



TRACKING HOP AROMA COMPOUNDS WITHIN HOP VARIETIES AND BEER

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PRESENTATION OVERVIEW

- Hop Aroma Compounds
- Hop Aroma Compound Extraction and Analysis Techniques
- Analysis Instrumentation for 2018 Harvest
- 2018 Harvest Hop Aroma Data
- Beer Analysis Data
- Conclusions
- New Analysis Instrumentation for 2019 Harvest



CURRENTLY REPORTED

- Total oil 0.5 – 3.0% reported as ml/100 g
- Reported as % Area of Chromatogram
 - Qualitative representation of the oil composition by GC
 - β -Pinene – 0.1-2.0%
 - Myrcene-most abundant 20-60%
 - Linalool – 0.1 – 1.0%
 - Caryophyllene – 5-20%
 - Humulene- 5-20%
 - Farnesene – 0-10%
 - Geraniol – 0.1-1.0%

HOP AROMA

- Total Oil Content in Hops 0.2 - 3%
- Hop Aroma
 - Perceived Hop Aroma depends on oil composition
 - Hundreds of compounds contribute to hop aroma
 - Factors that affect hop aroma composition
 - Variety (genetics)
 - Growing Region
 - Agronomics
 - Ripeness
 - Kilning
 - Processing
 - Storage

HOP AROMA IN BEER

- Hop aroma perceived in beer is not the same as hop aroma perceived in hops
- Factors that affect extraction of hop aroma compounds in beer include:



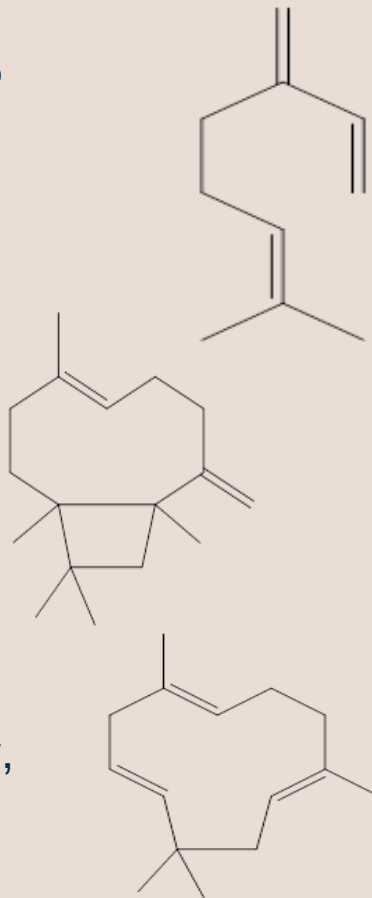
- Contact with the liquid
- Chemical Structure of the Hop Compound
 - Polar and nonpolar
- When the hop addition occurs
 - Kettle
 - Late kettle or whirlpool
 - Dry hopping
- Beer Style
 - Yeast
 - pH
 - Gravity
 - Alcohol
 - Haze
 - Temperature

COMPOSITION OF HOP AROMA

- Nonpolar compounds – Hardest to extract
 - Terpenes (Hydrocarbons) 80% of hop aroma
 - Monoterpenes (C10's)
 - Sesquiterpenes (C15's)
 - Aliphatic Hydrocarbons <1% (straight chains nonaromatic rings)
- Polar compounds – Easier to extract
 - Esters 15%
 - Carboxylic acid 1%
 - Terpene Alcohols 1%
 - Sesquiterpene Oxides 1%
 - Aldehydes and Ketones 1%
 - Thiols (sulfur containing compounds)

MAJOR TERPENES

- Monoterpenes
 - Myrcene (most abundant in hops)
 - Aroma profile: herbal, spicy, geranium, woody, carrot
- Sesquiterpenes
 - β -Caryophyllene
 - Aroma profile: cedar, spicy, floral, turpentine
 - Humulene
 - Aroma profile: grassy, floral, spicy, woody, herbal



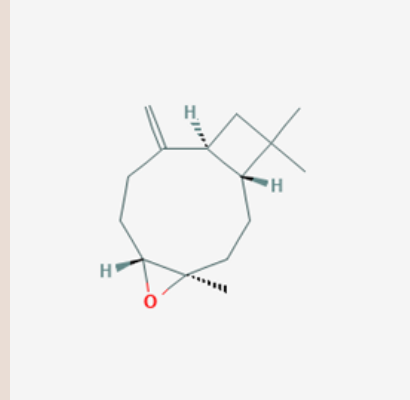
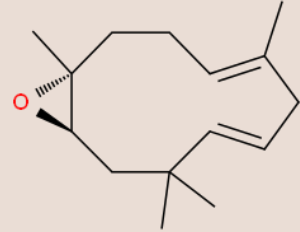
Dry Hopping extracts these compounds (pine, woody)

Late kettle and whirl pool very small amounts survive, some evaporate, some convert/oxidize to other compounds.

Lost in fermentation, from CO₂ Scrubbing or lost in biomass

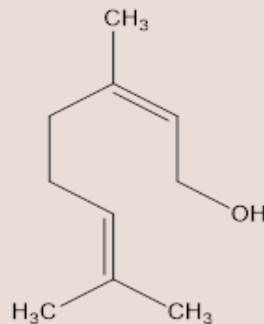
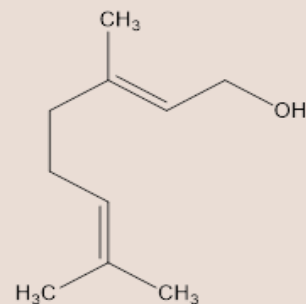
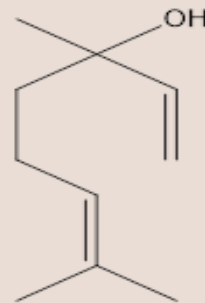
SESQUITERPENE OXIDES

- Humulene Oxide
 - Aroma profile: musty, floral, spicy, woody, herbal
- Caryophyllene Oxide
 - Aroma profile: musty, floral, spicy, woody, dry
- Both compounds form during hop storage and are a sign of oxidized hops
 - Late kettle, whirl pool additions and dry-hopping known to bring spicy or noble character to beer



