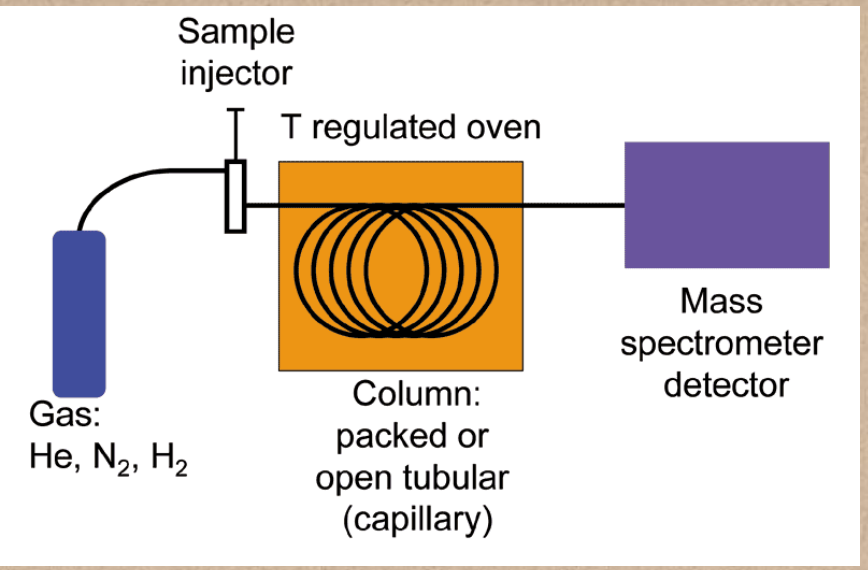
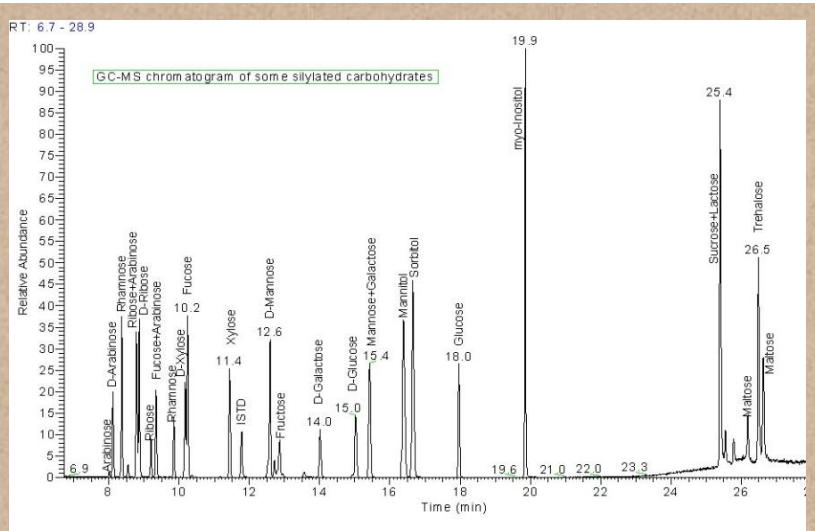
STONE®
BREWING CO.

Bourbon Barrel and Oak Flavor Compound Analysis

Gas Chromatography/Mass Spectrometry





Not Pictured:
Analytical to digital conversion equipment.

Calibrated with known standards.
Precise identification of specific compounds.
Validated this method in a past life using HPLC and GC-MS!

