37

2017 ASBC Annual Meeting

Identification of Hop Varieties and Growing Region by Gas Chromatography-Sulfur Chemiluminescence

Ryan D. Foster, Stephanie J. Conn, Darren A. Gamache / Virgil Gamache Farms Inc. Toppenish, Washington

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

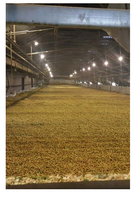
Study Objectives:

- Generate a method to distinguish hop varieties that does not involve genetic testing
- Improve on prior publications that focus on terpenes for hop characterization
- Determine if sulfur compounds found in hops are able to be used to determine in which region the sample was grown

Project Background:

There are many differing opinions on the effect of growing region on hop quality. One large opinion is that a hop variety grown in varying places around the world, or even country, will present differences in the aroma notes.

Over the course of a few years Virgil Gamache Farms Inc. has expanded to growing VGXP01 in 3 different states and within those states, 4 distinct growing regions. Every year there were distinct aroma differences found in each growing region that the other locations, where the same root stock was being grown, could not be duplicated. Yet, each region is consistent on a year to year basis within that area. Historically attempts to analyze these differences by use of the terpenes has led to inconclusive results.



The inability to create reliable interpretation of the terpene data led to the need to find another analysis technique that was able to more efficiently characterize samples as having the same aroma notes or differing ones. At the same time that these questions were being raised, the importance of another class of compounds in hop sensory was beginning to develop; polyfunctional thiols. By adding a sulfur chemiluminescence detector to the GC the user was now able to detect these compounds at lower than 25ppt. With these low detection levels, the nuances of the sulfur compounds that dictate so much of what is perceived by the nose can be analyzed.

Once the hop samples were being analyzed in mass by this new technique it was apparent that there was a discernable differences between both variety and growing regions within those varieties. This observation led to the idea of creating a database of samples to determine if the sulfur spectrum could be used as a fingerprint to identify hop samples. If this was proven to be true then the same approach could possibly be used to determine the region in which the sample was grown.

Based on this question the collection of samples from farmers around the region and world began to form a database different varieties to test the hypothesis. Preliminary results from the study are being presented in this poster with more work to follow based on the initial findings and feedback of the community.

Experimental Method:

Variety Selection:

Samples for this study were chosen to be in pellet form. This decision was made based on the availability and increased storability of pellets over whole cones. The varieties selected to build the proof of concept database were chosen based upon perceived popularity in the brewing world. Experimental varieties were not selected for the initial testing. To test the theory behind regional growing differences, Cascade was selected based upon its frequency of planting. Regional identifiers were added to each sample. The identifier represents the smallest region that it can be attributed to with certainty. Local Region < State < Country

Sample Prep:

The hop samples were massed out in 2g increments and blended to form a hop tea. Then 1.8g of tea was diluted to 10ml in a vial and a Gerstel Twister™ stir bar was added. This was then allowed to stir for 1 hour to adsorb the components in the hop tea.

GC-SCD Analysis:

The GC that was used to generate the hop spectral data consists of an Agilent 7890A+ with an FID/SCD combo detector. Sample introduction was achieved by desorption of the Twister™ stir bar by use of the Gerstel TDU. The desorbed sample was separated on an Agilent DB-Sulfur SCD column. The oven is ramped from 40°C to 260°C at a rate of 10°C/min.

Library Building:

Upon completion of GC run the SCD data was processed through Agilent MassHunter software. The software was used to find the 40 largest peaks in the sample. These 40 peaks were then put into Microsoft Excel under the name of the hop used to generate the data. This generated library enables the statistical analysis of multiple varieties against one another to determine the best match.

Data Processing and Statistical Analysis:

The analysis was completed through the use of Microsoft Excel. The spectral peaks of an unknown sample were compared to each known sample. A similarity score was generated for each comparison. The highest similarity score generated is the suggested variety of the unknown sample. To generate the score an algorithm was developed to locate peaks with the same retention time in the known samples and then determine a score based upon the similarity of the peak ratio as compared to the peak located at 10.6 minutes.

Results and Discussion:

Variety Matching:

After the library was assembled a few known samples were run to make adjustments to the matching score calculation. Once this was completed 4 samples were purchased from a local home brew store. The selected varieties were YCR 14(A), Centennial(B), HBC 394(C), and VGXP01(D). These were then run and processed through the Microsoft Excel library. Below are the results of each analysis and the top matches

A	Variety	Match Score
1	YCR 14 (USA)	24.27
2	Bodicea (ENG)	-1.92
3	Riwaka (NEZ)	-2.10

B	Variety	Match Score
1	Centennial (USA)	26.49
2	Willamette (AUS)	-0.94
3	Hopsteiner#01210 (USA)	-0.96

C	Variety	Match Score
1	HBC 394 (USA)	26.67
2	YCR 14 (USA)	-2.32
3	Bitter Gold (USA)	-3.23

D	Variety	Match Score
1	VGXP01 (WA)	27.96
2	Cascade (ARG)	-0.81
3	YCR 14 (USA)	-3.79

Regional Matching:

Only preliminary work was completed on this portion. It was shown that the library is able to distinguish between samples of Cascade from different regions. It was tested by running a second sample of Cascade from Argentina and comparing the match score to the other samples of Cascade to determine which region it was grown in.

Ranked	Match Score
Cascade (ARG)	19.08
Cascade (AUS)	11.55
Cascade (CAN)	14.51
Cascade (MI)	11.80
Cascade (WA)	13.87

Conclusions:

Variety Matching:

Proof of concept has been proven. The database was able to match 4 out of 4 random samples purchased from a local home brew store. Some library samples need to be rerun to increase the number of detected peaks to allow for better matching. Using the sulfur peaks has shown to be more repeatable than using the terpene data.

Regional Matching:

Proof of concept is shown to be viable. The database was able to distinguish Cascade from 5 different regions. This is planned to be expanded to determine the accuracy of the method.

Contact Authors:

Ryan D. Foster
Ryan@vgfinc.com
1-(509)-865-6422

Stephanie J. Conn
Stephanie@vgfinc.com
1-(509)-865-6422

Darren A. Gamache
Darren@vgfinc.com
1-(509)-865-6422