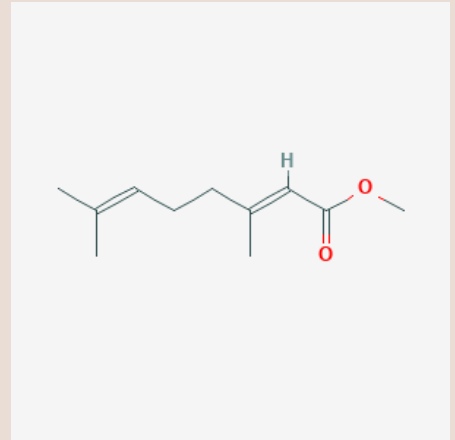
TERPENE ALCOHOLS

- Linalool
 - Aroma profile: floral, fruity, citrus, sweet
 - First hop oil discovered in beer
 - Survives the brewing process – kettle, whirl pool and dry hopping
- Geraniol
 - Aroma profile: geranium, floral, lemon, lime
 - Survives the brewing process
 - Involved in biotransformation
- Nerol
 - Aroma profile: floral, lemon, lime

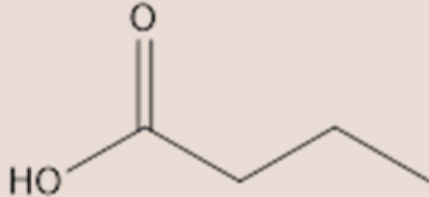


ESTERS AND CARBOXYLIC ACIDS

- Esters-Third most abundant compounds in hops 15%
 - Aroma profile: fruity
 - Methyl geranate
 - Survive brewing process, but can thermally degrade

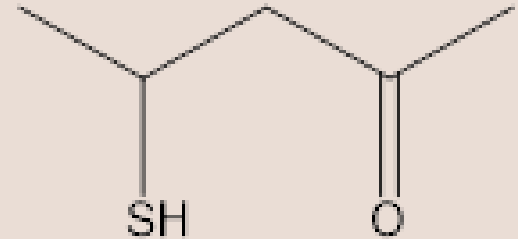


- Carboxylic acids
 - Aroma profile: cheesy
 - Butanoic acid
 - Can survive brewing process, but during fermentation can be turned into ethyl esters



THIOLS

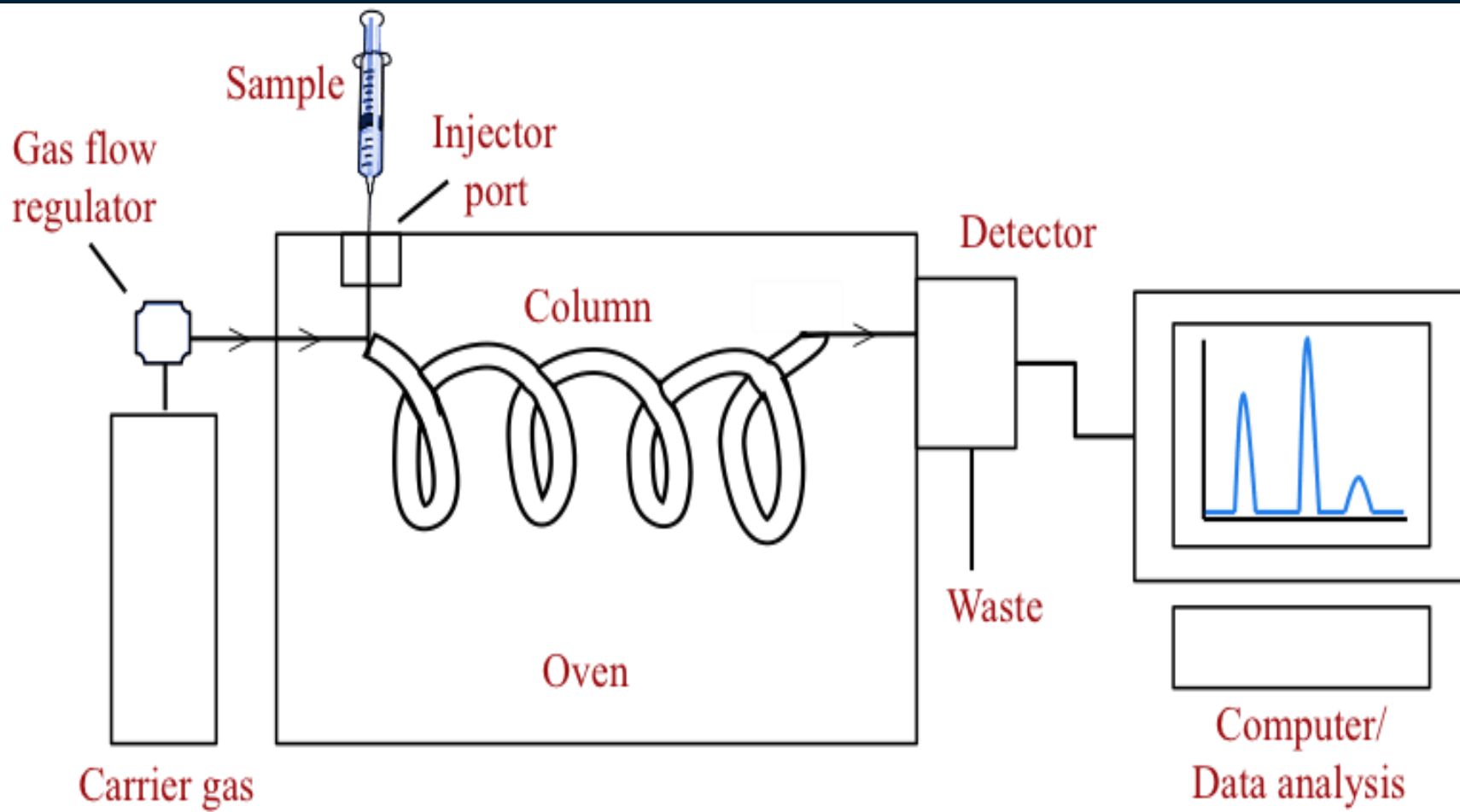
- Sulfur containing compounds that generally cause off odors like onion, garlic, cheesy, and over cooked vegetable.
- 4-Mercapto-4-methylpentan-2-one (4MMP)
 - At low concentrations (1.5 ppt) it has a pleasant aroma of black currant or muscat.
 - At high concentrations, it has an offending aroma of very bad body odor or cat urine.