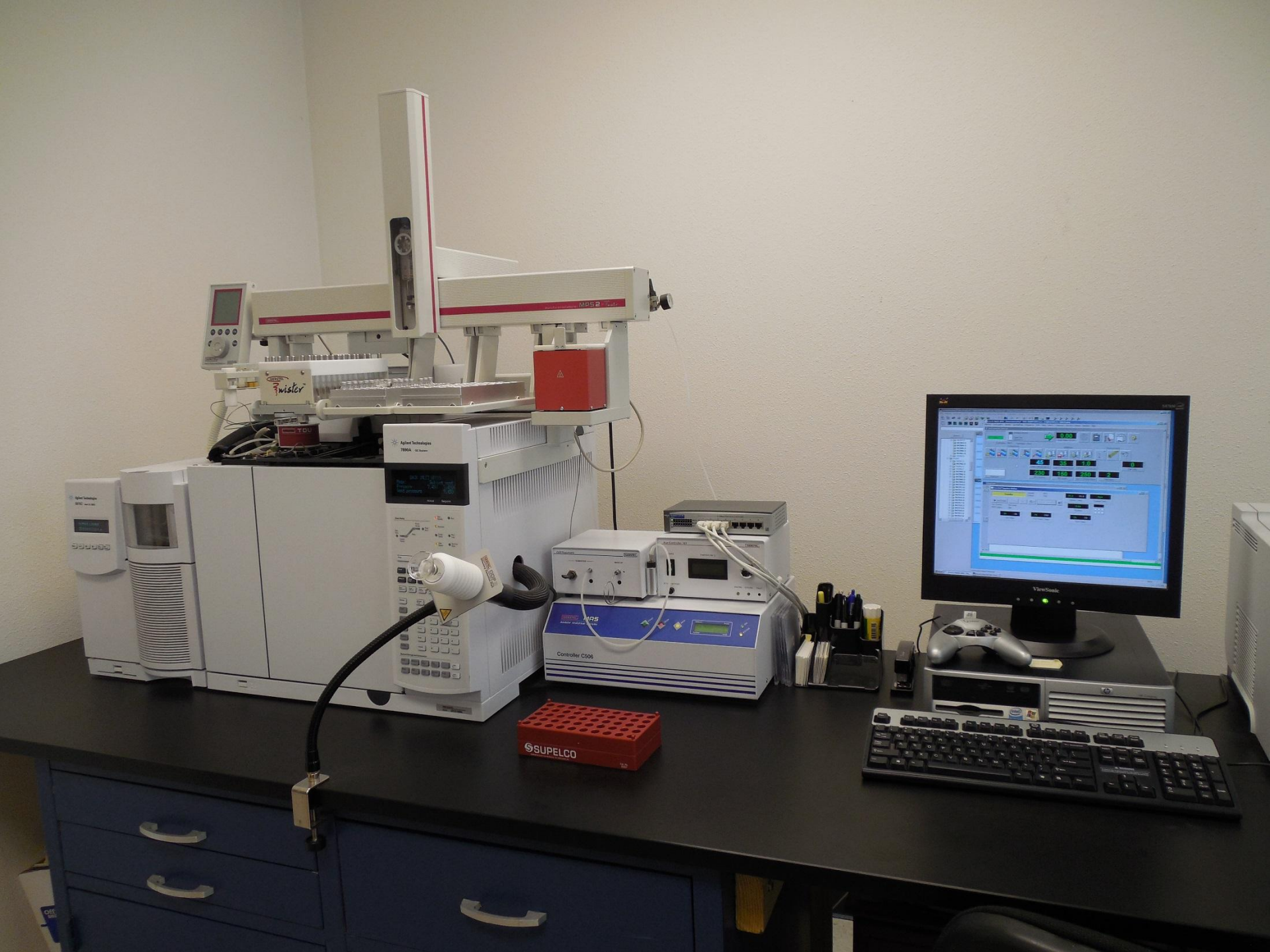
Sample Prep and Analysis

Samples prepared with a 30 ml sample treated with 2 ml aliquot of Dichloromethane and tumbled for 24 hours at 8 RPM.

Dichloromethane is then extracted by centrifugation at 1500 RPM for 5 minutes.

Internal Standard of 50 ppm Vanillin-d3 injected.

Sample is run on an Agilent GC/MS unit using a Restek RTX-Wax column.


MPS2
Twister
Agilent Technologies
7890A
Controller C506
ViewSonic
SUPELCO

Quality Control

Traditional sampling was ineffective. We would sample each barrel for micro, analytical, and sensory and still end up with spoilers in the tank!

Full testing of each barrel not sustainable.

More effective was tasting and pH testing of each barrel just prior to racking out.

Confirmation micro check on tank.

Toasted/Charred and Raw Oak Flavors

Raw Oak Compound Flavors

- Spice
- Wood Sugars
- Coconut
- Raw Wood/Pencil Shavings
- Others

Toasted/Charred Compound Flavors

- Furans: Caramels, Acrid pungency, toasted notes
- Smoke aromas
- **Vanilla: 3 different types of vanilla compounds!**
  - In addition to fresh vanilla flavors, lifts other flavors
- Others

A Bourbon Barrel Test

A strong ale using a single recipe aged in three types of bourbon barrels presented a unique opportunity to monitor for flavor and chemical analysis.

The Data set included:

- Set 1: never used, virgin bourbon barrels freshly charred, racked to barrel in Nov 2012
- Set 2: Bourbon barrels previously housing 10 year old bourbon, racked to barrel in Nov 2012*
- Set 3: Bourbon barrels previously housing a high gravity dark beer, racked to barrel in Aug 2012*

*Both of these sets of barrels contained the same 10 year old Kentucky bourbon prior to beer fill.

The Chemical Analysis

- Raw Oak Compounds:
  - cis-Lactone
  - trans-Lactone
- Furans:
  - 5-Hydroxymethyl Furfural
  - 5-Methyl Furfural
  - Furfural
  - Furfuryl Alcohol
- Smoke and Spice Compounds:
  - Guaiacol
  - Eugenol
  - trans-Iso Eugenol
  - cis-Iso Eugenol
- Other Pyrolosis Products
  - Vanillin

Flavor Thresholds and Flavor Descriptors

Wine and Spirit Flavor Thresholds in ppb.
Beer Thresholds have not been experimentally derived.

Compound	Flavor Imparted	Flavor Threshold
5-Methyl Furfural	Toast/Butterscotch/Caramel; Acrid in very high concentrations	1000
5-Hydroxymethyl Furfural	Toast/Butterscotch/Butter/Caramel	1000
Furfural	Bread/Toast/Butterscotch/Caramel; Acrid in very high concentrations	3000
Furfuryl Alcohol	Bready/Burnt; Acrid in very high concentrations	8000
Vanillin	Natural Vanilla	50
trans-Lactone	Fresh Oak/Coconut	20
cis-Lactone	Fresh Oak/Coconut (stronger isomer?)	20
Eugenol	Spice/Clove	10
Guaiacol	Smoke	10
trans-Iso Eugenol	Spice/Clove/Carnation	10
cis-Iso Eugenol	Spice/Clove	10

