APPLICATION NOTE

Gas Chromatography

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Aroma Study of Potable Spirits

Introduction

The production of whisky requires maturation in wooden casks for the full development of the finished product's character. Subtle differences in the casks' conditioning can produce quite different flavors and aromas that require skillful blending to achieve a consistent product. The PerkinElmer TurboMatrix™ headspace trap system coupled with a Clarus® SQ 8 GC/MS and SNFR™ olfactory port is an effective means of identifying low concentration volatile organic compounds (VOCs) in potable spirits.

Manufacturing whisky is a lengthy process due to Scottish law, which mandates that the distilled spirit be matured in oak casks for a minimum of three years and one day before it is bottled. During the maturation process the spirit takes on a distinct character in each cask, which must then be blended to give the recognized finished product. Much of the blending is performed by the master blender, a craft that can take 12 years in apprenticeship. One of the key characteristics of whisky enjoyment is the aroma from the spirit with a recently designed copita (a tulip-shaped sherry glass), having been developed to maximize this experience. Functional groups that give character to whisky include alcohols, esters, acids and carbonyls, and the odor thresholds of these analytes of interest vary greatly by each group.

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Work by Salo[1] et al. explained that the majority of whisky's odor contribution comes from carbonyl compounds. Yet it is interesting to note that, while carbonyl compounds are the most prevalent odor components, of the compounds present they have the smallest combined mass with alcohol being a major component as whisky is legally required to be a minimum of 40% alcohol by volume.

There is usually some discussion among consumers as to the correct way to enjoy whisky. The range of opinions include; neat from the bottle with no change, in a chilled glass, over ice to chill the spirit or with the addition of some volume of room temperature water. The most common comment about ice is that the ice will melt adding water to the whisky. Not unsurprisingly the effect of temperature on the partitioning of flavor components into the headspace above the spirit is rarely discussed. When attempting to determine water's influence on the consumer experience, headspace sampling provides the capability to capture those headspace components and closely mimic the customer experience as they were enjoying a dram. After GC separation a mass spectrometer can identify those components that the consumer experiences at an olfactometry port enabling a detailed analysis of the direct customer experience

One of the unique challenges with headspace sampling versus the human interaction is determining the sample volume. Given the many compounds and the wide variation in their odor thresholds, to compare the headspace results with the direct sampling of the human nose from the glass a large injection of vapor is desirable. To achieve that goal the headspace vapor is collected on an absorbent trap using the TurboMatrix HS trap system.

In this application note, the VOCs in single malt whisky were investigated. Sample preparation simply involved dispensing a fixed volume of whisky into a sample vial and sealing it. The headspace vial was then sampled for GC separation with MS and olfactometry detection Figure 1.

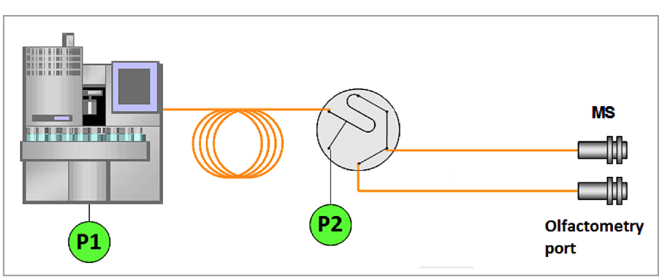

Figure 1. Instrumentation overview with headspace sampling, GC separation with MS and olfactometry detection.

Experimental Conditions

The PerkinElmer TurboMatrix HS trap increases the headspace volume that can be sampled by evacuating the entire sample vial onto an adsorbent chemical trap. A significant advantage of the HS trap is the capacity of the trapping material, which is greater than that yielded by other techniques such as SPME. The selected trap is an air monitoring trap, which has excellent trapping properties for a wide variety of compounds from different functional groups. The trapping material is also hydrophobic, which assists with water management from the sample. This sample preparation consisted of 3 mL of sample pipetted into a vial and capped. The vials were thermostatted at 35 °C to mimic being held in a manner consistent with a consumer. Full experimental conditions are described in Table 1.