ANALYSIS TECHNIQUE FOR AROMA COMPOUNDS

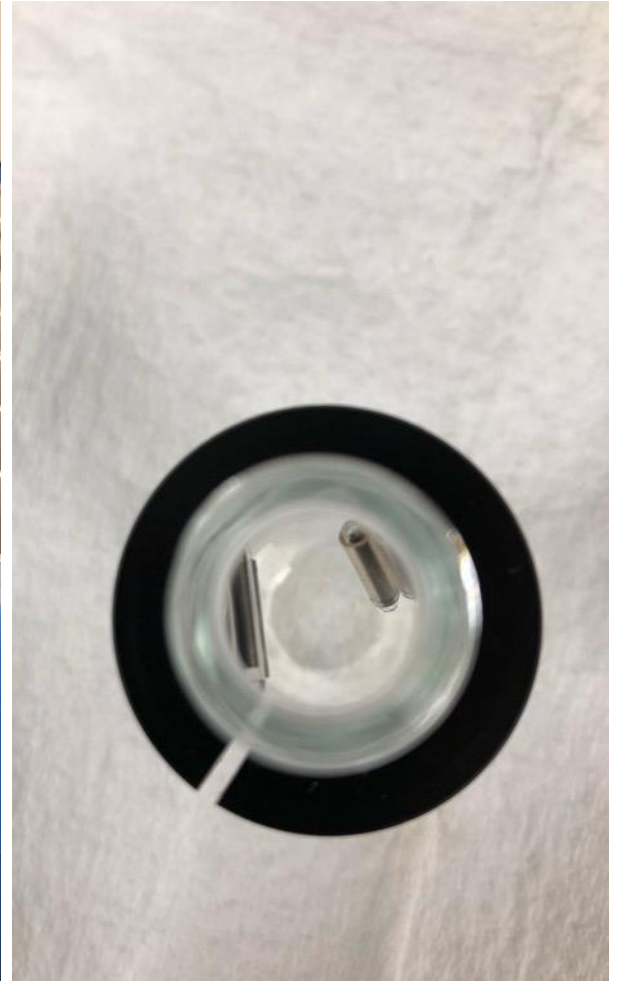
Gas Chromatography: Generally considered the best instrumental analysis technique for the analysis volatile compounds.

- Chromatography – is a separation technique that consists of a mobile phase and a stationary phase, and the analytes are separated by their individual affinities/attraction for the mobile phase and stationary phase. Each analyte will take a different amount of time to travel through the stationary phase, which is called the retention time.
 - Mobile phase is the medium used to carry analytes through the stationary phase
 - Stationary phase is a medium that the compounds interact depending on their affinity for the medium
- Gas Chromatography – uses gas as a mobile phase called a carrier gas usually helium, so the analytes have to be heated into their gaseous state to be carried through the stationary phase. The stationary phase is called a column that can be either packed (filled with material) or capillary (open tubular).



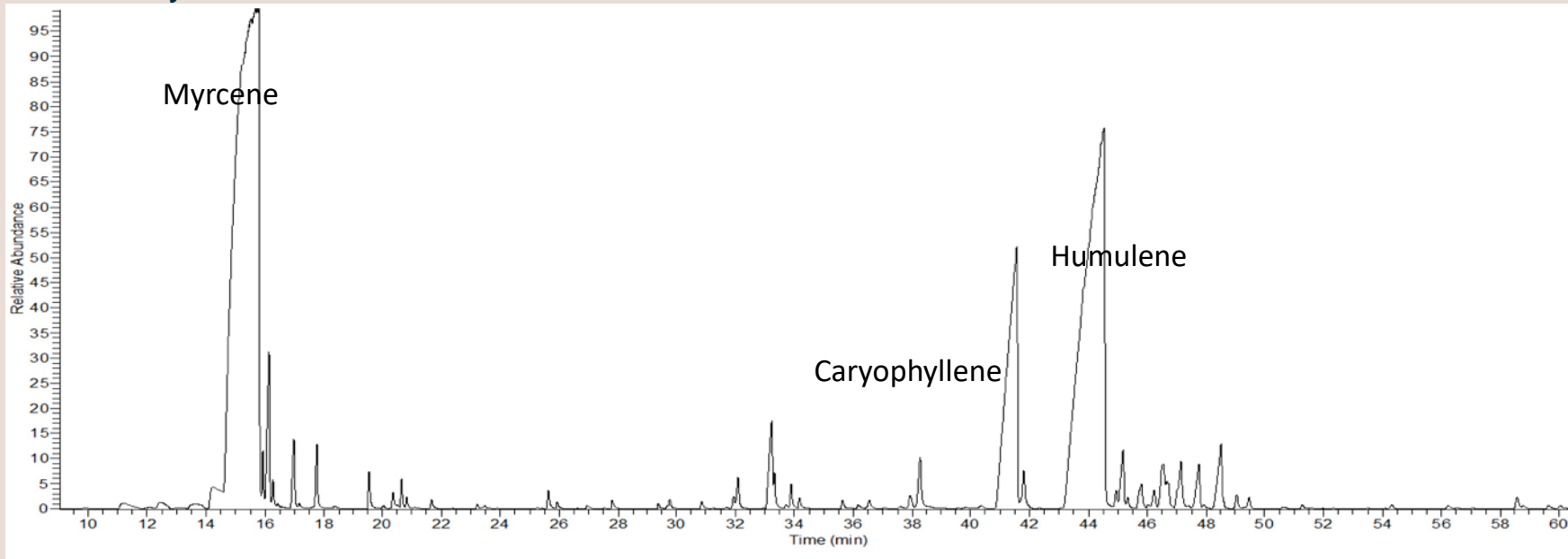
AROMA COMPOUND EXTRACTION TECHNIQUES

- Distillation
 - Boiling the hops/hop products in water for a set amount of time to distill and collect oil.
- Liquid Injection
 - The oil is mixed with a solvent and then directly injected into the injection port.
- Solid-Phase Microextraction (SPME)
 - A fiber coated with an extracting phase that will extract different analytes from different types of media.
- Headspace (HS)
 - The sample is heated while being agitated and then a syringe will extract the analytes from the headspace above the sample and inject into the injection port.
- Dynamic Headspace (DHS)
 - The sample is agitated and heated while the headspace is purged under a controlled flow of inert gas to provide more efficient extraction conditions.
- Twister Stir Bar Sorptive Extraction (SBSE)
 - A magnetic stir bar covered in a sorbent material (PDMS) that extracts and concentrates analytes.
 - It is solvent-free and more sensitive than SPME.