Actual Analysis

		Brand New Bourbon Barrels				1st use after Bourbon Barrels				2nd use after Bourbon Barrels			
		3 month concentration		7 month concentration		3 month concentration		7 month concentration		7 month concentration		10 month concentration	
	Flavor Threshold (ppb)	ppb	OAV*	ppb	OAV*	ppb	OAV*	ppb	OAV*	ppb	OAV*	ppb	OAV*
5-Methyl Furfural	1000	110	0.1	90	0.1	40	0.0	50	0.1	50	0.1	50	0.1
5-Hydroxymethyl Furfural	1000	1400	1.4	2000	2.0	1100	1.1	2600	2.6	1800	1.8	2900	2.9
Furfural	3000	620	0.2	490	0.2	290	0.1	560	0.2	680	0.2	650	0.2
Vanillin	50	740	14.8	380	7.6	380	7.6	300	6.0	570	11.4	270	5.4
Guaiacol	10	20	2.0	20	2.0	9	0.9	10	1.0	10	1.0	10	1.0
trans-Lactone	20	10	0.5	20	1.0	10	0.5	20	1.0	10	0.5	20	1.0
cis-Lactone	20	70	3.5	150	7.5	130	6.5	210	10.5	90	4.5	120	6.0
Fufuryl Alcohol	8000	6100	0.8	7100	0.9	5200	0.7	6300	0.8	6000	0.8	6900	0.9
Eugenol	10	10	1.0	20	2.0	5	0.5	8	0.8	4	0.4	5	0.5
trans-Iso Eugenol	10	5	0.5	40	4.0	3	0.3	20	2.0	2	0.2	20	2.0
cis-Iso Eugenol	10	6	0.6	8	0.8	4	0.4	5	0.5	4	0.4	4	0.4

* Odor Activity Values: number of times past the minimum flavor threshold.

