Flavor and Aroma Profile of Hops Using FET-Headspace on the Teledyne Tekmar Versa with GC/MS

Application Note

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Abstract

To brewers and the brewing industry, hops is an important beer component because of the flavor and aromas imparted during the hops addition process. Consequently, anticipating and/or validating the flavor profile of a particular variety of hops, based on analytical techniques, has become an increasingly useful tool in the head brewer's repertoire.

Hops flavors and aromas are caused by many different classes of compounds including those known as terpenes. In this application note, the flavor profile of five types of hops will be identified using Full Evaporation Technique (FET) Headspace on a Teledyne Tekmar Versa Automated Headspace vial sampler connected to a GC/MS (Gas Chromatograph/Mass Spectrometer) for chromatographic separation and detection.

Introduction

Hops have become a signature flavor component of American craft beer styles beginning with use of the Cascade variety, the first American-bred aroma hops.[1] With over 125 different types of hops varieties throughout the world, the options for hops-based flavors are broad and continually evolving.[2] The addition of hops to the brewing process affects the resulting beer in three distinct ways, adding bitterness, flavor (Citrus, Floral, Pine Resin) and aroma during the dry hopping process. The ability to quantify the flavor and aroma components of each hops variety can greatly assist in product development as well as ongoing quality control.[3]

This application note will focus on the flavor profile of five different types of hops by identifying the terpenes contained in their essential oils. A list of terpenes is shown in Table I, with the most prevalent being: Myrcene, Humulene, and Caryophyllene.

Table I Compound Name and Associated Nose Aroma[4]

Compound	Nose Aroma
Caryophyllene	Woody
Citronellol	Citrusy, Fruity
Farnesene	Floral
Geraniol	Floral, Rose, Geranium
Humulene	Woody, Piney
Limonene	Citrusy, Orange
Linalool	Floral, Orange
Myrcene	Green, Resinous, Piney
Nerol	Rose, Citrusy
Pinene	Spicy, Piney
3 mercaptoheyl Acetate	Muscat, Passion Fruit

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A Teledyne Tekmar Versa Automated Static Headspace vial sampler will be used to develop a Full Evaporation Technique (FET) for the profiling of the terpene compounds present in the hops samples. By using static headspace, only the volatile component will be transferred to the GC, leaving the nonvolatile components that can foul the GC injection liner, in the headspace vial.

Experimental Instrument Conditions

For this study, the Versa was coupled with a GC/MS system. Helium was used as the GC carrier gas, as well as the Versa pressurization gas. The Method Optimization Mode (M.O.M.) feature of the Versa's TekLink software was used during method development to determine optimal instrument parameters for the analysis. The GC was equipped with a Restek® 5MS column with dimensions of 30 m length x 0.25 mm ID x 25.0µm film thickness. The GC/MS parameters are shown in Table II and Table III. Table IV shows the Versa instrument parameters.

Table II GC Parameters

Column	5MS, 30 m x 0.25 mm ID x 25.0 µm
Oven Program:	60°C for 0.1 min, 12.5 °C/min to 280 °C with a 2.5 min final hold
Inlet:	180 °C
Column Flow	2 mL/min, Average Velocity 33 cm/sec
Gas:	Helium
Split:	20:1
Pressure:	17.2 psi

Table III Mass Spectrometer

MS Source	276 °C
MS Quad	150°C
Solvent Delay	3.00 Min
EMV Mode	Gain Factor
Mass Range	35.0-550.0

Table IV Versa Instrument Parameters

Variable	Value	Variable	Value
Constant Heat Time	Off	Mixing Time	2.00 min
GC Cycle Time	30.00 min	Mixing Level	Fast
Valve Oven Temp	160 °C	Mixer Stabilize Time	0.50 min
Transfer Line Temp	160 °C	Pressurize	20 PSIG
Platen/Sample Temp	190°C	Pressurize Time	2.00 min
Platen/Sample Temp & Time	Varied during study	Pressurize Equil Time	0.25 min
Platen Temp Equil Time	0.10 min	Loop Fill Pressure	15 PSIG
Sample Equil Time	10.00 min	Loop Fill Time	2.00 min
Mixer	On	Inject Time	1.00 min