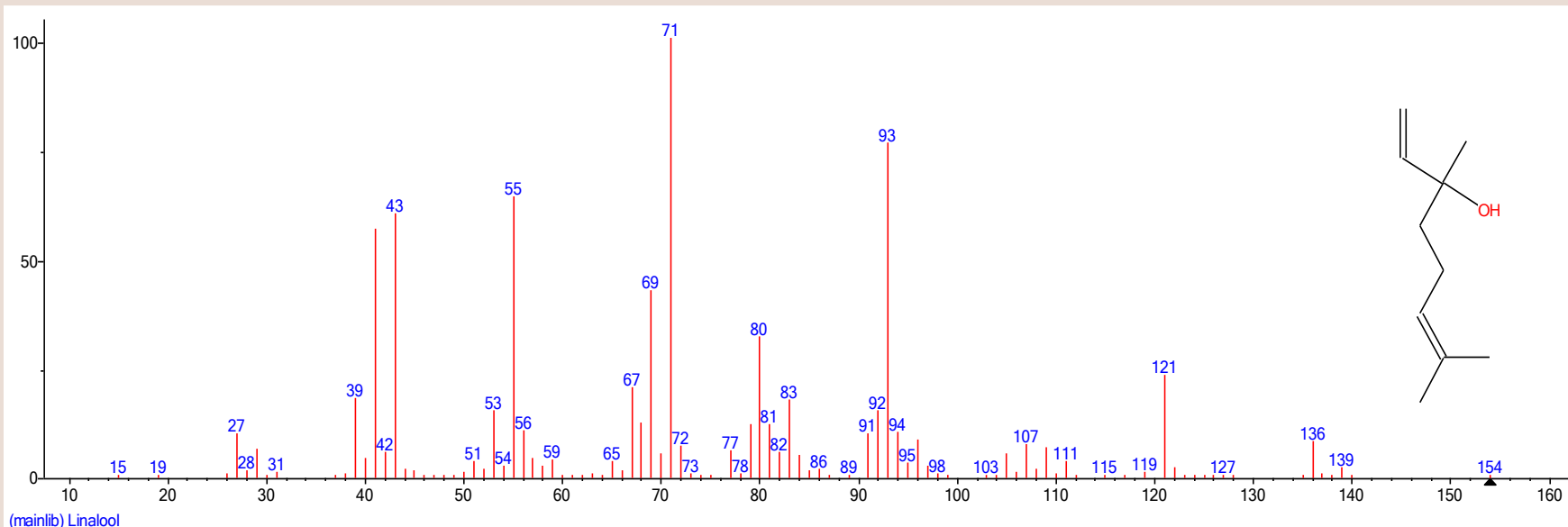
GC DETECTORS

Flame Ionization Detector (FID): A universal detector that combust the analytes once the pass through the column. Identification of compounds is restricted by retention time, and verified by referenced standards.



GC DETECTORS

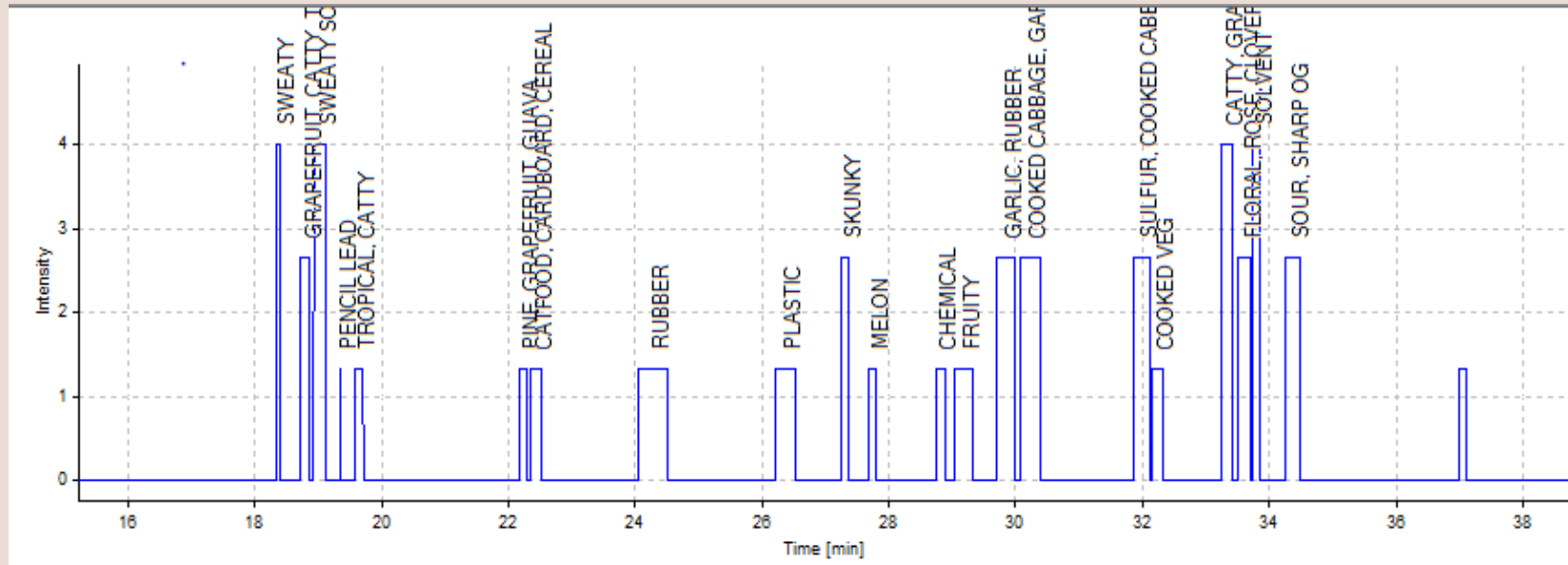
Mass Spectrophotometer (MS): A precise and accurate detector. Once the compounds have passed through the column they are fragmented by applying a electron voltage. The fragmented ions create a Mass Spectra (finger print) of the compound that can be compared against national data bases. Identification is completed by retention time, mass spectra libraries and reference standards.