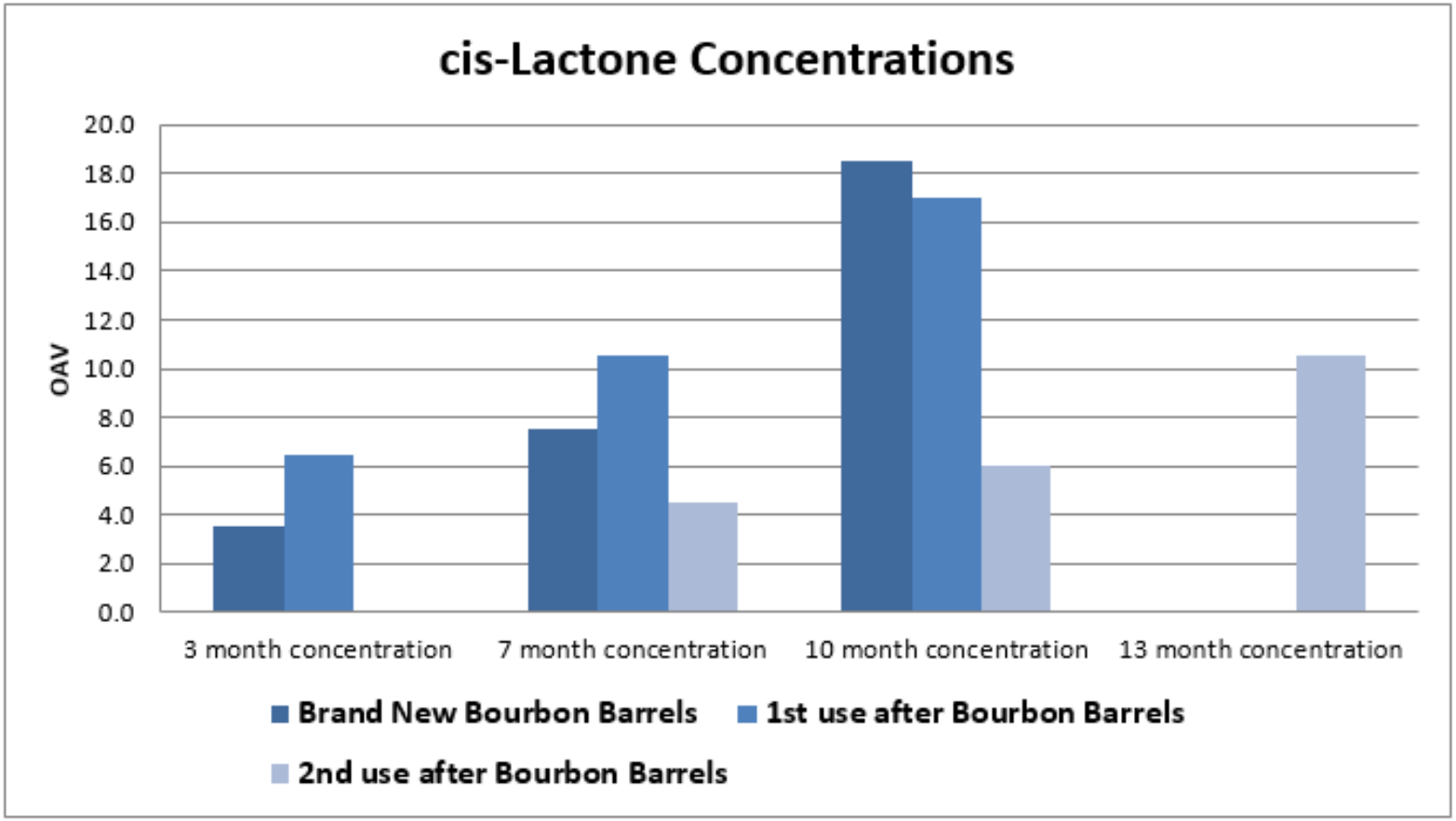
Making Sense of the Data

Raw data converted to Odor Activity Values

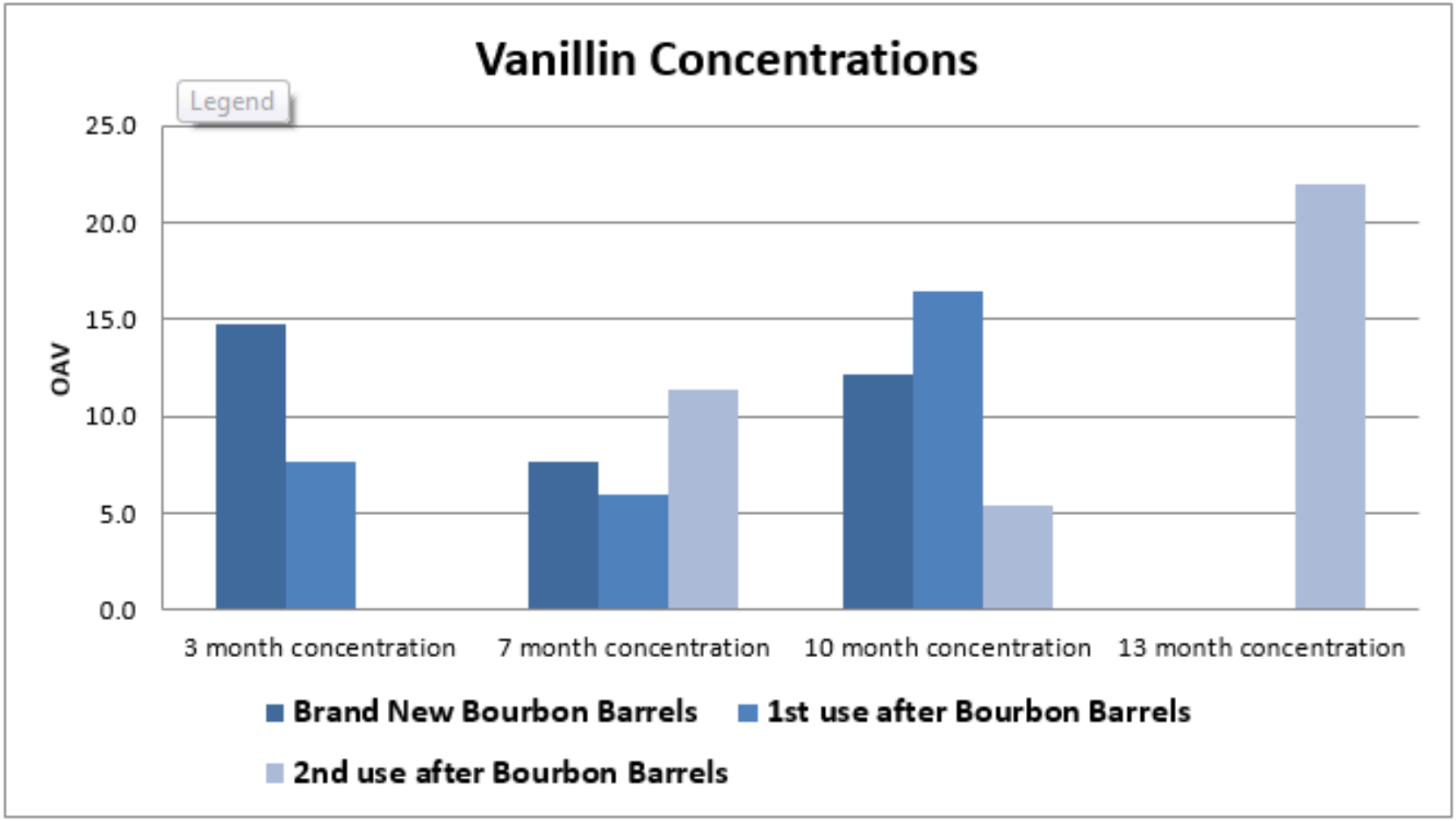
Not all compounds analyzed were significant from the previous slide. Significant compounds included:

- cis-Lactone
- Vanillin
- 5-Hydroxymethyl Furfural
- To a lesser extent Guaiacol, Eugenol, and trans-Iso Eugenol