Table 1. TurboMatrix HS-110 Trap

Needle	100 °C
Oven	35 °C
Transfer line	120 °C
Trap Low	30
Trap Hi	300
Vial pressurization	1 minute
Vial desorb	3 minutes
Dry purge	10 minutes
Trap hold	5 minutes
Desorb	0.1 minutes
Thermostat	15 minutes
GC cycle time	72 minutes
Carrier pressure	52 psi
Desorb pressure	52 psi
Vial pressure	40 psi

Table 2. GC Conditions Injectors

GC conditions injectors	Both at 250 °C
Oven program	40 °C (no hold) ramp 4 °C/min to 240 °C (hold for 8 minutes).
Column	60 m x 0.32 id wax column

Table 3. MS Conditions

Transfer line temperature	200 °C
Source temperature	180 °C
Mass range	30 – 300 m/z
Scan time	0.2 sec
Interscan delay	0.1 sec
Ionization mode	EI+
Run time	58 minutes

Swafer Micro-Channel Flow Technology

The S-Swafer™ employed here allows for the manipulation of the column flow rate and sample separation without impacting the active split between the mass spectrometer and olfactory port. Split ratios and flows are results of the selected transfer line geometries and carrier gas pressure(s). The addition of the second pressure source regulates the splitting and maintains the engineered configuration independent of the column head

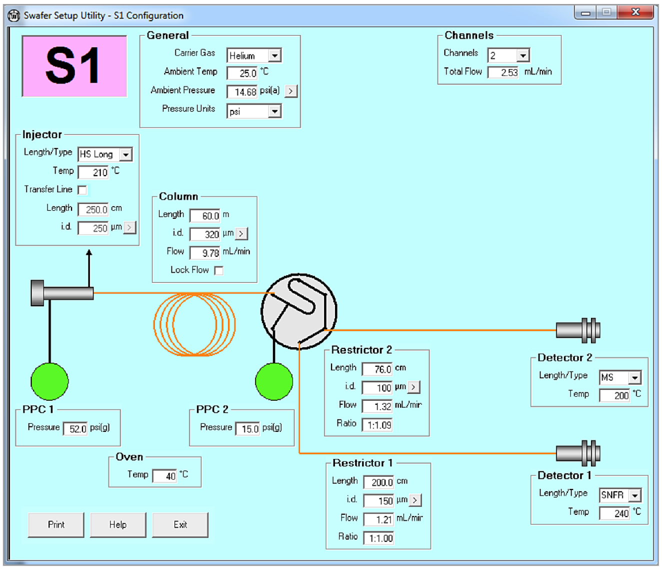

Figure 2. Swafer™ utility software describing dimensions and calculated flows.

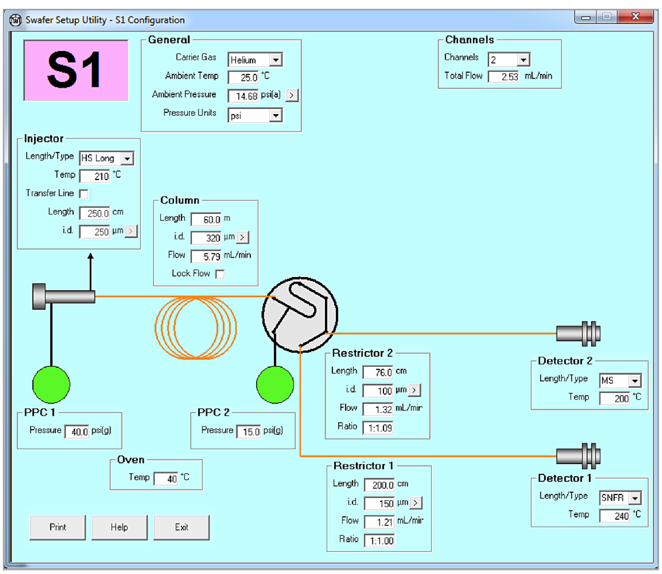

Figure 3. Swafer™ utility software describing dimensions and calculated flows. The adjusted column pressure, PPC1, has not changed the flow rates to either detector giving more freedom to adjust the separation conditions.

pressure and maintains a stable flow into the MS detector and olfactometry port. Independence from the column head pressure increases the flow rate options available to a chemist in the separation. The separation is critical from both an identification and a human interaction standpoint. It can be desirable to have a greater separation than is typical for GC to give a human analyst the opportunity to identify what they are experiencing as certain components are persistent and can mask other more subtle scents of less intense compounds. Therefore, a 60 m x 0.32 id wax column was used with a GC oven program starting at 40 °C and ramping 4 °C/min to 240 °C (hold for 8 minutes).