(mainlib) Linalool

GC DETECTOR

Olfactory Detection Port (ODP): This detector requires individuals that have a good nose. As the compounds pass through the column one identifies the compounds by smell. This is generally in conjunction with one of the above detectors



2018 HARVEST HOP AROMA DATA

- Analysis completed on the GC-MS, each variety had a minimum of 9 lots tested.
- Twister SBSE extraction method used.
- Major Terpenes (content %w/w)
- Linalool (ppm)
- Geraniol (ppm)
- Linalool and Geraniol (ppm)
- Relative total ester content (area counts)

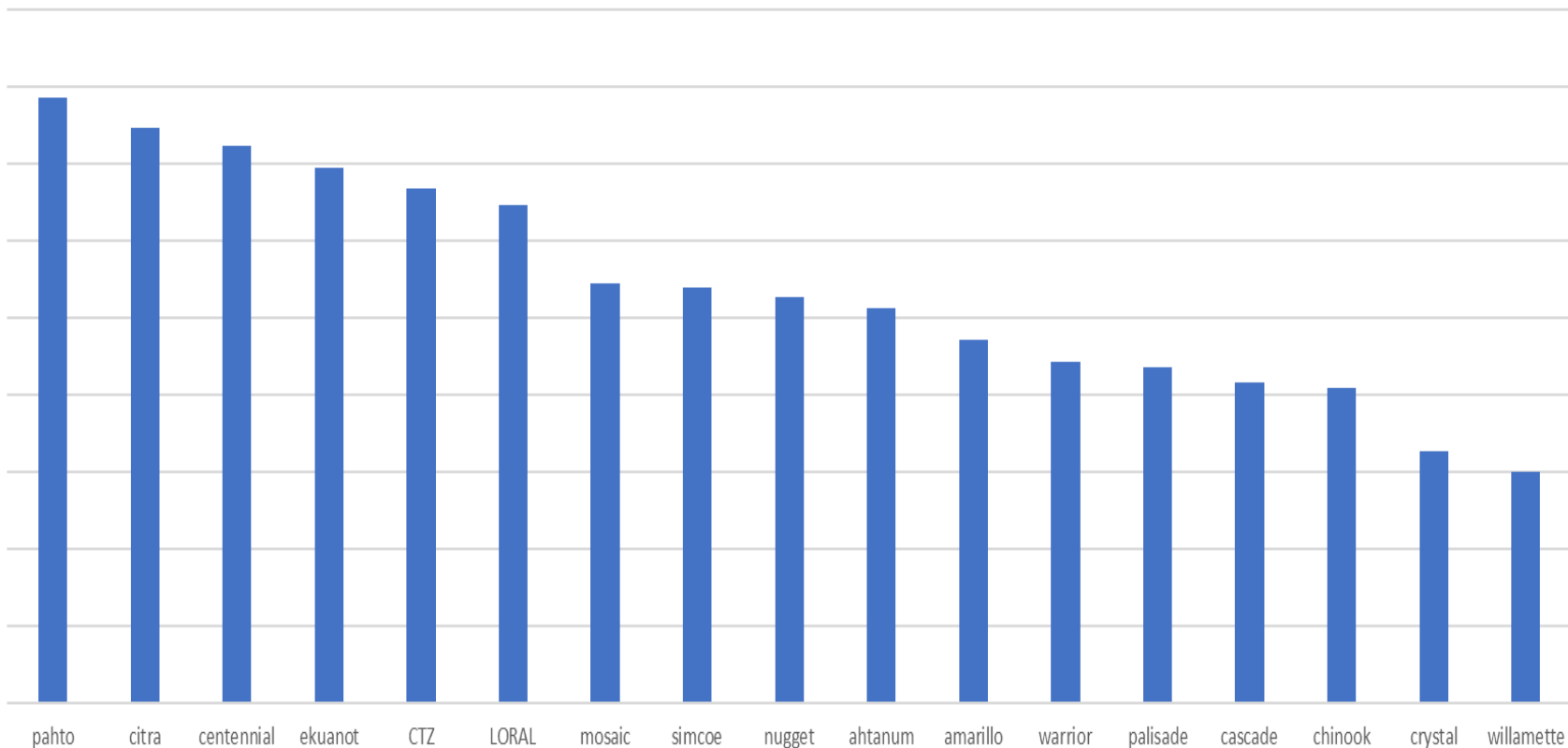


2018 HARVEST INSTRUMENTATION

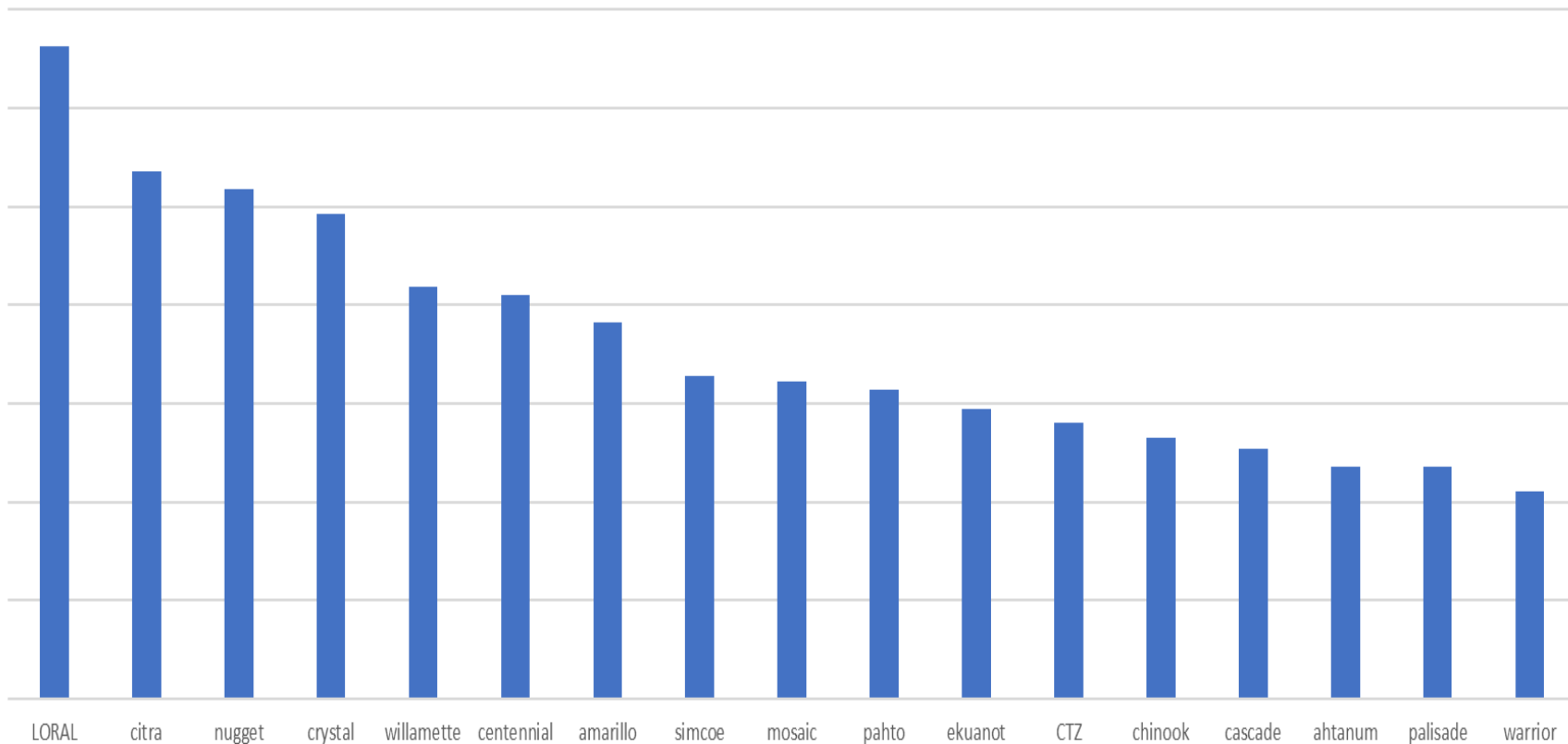
- Agilent 5975B GC/MSD
- Gerstel MPS
- Gerstel Olfactory Detection Port (ODP)