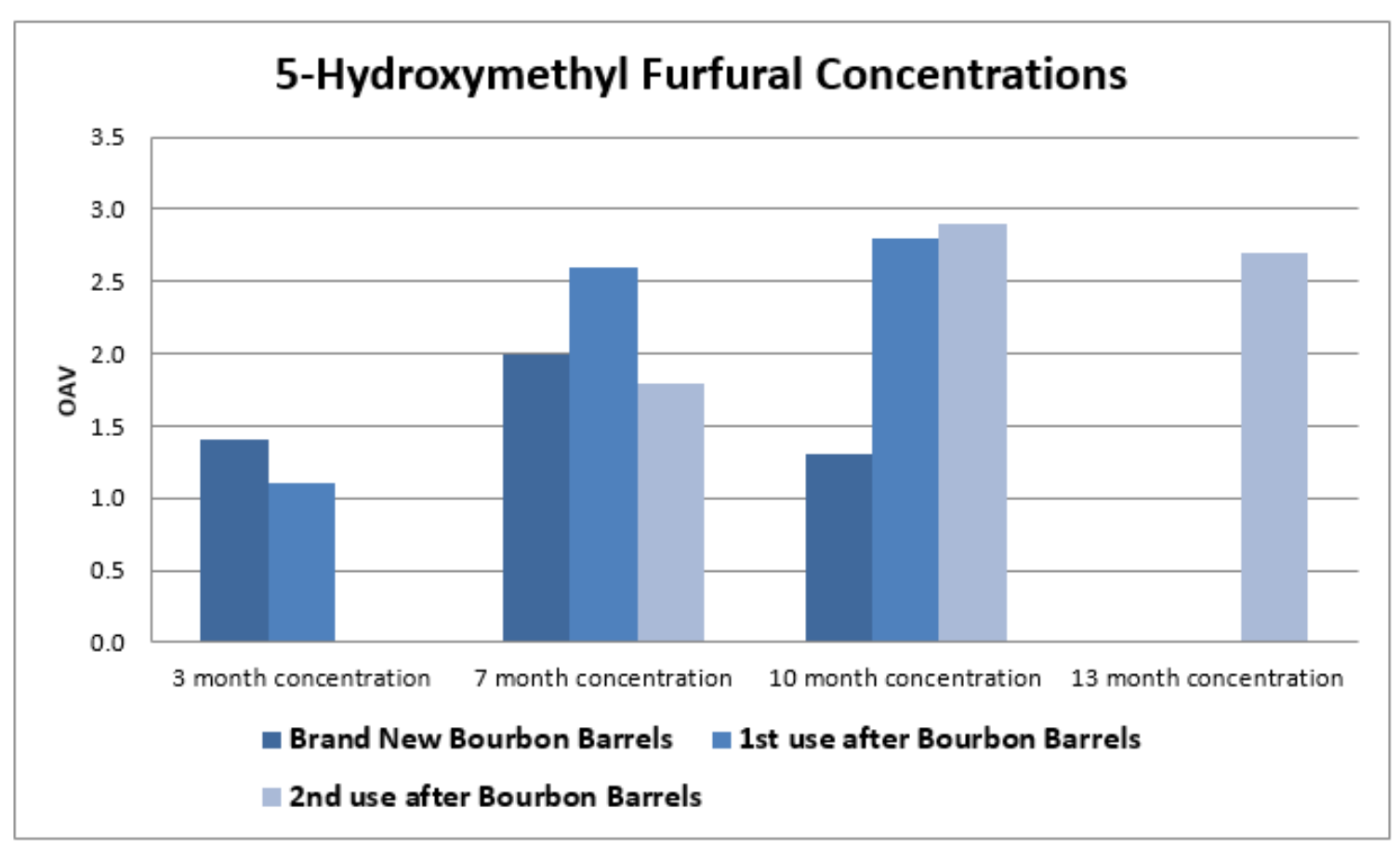
cis-Oak Lactone



Vanillin

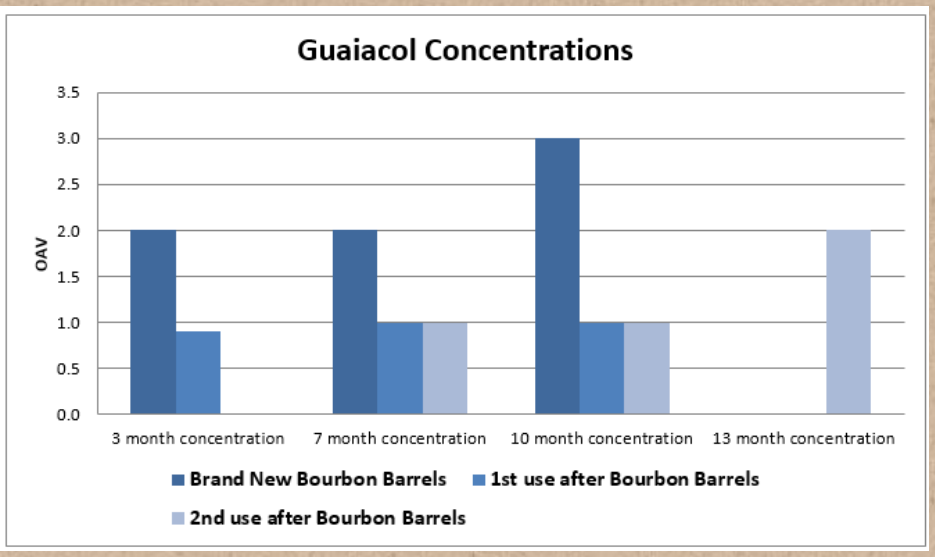

Vanillin Concentrations
Legend
25.0
20.0
15.0
10.0
5.0
0.0
OAV
3 month concentration
7 month concentration
10 month concentration
13 month concentration
Brand New Bourbon Barrels
1st use after Bourbon Barrels
2nd use after Bourbon Barrels