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Sample Preparation

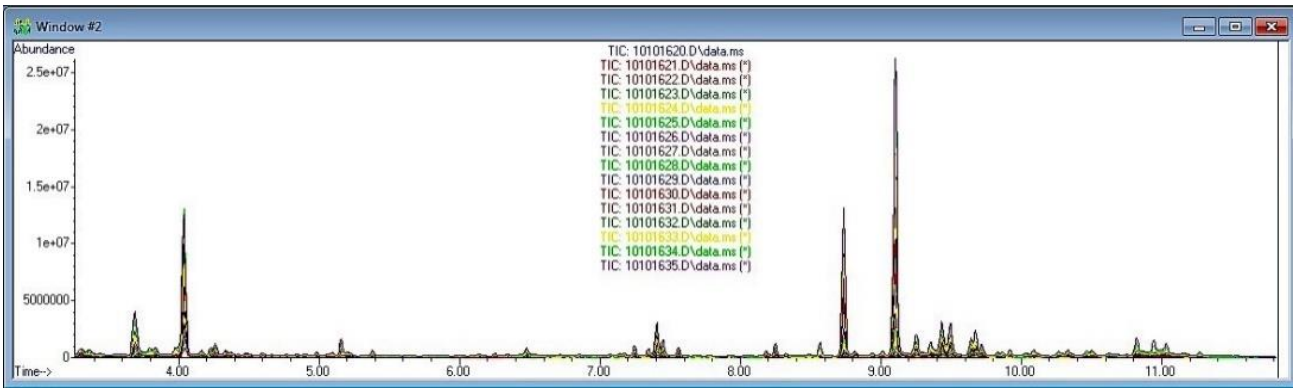
Whole cone hops from five varieties (Cascade, Centennial, Nugget, Mosaic and CTZ) were purchased from a local home brewing store. These hops were ground into a fine powder using a knife mill. The samples were then frozen until the time of analysis. 10.0 mg of each variety was added to a headspace vial for the FET analysis.

Results

M.O.M Optimization

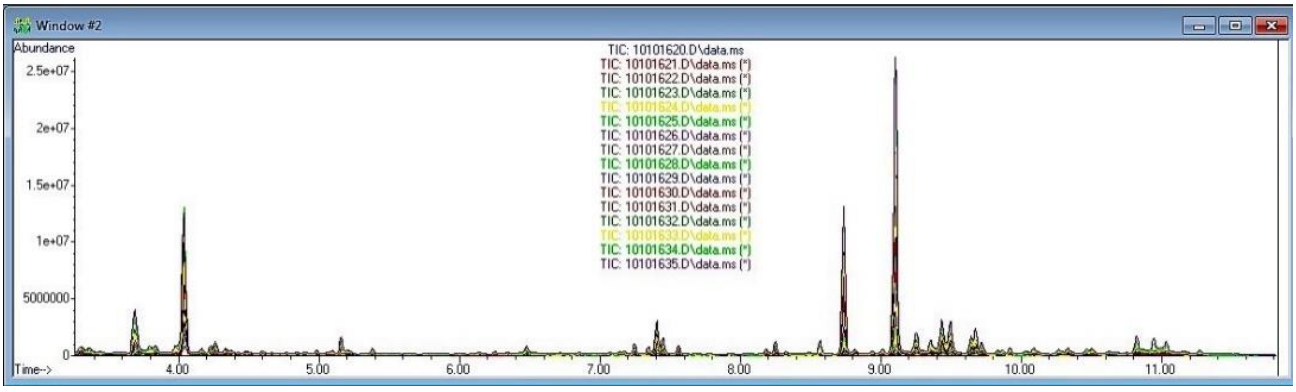
Prior to sample analysis, two studies were run using the M.O.M. feature of the Versa's TekLink™ software. The first study was to determine the optimum platen/sample temperature. The temperature study was evaluated from 40-190°C in 10° increments, after which it was determined that 190°C was the best choice (Figure 1).