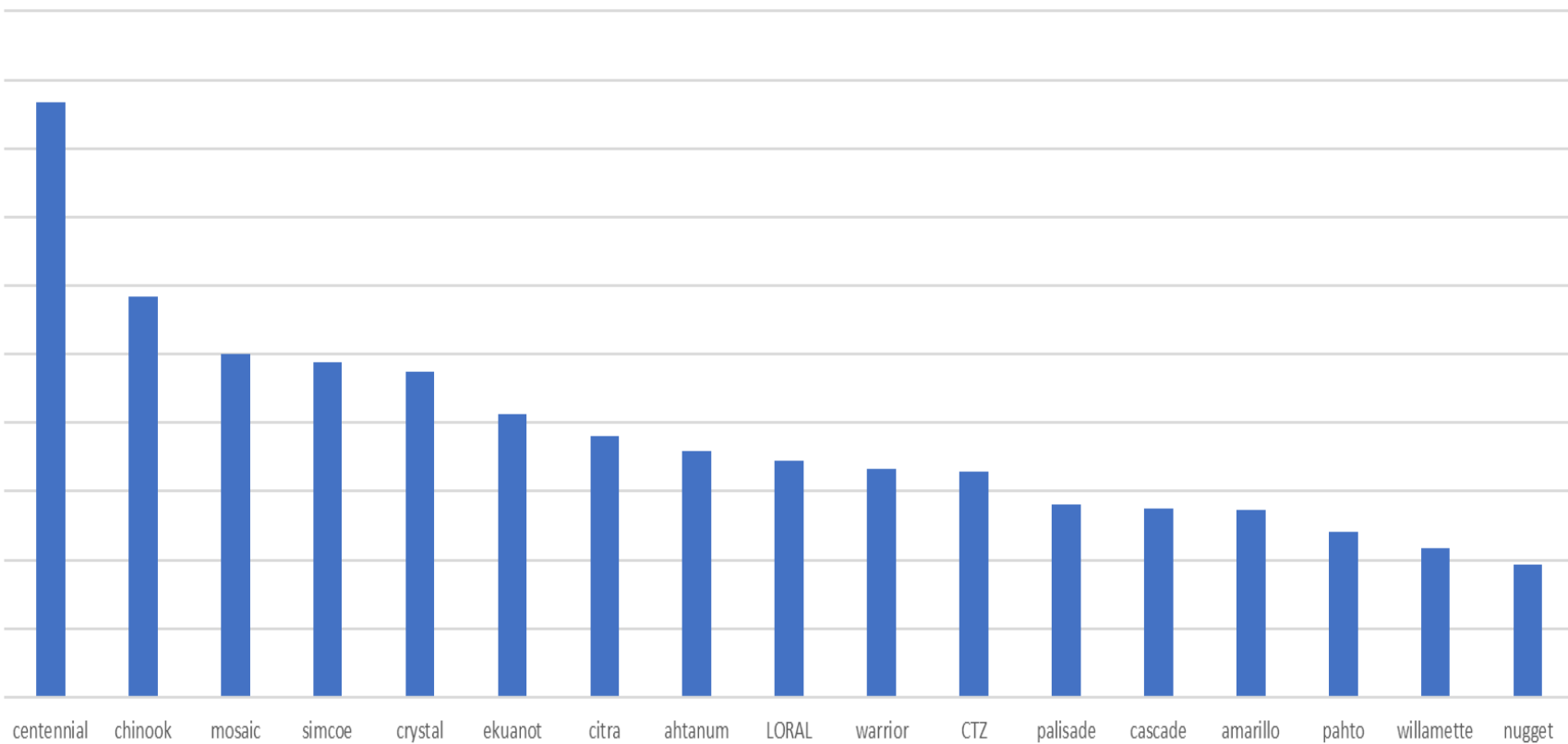
Hop varieties ranked by major terpenes (Myrcene, Caryophyllene and Farnesene) content %w/w