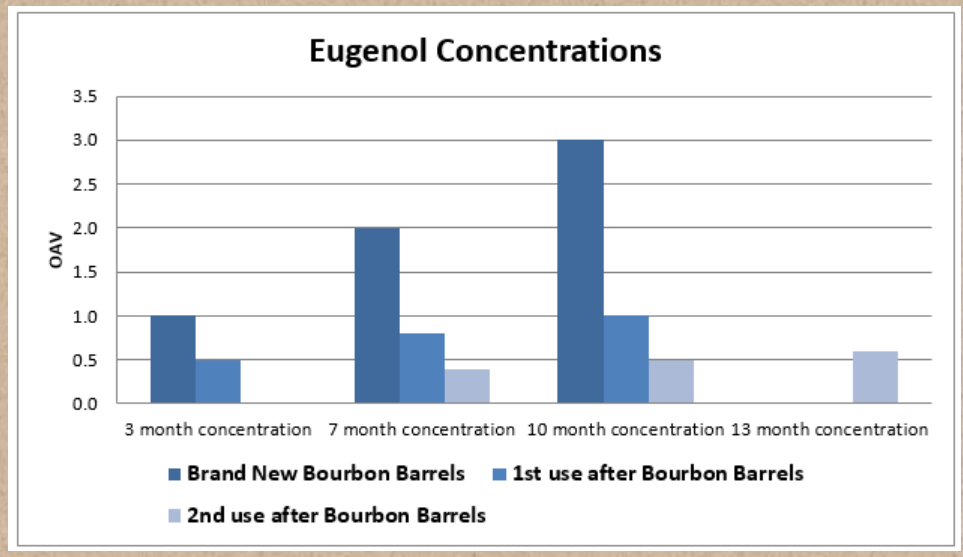
The Only Significant Furan Compound in this Study



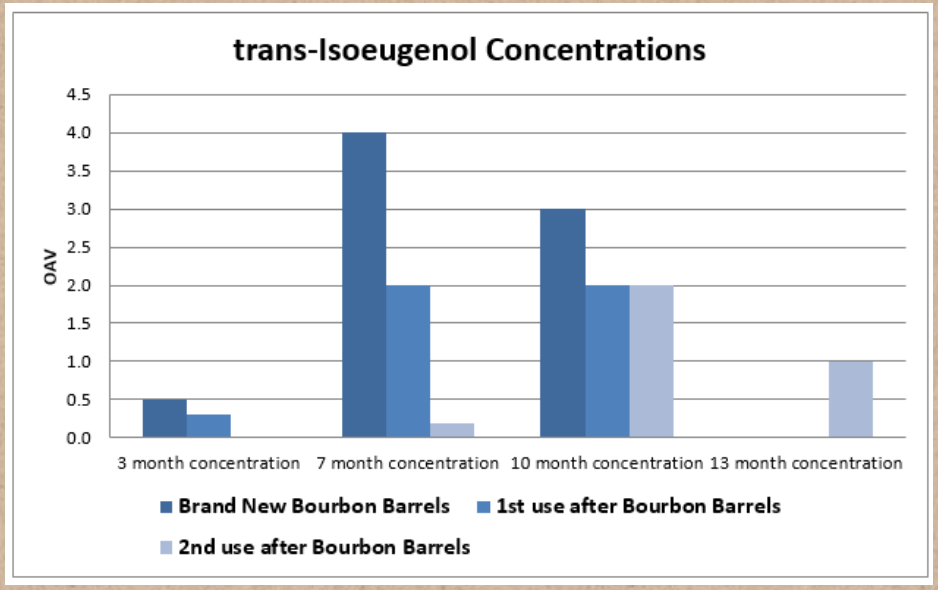
Note: Some distillers use 5-Hydroxymethyl Furfural as an aging analytical marker! Found in many foods.

Guaiacol and Eugenols





Guaiacol and Eugenols Cont.



Eugenols and Guaiacol were far less significant in used barrels, with Guaiacol and Eugenol below the flavor threshold in used barrels.

Explains the frequent lack of “wood spice” in bourbon barrel aged beers.

Preliminary Conclusions!

Even 2nd use barrels contain significant Vanillin levels that can be extracted from aging, at 22 times the flavor threshold after 13 months.

Vanillin levels on virgin bourbon barrels dropped over time.

- Possible reasons are analytical error, oxidation of vanillin with age, or different representative samples.

According to this analysis, we can expect strong wood flavor from bourbon barrels in as little as 3 months.

Quality Control Pass Rate

Time in Barrel	2 months	3 months	4 months	6 months	10 months	13 months	20 months
Number of Barrels	159	126	8	38	68	6	74
Failure Rate	0%	0%	0%	0%	18%	100%	49%

Microbiological Stability is solid up to 6 months after racking to barrel in our process.

Conclusions

There is a ton of Vanillin at 7.6 times the flavor threshold, as well as Cis-Oak Lactone at 6.5 times the flavor threshold at only 3 months of aging in a freshly emptied of bourbon barrel.

In our process, micro stability is solid at up to 6 months of aging.

There is a lot of flavor in 2nd use barrels.

Some oak impact is probably coming from the bourbon in the barrels, but most is likely from the wood: see virgin barrel data!

