaluate, focus on your **TARGETS** rather than your interest/liking
- Going with the firey-est Mosaic in the whole cone will only lead to vegetal heart-ache in the pellets
- Using blinded data helps you overcome the ‘loudest voice in the room’

Just do it!

But why collect all these data?



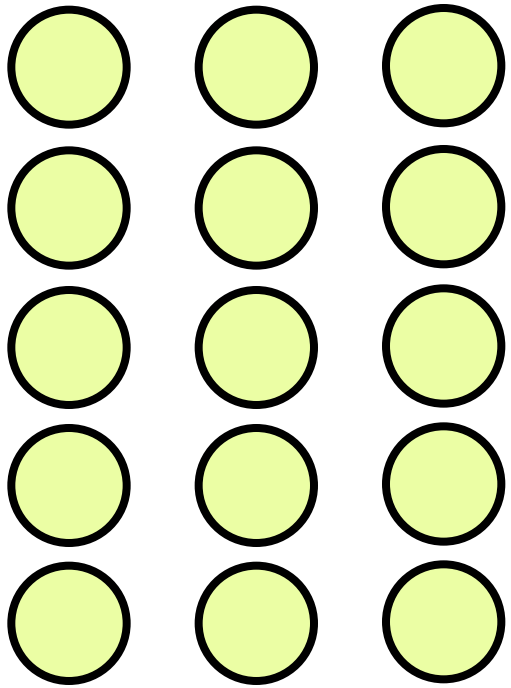


Sensory Plus - Selection process

HARVEST INTAKE

SELECTION

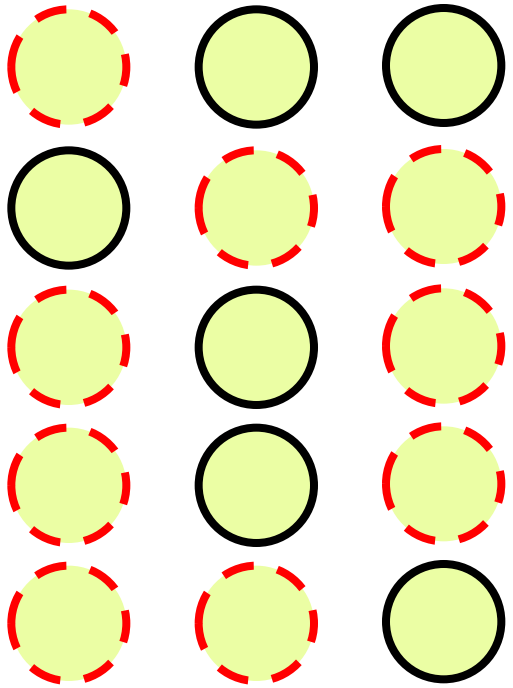
SENSORYPLUS RE-SCREEN/BUILD BLEND



Example: Fifteen lots of Citra are received during intake. At least four are needed for previously established allocation of Citra LUPO**MAX**