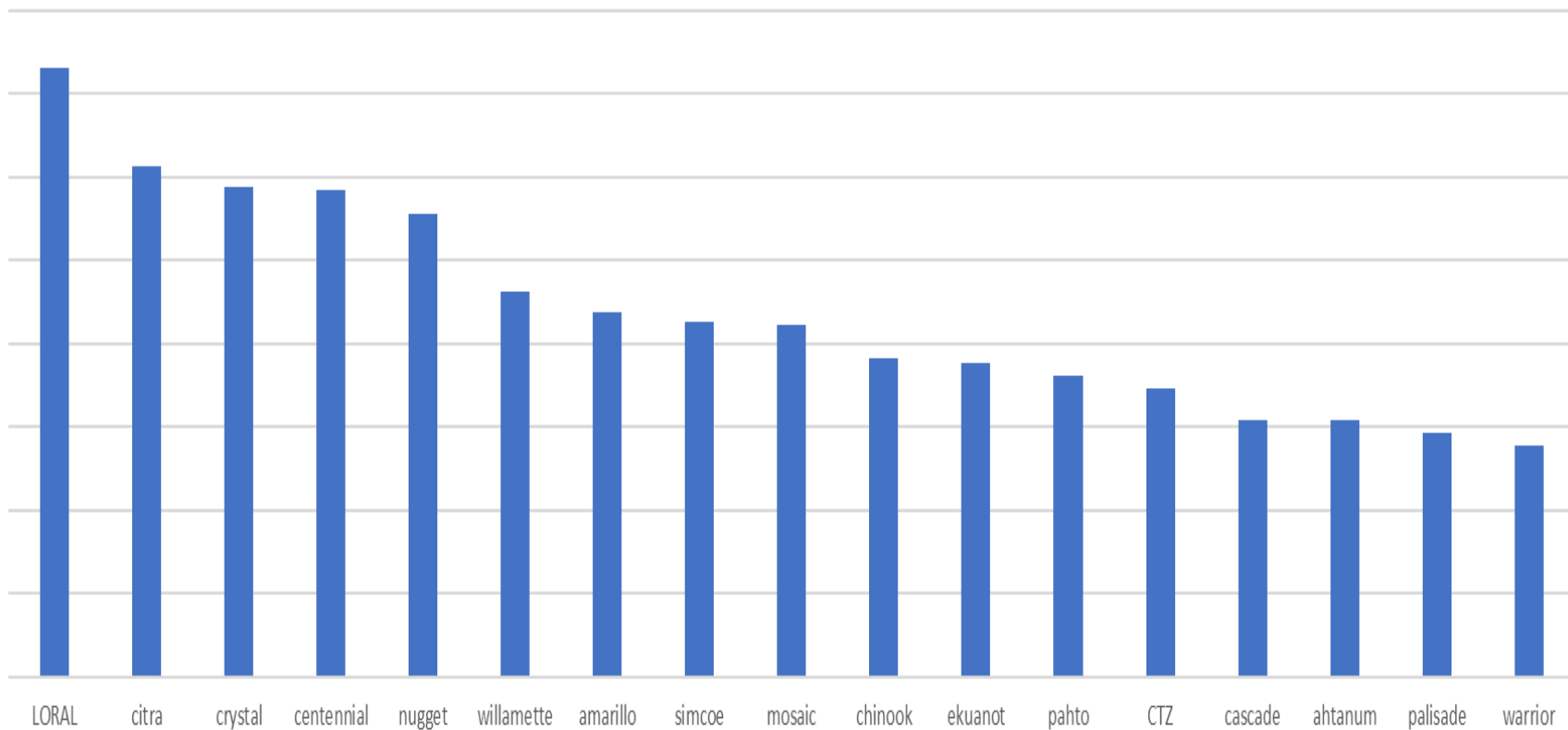
Hop varieties ranked by linalool content ppm



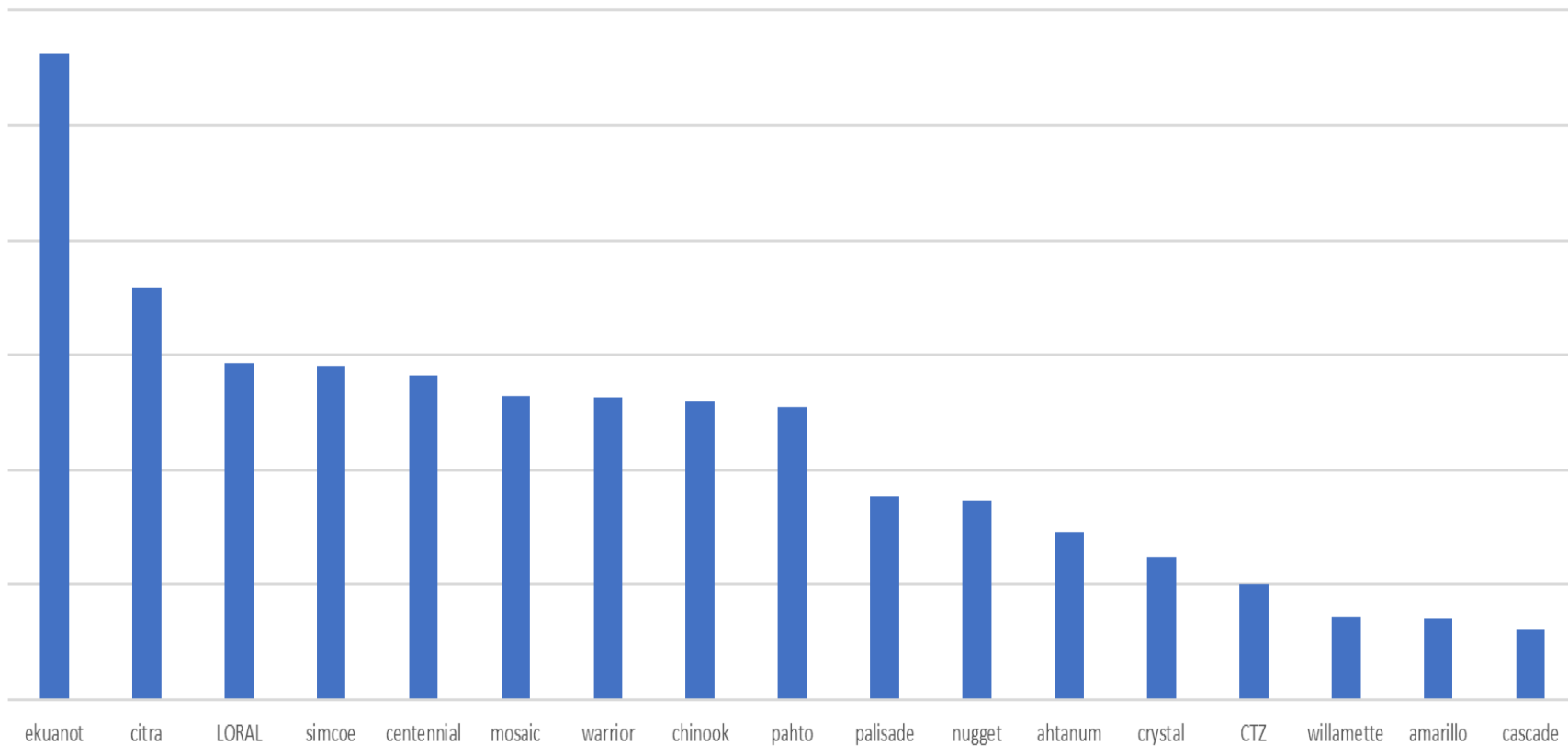
Hop varieties ranked by geraniol content ppm