Finally, Some Opinions

The difference between 6 and 15 times the flavor threshold for vanillin or other barrel aging flavors is not perceived in the same linear way: not 2.5 times more intense.

A nice malty or very dark beer at three months of bourbon barrel aging tastes delicious, and is free of soy sauce like flavors from extended aging!

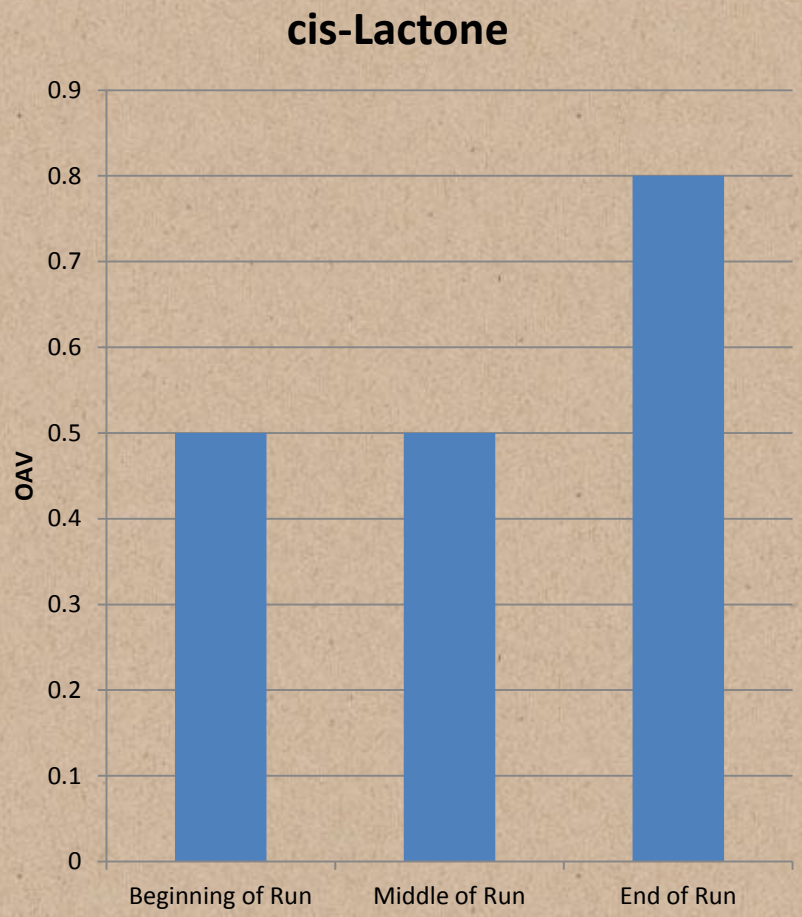
Lengthy aging has it’s place, and we still do it, but I don’t think it is always necessary or always worth the risk.

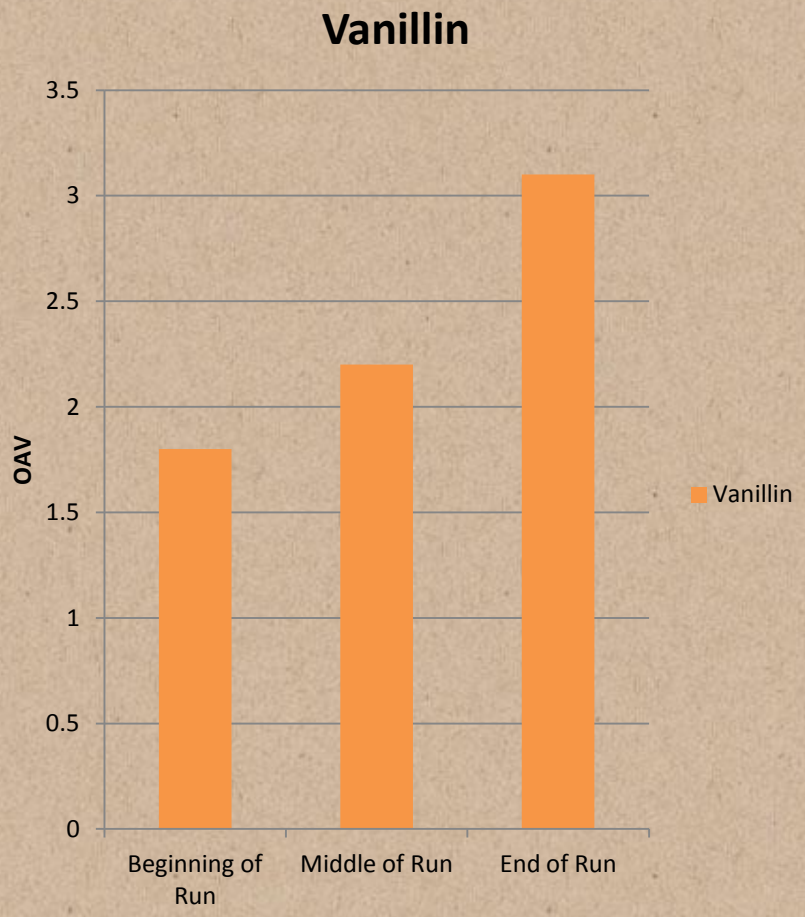
Oak Chip Beer Test

One of our beers made with added oak chips had some batch to batch consistency issues with the oak intensity levels.