Sensory Plus - Selection process

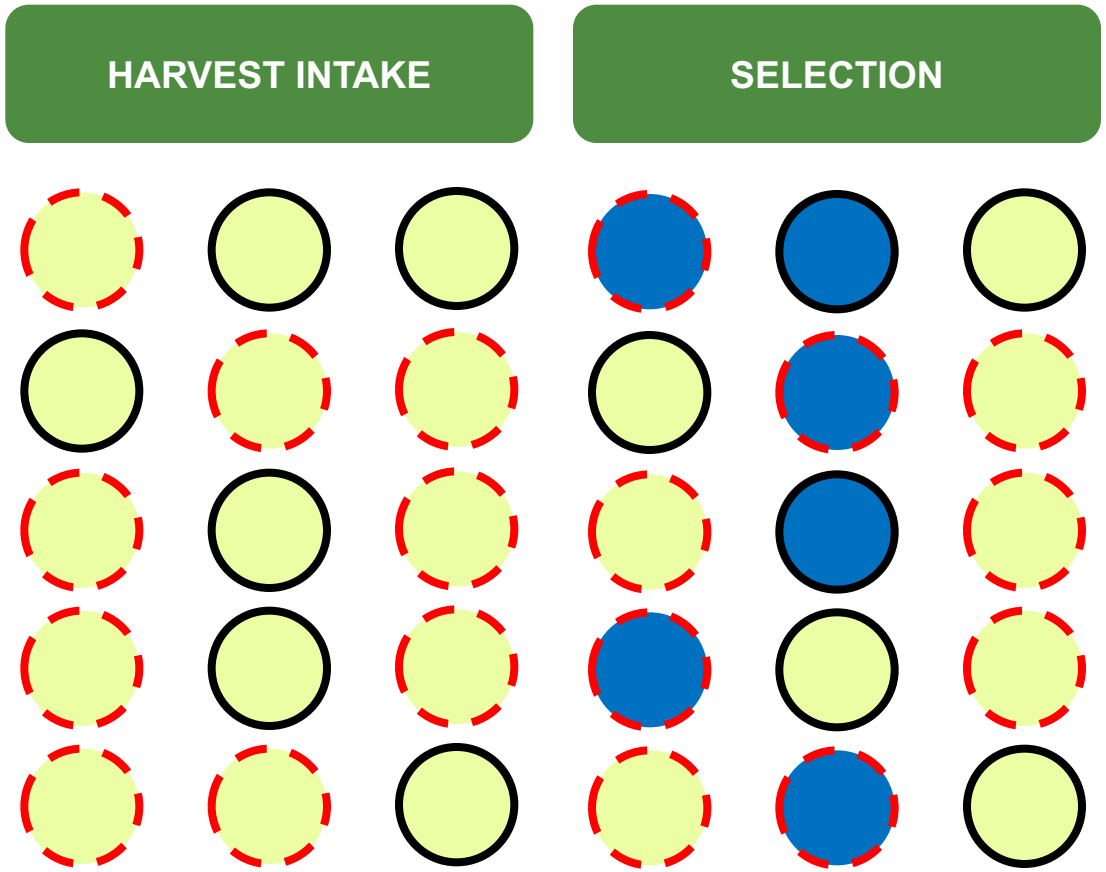
HARVEST INTAKE | SELECTION | SENSORYPLUS RE-SCREEN/BUILD BLEND



Based on sensory evaluation during intake all potential LUPO**MAX** candidates are flagged (red).

All lots are presented to customers for Selection to prevent negative perceptions regarding “stealing” the best lots for LUPO**MAX**.