Hop varieties ranked by geraniol + linalool content ppm

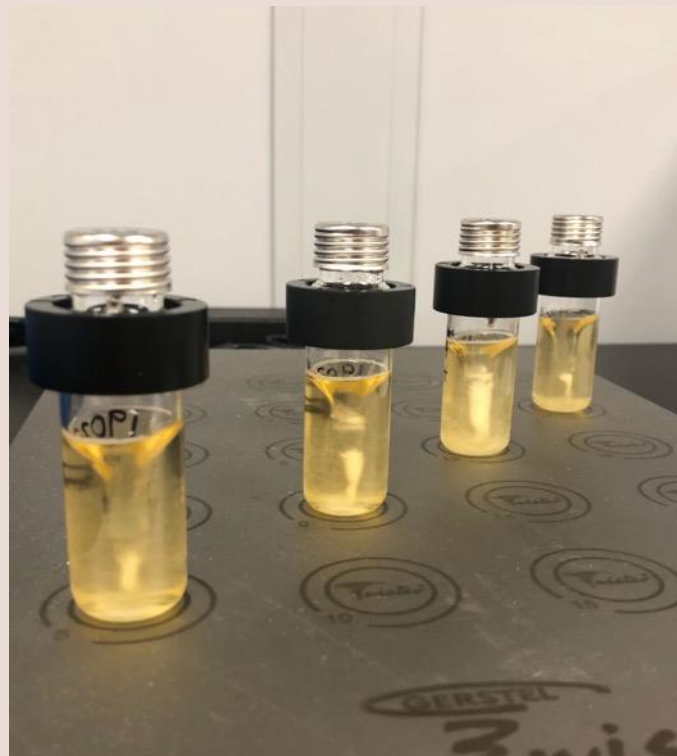


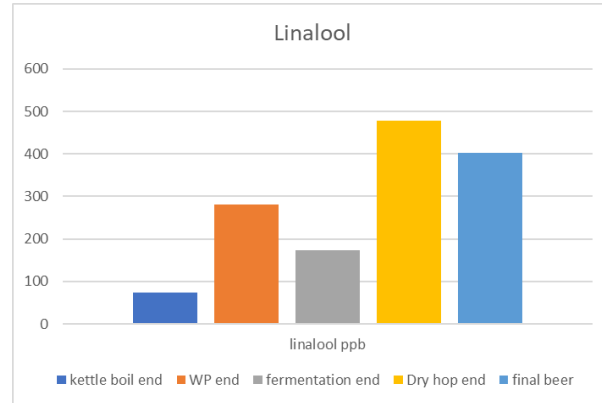
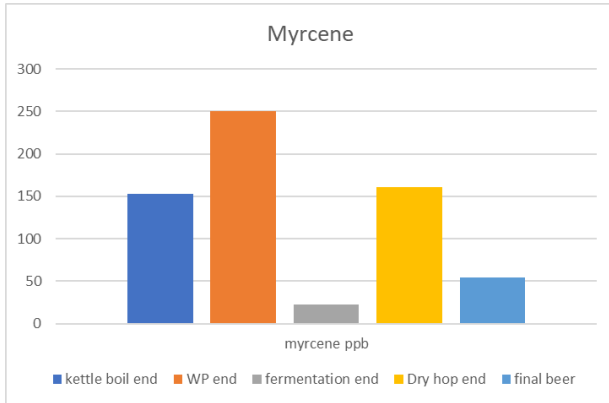
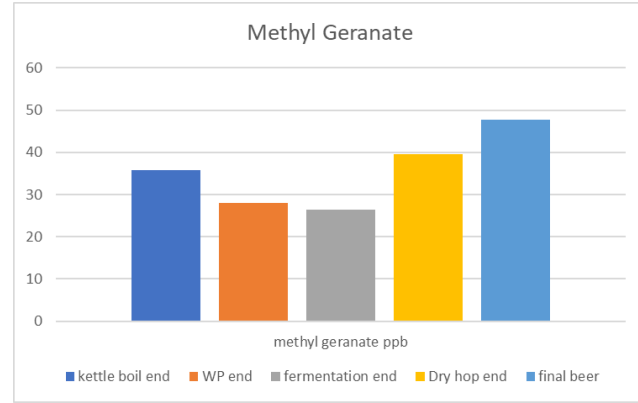
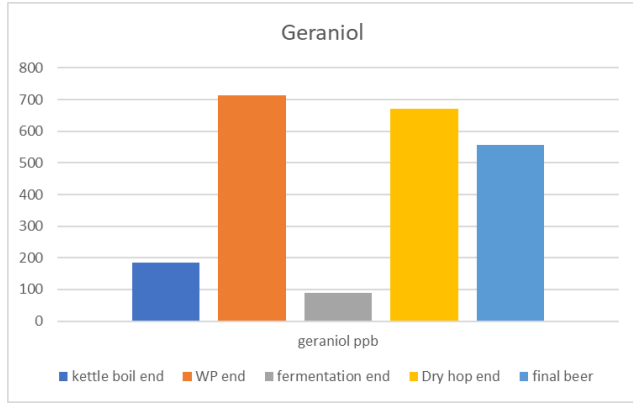
Hop varieties ranked by relative total ester content area counts(10^{-6})/g



BEER ANALYSIS DATA

- Data gathered from samples collected throughout the brewing process, focusing on the specific points below.
 - End of the kettle boil
 - End of whirlpool
 - Terminal gravity
 - Post-dry hopping
 - Final Package
- Looking at the most abundant aromatic compounds that make it into the final beer.





CONCLUSIONS

- Hop aroma is not equal to total oil content
 - Composition of the hop aroma
 - Consists of hundreds of compounds
 - Compounds aren't singular, they work together to create the hop aroma
- Hop aroma in beer is an extraction
 - Depends on the contact with the liquid
 - Depends on the nature of the compounds
 - Before fermentation – polar compounds are best, but biotransformation, oxidation, and degradation occur
 - After fermentation – best place to extract nonpolar compounds

CONTINUED RESEARCH AND ANALYSIS

- Complexity of hop aroma requires several years of research and data collection
- Collect data on each cultivar
 - True average
 - Growing region affects
 - Agronomics
 - Ripeness
- Implementation of new analytical instrumentation
 - GC/MS Q-TOF with sulfur chemiluminescence detector (SCD)





**YAKIMA
CHIEF
- HOPS -**

**Thank you for
listening!**

Questions?