Figure 1 Temperature Study 40-190°C



A second study was conducted to determine the optimum sample equilibration time. The sample equilibration time was varied from 5-35 minutes, after which it was determined that 10 minutes was the best choice (Figure 2).

Figure 2 Sample Equilibration 5-35 Minutes



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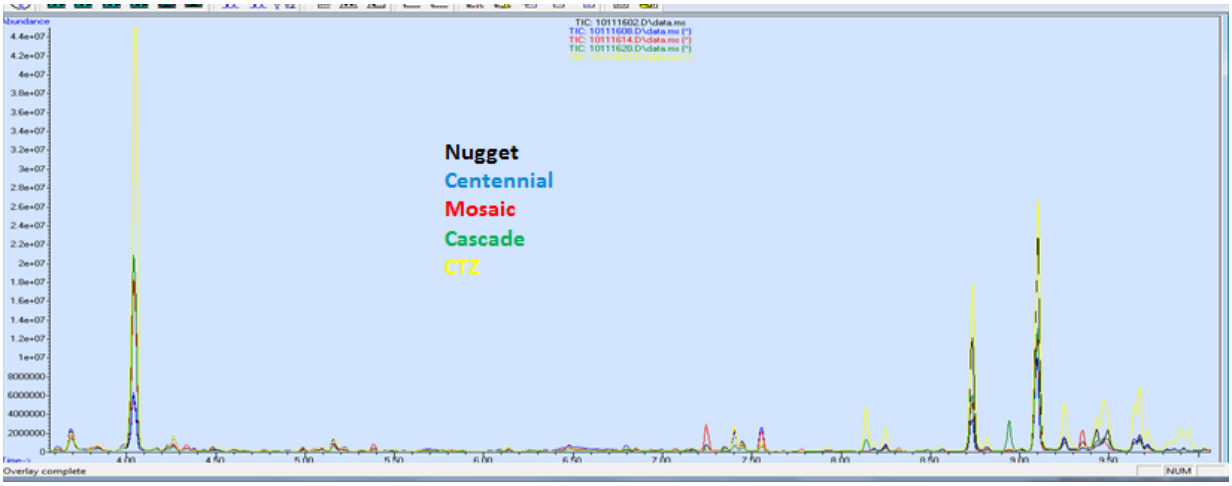
Flavoring Profile Study

Once the optimal method was determined, the hops samples in sealed vials were loaded in the Versa carousel and analyzed. Total Ion Chromatograms (TIC) were used to give a qualitative representation of terpenes in five different hops samples. Figure 3 shows the TIC overlay of all five hops samples.

Figure 3 Total Ion Chromatogram of Five Hops Samples



It was determined from the TIC that the major compounds identified in the hops samples were Myrcene, Caryophyllene and Humulene, all of which are key to defining the flavor and aroma of the resulting beer. Myrcene is known to provide herbal and resinous aroma, while Humulene provides woody and piney aroma. Looking closer at an Extracted Ion Chromatogram (EIC), the CTZ hops can be seen to have a Myrcene concentration much higher than other varieties (Figure 4). This also can be seen for Caryophyllene and Humulene (Figure 5).