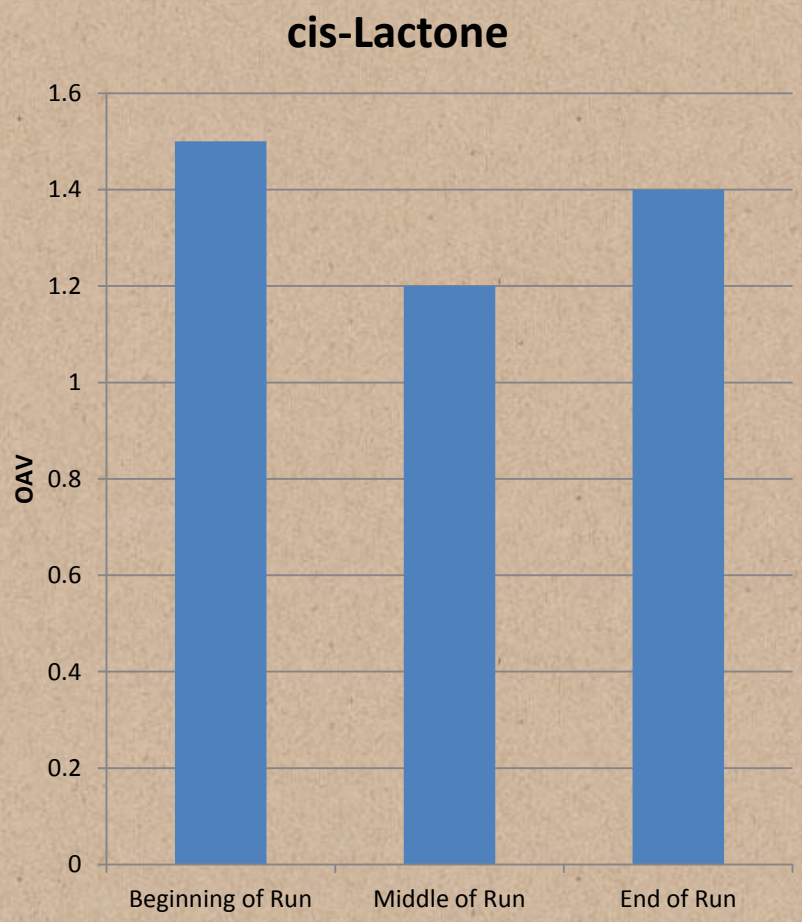
Mixing the tank by bubbling proved effective in improving oak flavor intensity and consistency, but what was really happening?

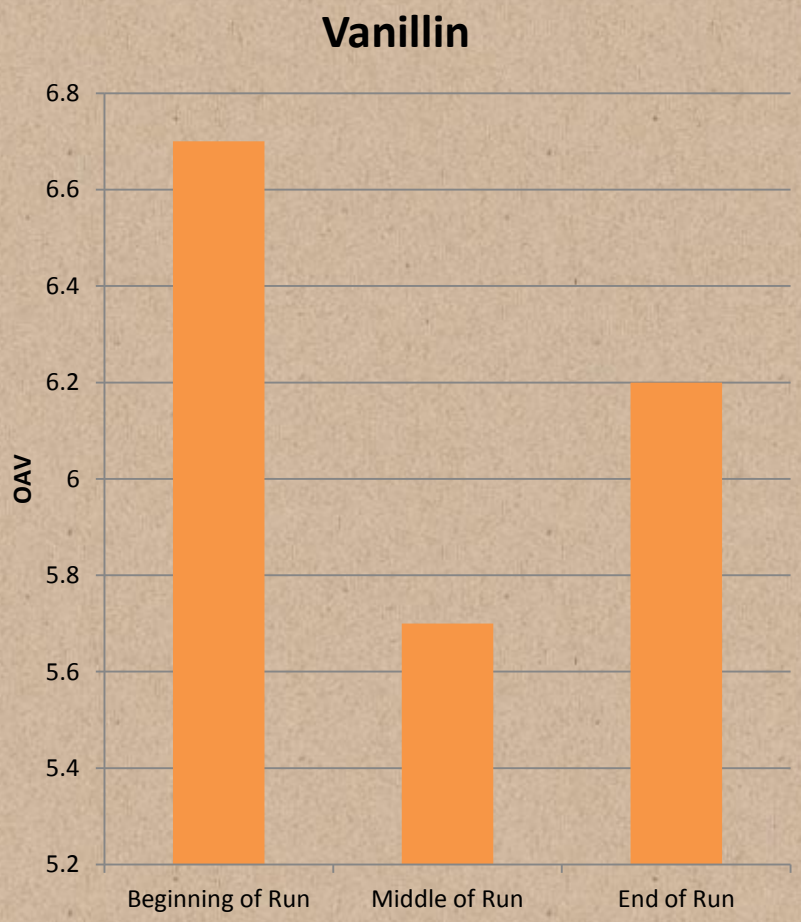
Oak Analysis: pre-Mixing





Oak Analysis: Post-Mixing





Acknowledgements

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The Executive Brewing Team: Mitch Steele, Steve Wagner

Mark Valentini of Analytical Sciences

Phil Burton of Barrel Builders

The Oak Trees that gave us their lives to make these amazing vessels that make such outstanding beer!

Questions?

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