Swafer™ utility software shown in Figure 2 details the dimensions and calculated flow rates that were employed in the study. The screen capture in Figure 3 demonstrates that changing the column head pressure from 50 psig to 40 psig adjusted the analytical column flow rate but had no impact on the flow rates to both detectors, and thus no impact on the split ratio between the detectors.

Results

The chromatogram in Figure 4 shows the comparison of a neat 12 year old single malt Glenlivet® scotch and the same scotch with water added. There are obvious differences in the alcohols and ester concentrations in the headspace.

The ethyl decanoate has a fruity fragrance, with a more subtle fruity odor and a somewhat waxy odor as well. Characteristic whisky odor is 3-methylbutan-1-ol with 2-methylpropan-1-ol, which has a malty odor. The addition of water to neat whisky has a significant increase in those compounds in the headspace.

The addition of increased volumes of water, in this case 2 mL Figure 5, further highlights the impact on the selected odor compounds. Ethyl octanoate, ethyl decanoate and 3-methylbutyl acetate show increased concentration in the headspace (all of which have fruity odors), whereas the alcohols are decreased in concentration as the partition changes to flavor the whisky with water. Such changes make the whisky smell fruitier. Another

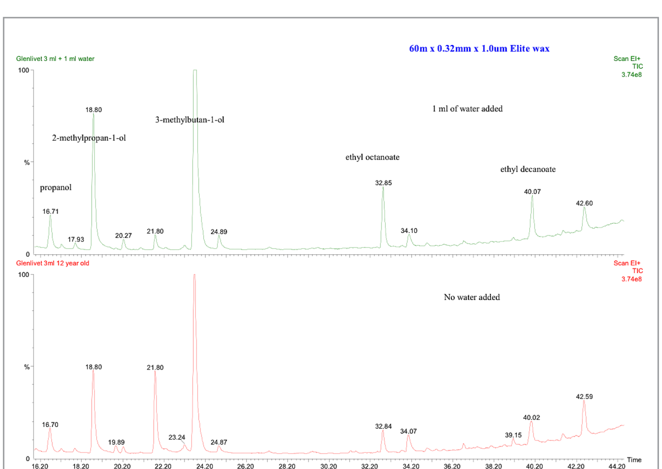

Figure 4. The effect of water to a sample of Glenlivet® is apparent with the increase of ester and alcohol compounds in the headspace.

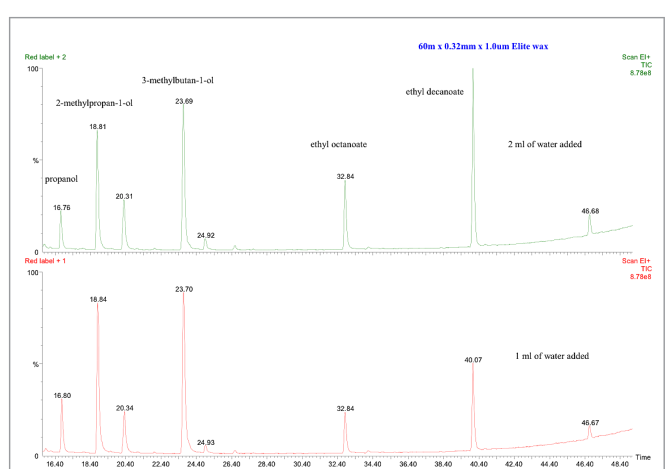

Figure 5. The effect of water to a sample of Glenlivet® is apparent with the increase of ester and alcohol compounds in the headspace.

interesting observation is that alcohol can desensitize the nose and can be recognized as a tingling sensation. Reducing the ethanol in the headspace then limits the desensitization further allowing enjoyment of the compounds present in the case of blended whisky there are also changes to the headspace due to the addition of water (see Figure 6). The changes are primarily the increase of analyte concentration in the headspace but the compounds at 33.98 and 34.94 minutes decrease in the headspace. The balance of flavors and odor compounds is changed by the addition of water.