Figure 4 Zoomed in EIC of Myrcene

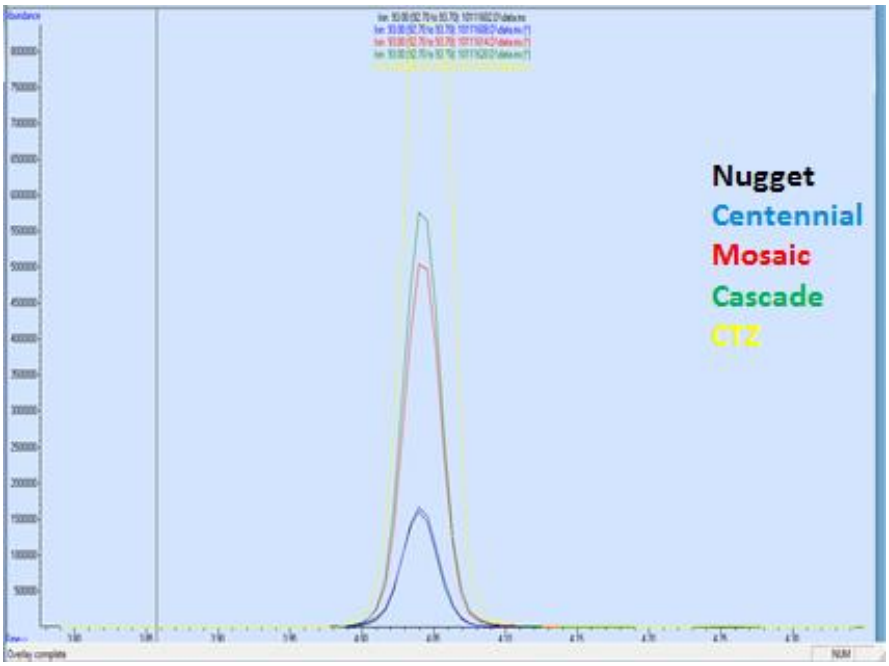


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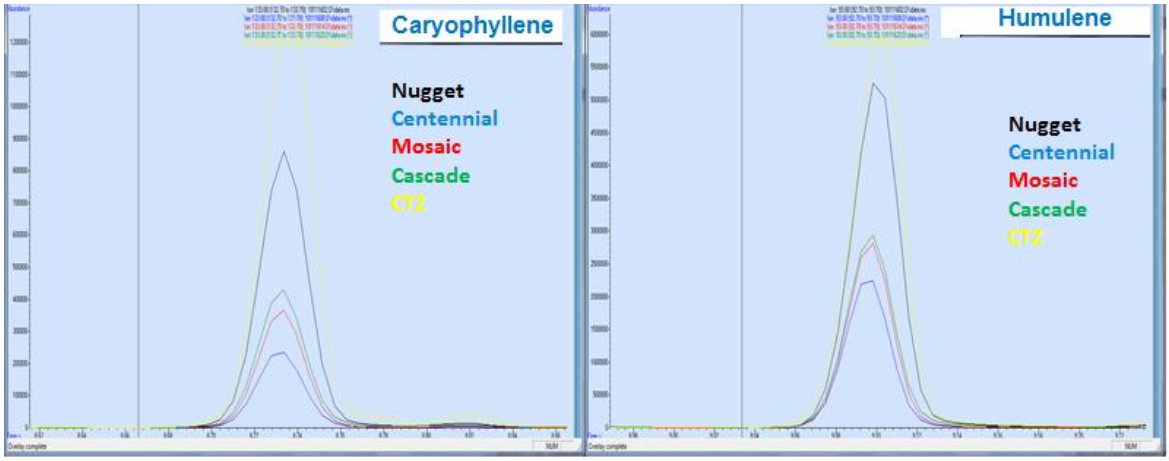
Figure 5 Zoomed in EIC for Caryophyllene and Humulene



Conclusion

The Teledyne Tekmar Versa Automated Static Headspace vial sampler coupled with GC/MS successfully used a Full Evaporation Technique (FET) to quantify terpene compounds in hops samples. By using static headspace, the GC injection liner was protected from nonvolatile sample components. Sample quantity was small, using the FET (10.0 mg) and sample preparation was minimal. This configuration provided a simple and effective flavor profiling solution for hop analysis.

References

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