Sensory Plus - Selection process

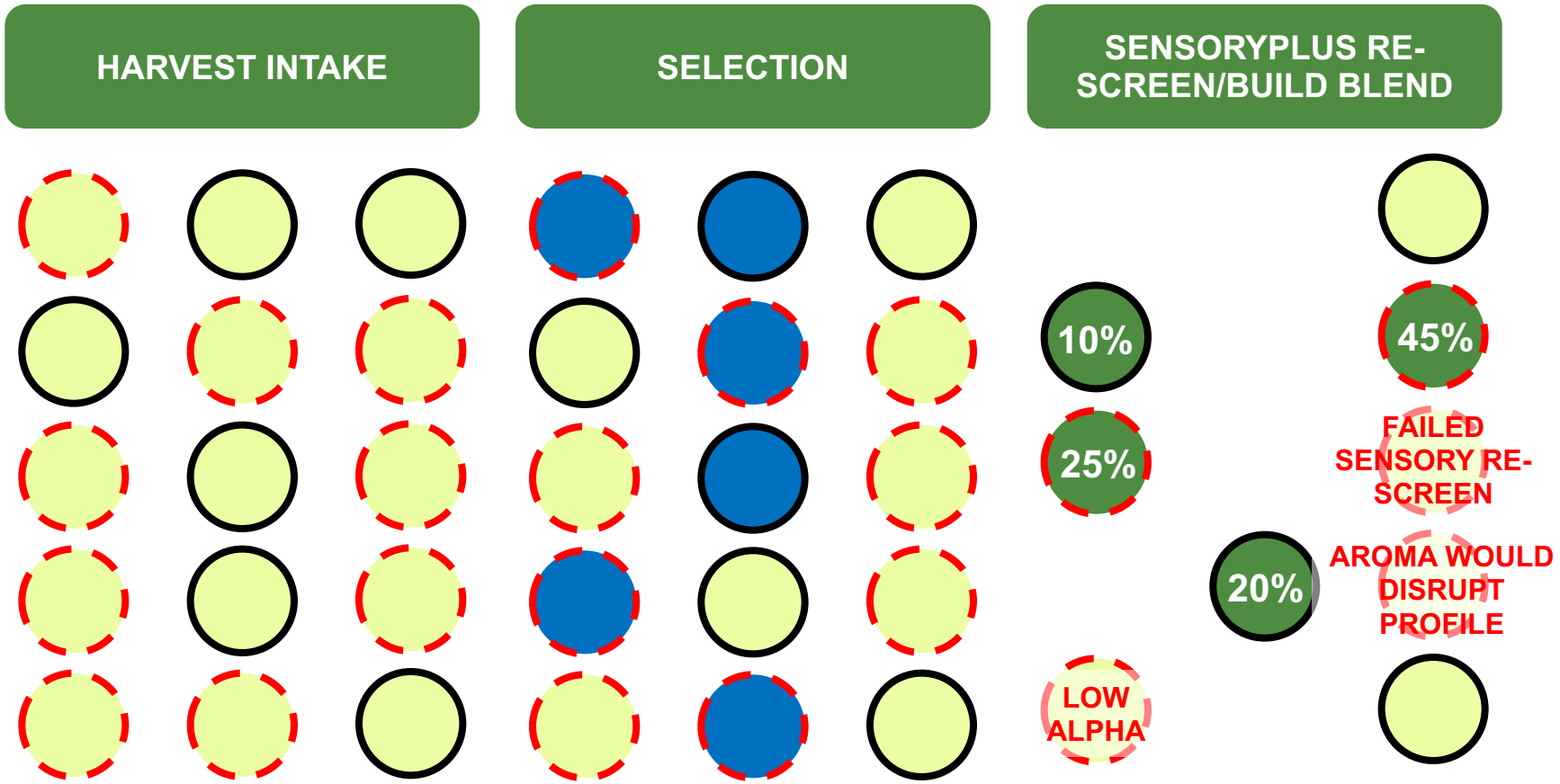


Customers selected (blue) six of the 15 lots, including half of the flagged lots.

New bale samples are cut for SensoryPLUS rescreening based on initial sensory.

Technical specifications are provided by QC.

Sensory Plus - Selection process



In the end

- There are a lot of options regarding how to approach a selection scenario –
- Experience is hugely important, but having a strong plan when you're new will give you a leg-up
- Consistent training and re-training are **KEY!**
- It doesn't take a lot of investment (relatively speaking) to get huge dividends in improved quality

We literally want you to be satisfied with your hops

Let’s do this

Centennial




Centennial is typically described as having a "strong citrus and fruity" character with notes of "Orange," "Lime," "Cherry," "Floral," and "Pine Resin."

	Typical	Today's Sample
Alpha %	9.5 - 11.5	9.48
Beta %	3.4 - 4.5	3.4
HSI	0.275 - 0.31	0.318
Total Oil (mL/100g)	1.5 - 2.5	1.8

Cashmere

Cashmere is typically described as having a "strong citrus and sweet fruit" character with notes of "Lemon," "Lime," "Ripe Melon," "Stone Fruit," and "Thyme."

	Typical	Today's Sample
Alpha %	7.7 - 9.1	6.89
Beta %	3.5 - 4.5	6.61
HSI	0.25 - 0.265	0.274
Total Oil (mL/100g)	1.2 - 1.4	0.8

Citra

Citra is typically described as having a "strong citrus and tropical" character with notes of "Grapefruit," "Lime," "Mango," "Passionfruit," "Generic Floral" and "Sweaty" or "Catty"

	Typical	Today's Sample
Alpha %	11.0 -13.0	14.1
Beta %	3.4 - 4.5	3.69
HSI	0.25 - 0.281	0.327
Total Oil (mL/100g)	2.2-2.8	2.5

HBC 586

HBC 586 is typically described as having a "tropical, citrus, and slightly spicy" character with notes of "Mango," “Guava” "Lychee," and "Mandarin Orange," "Berry Jam," and "Fresh-Cut Serrano Peppers.”

	Typical	Today's Sample
Alpha %	12.0 - 13.0	11.46
Beta %	7.5 - 8.5	7.29
HSI	0.26 - 0.28	0.318
Total Oil (mL/100g)	1.2 - 2.5	1.8


Q&A