A comparison of Glenlivet® with Dewar's® and Jim Beam brands (Figures 7 and 8, respectively) shows the distinct qualitative and quantitative differences between samples.

Conclusion

The addition of water to whisky changes the partitioning of the odor compound(s), which changes their concentration in the headspace and, by extension, in the liquid. Remaining compounds will impact the "mouth feel" and balance of the finished product and as such, the addition of water becomes very much a matter of taste.

Given the different starting materials and the fact that the "magic" of aging whisky differs from brand to brand, a consumer may add more water to some whiskies than to others.

References

1. P. Salo, L. NyKanen, and H. Suomalainen, J. Food Sci., 1972, 37, 394.

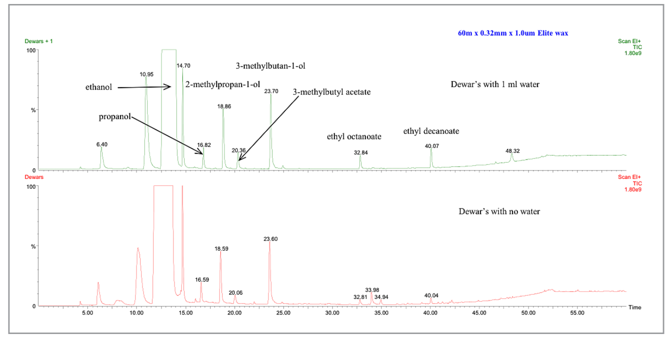

Figure 6. Blended Dewar's® whisky with and without water.

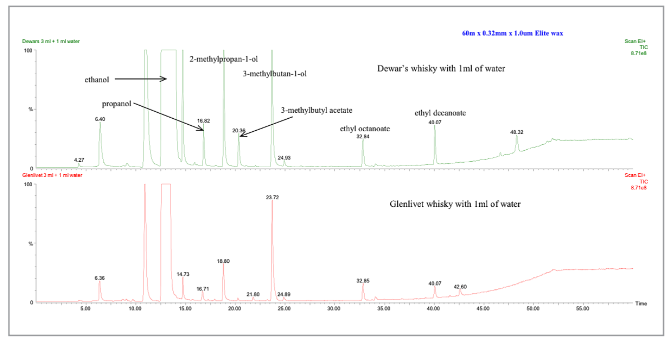

Figure 7. Comparison of Dewar's® and Glenlivet® with 1 ml of water added. Note that there are qualitative and quantitative differences between the headspace of two whiskies with the same amount of water added.

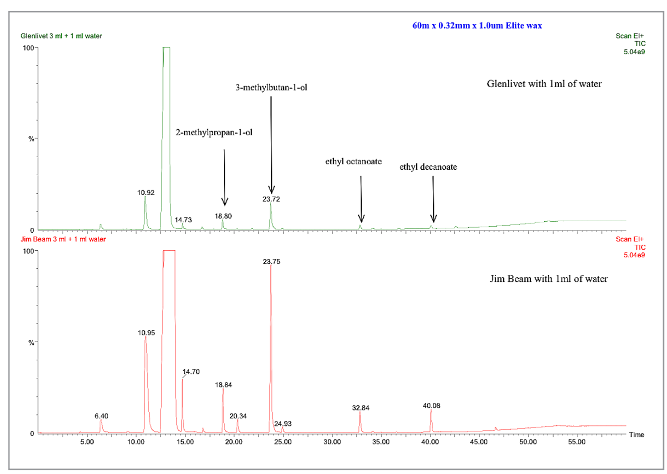

Figure 8. Comparison of single malt and bourbon whisky with water added.

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