The BooZi Device's Effect on Aroma Compounds in Distilled Spirits

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The BooZi is a commercially available flavor-modifying device that claims to remove the negative flavor agents (congeners) from a number of different types of distilled spirits and wines. SPME was utilized for the extraction of the volatile and semi-volatile compounds within each sample. The analysis of the compounds found in the samples following exposure to the BooZi device were analyzed using a GC-MS. The most significant changes regarding the aroma profile of the distilled spirits were noticeable following 96 hours of exposure. The BooZi device was shown to be effective in reducing the concentration of a number of compounds, including 21 compounds having statistically significant changes. It was determined that the reduction of the compounds is associated with the mass of the product and the exposure time. This study has shown the effectiveness of the BooZi device in reducing the congeners within the distilled spirts samples tested. This will likely have an impact on the spirits' flavor and aroma.

Keywords: aroma; gas chromatography; mass spectroscopy; solid-phase microextraction; liquor; molecular sieve

Introduction

BooZi, is a consumer product designed to reduce impurities in liquids. The manufacturers of BooZi claims that the product has the ability to effectively remove chemicals (congeners) from a wide range of alcoholic and non-alcoholic beverages by making the beverage more "pleasant" to the consumer. Congeners provide flavor and aroma to alcohol and distilled beverages. The BooZi is designed as a molecular sieve, to absorb impurities, while being passively exposed to the beverage. With the elimination of these negative chemicals the beverage would ultimately provide a more enjoyable consumption experience and therefore reducing the negative effects of over consumption. To address these claims, an independent analysis of the effectiveness regarding the BooZi device's ability to remove a number of volatile and semi-volatile aroma compound in a wide range of distilled spirits was undertaken and reported here.

Distilled spirits are characterized in part by the volatile and semi-volatile compounds present in the aroma profiles; this includes alcohols, esters, carboxylic acids, carbonyl compounds, and furan derivatives (Bortoletto & Alcarde, 2013; Lea & Piggot, 2003; M.C. Meilgaard, 1975; M. C. Meilgaard, 1982; Verstrepen et al., 2003). While a number of these compounds are common to a wide range of distilled spirits, they differ in the relative amounts present. This is partially due to the wide range of raw materials, fermentation metabolic pathways, distillation, aging, and exposure to aging containers such as oak barrels (Abad, 2016; Bryson, 2014; Christoph & Bauer-Christoph, 2007; Lea & Piggot, 2003; M.C. Meilgaard, 1975; Reazin, 1981; White & Zainasheff, 2010). These distinctions provide a wide range of chemicals which lead to the distinct flavor and aroma profiles attributed to each different type of distilled spirit. Negative congeners are also imparted into the distilled spirit. These compounds can negatively affect flavor perception, introduce unpleasant flavors and aromas, or may have potential negative effects on health from long term or chronic exposure (Blot, 1992; Damrau & Liddy, 1960; Pihl, Smith, & Farrell, 1984; Swift & Davidson, 1998).

The development of complex chemical aroma profiles of a wide range of distilled spirits has been the focus in recent years (Conner, Paterson, & Piggot, 1994; López-Vázquez, Herminia Bollaín, Berstsch, & Orriols, 2010). Currently, more than 300 volatile and semi-volatile compounds have been identified in the most common types of distilled spirits; gin, vodka, rum, brandy, and whiskey (Heymann & Ebeler, 2017; Lea & Piggot, 2003; Nykänen, 1986; Nykänen & Suomalainen, 1983). In addition, the correlation between key chemical species and aroma and flavors has been performed (Heymann & Ebeler, 2017). There have been several studies on the chemicals contained in the aroma of beverages and several acceptable methods for this analysis have been established (Ferrari et al., 2004; Fitzgerald, James, MacNamara, & Stack, 2000; MacNamara, 1984; Nascimento, Cardoso, & Franco, 2008; Ng, Hupé, Harnois, & Moccia, 1996; Rodrigues, Caldeira, & Camara, 2008).

Similar to beer and wine, distilled spirits are a major agricultural product manufactured throughout the world. The distinct flavors of these products are produced by raw materials, starter culture, fermentation, distillation and/or further processing, and maturation (Christoph & Bauer -Christoph, 2007; Lea & Piggot, 2003). Distilled spirits can be separated into two categories: 1.) distilled spirits and 2.) liqueurs. Distilled spirits generally have a higher alcohol content ranging from alcohol by volume (ABV) 30 – 50% (60 – 100 proof), while liqueurs are generally lower at ABV 15 – 45%. The flavor compounds associated with distilled spirits are produced not only by the fermentation of the raw products, but by distillation, storage, and aging. Liqueurs as previously stated tend to have a lower alcohol content, but also obtain their distinctive flavors from more than just the raw materials used during the fermentation process. Liqueurs are generally produced by blending or dissolving several different products together. Liqueurs can vary from high strength to lower strength specialty products, cream liqueurs, aperitifs, and mixed drinks(Lea & Piggot, 2003). The concentration of aroma compounds found in distilled spirits and liqueurs can vary greatly, along with the odor attributes and their perceived threshold levels within a product (Christoph & Bauer-Christoph, 2007).

The concentration of aroma compounds found within distilled spirits can vary from 0.1 to 1,000 ppm. Flavor compounds are traditionally produced during the fermentation process by the yeast (*Saccharomyces cerevisiae)* and other microorganisms that will metabolize the carbohydrates, amino acids, fatty acids, and other organic compounds. The yeast that carry out the primary fermentation process produce the primary flavor products ethanol, glycerol, and carbon dioxide, as well as the secondary products like aldehydes, ketones, higher alcohols, organic acids, and esters. The esters produced during the primary fermentation are "fermentation-by-products" or "congeners" (Bortoletto & Alcarde, 2013; Christoph & Bauer-Christoph, 2007). Esters are the largest group of flavor compounds with the most pleasant properties. Esters tend to play an important role in the flavor and aroma profile of distilled spirits due to the number of compounds found within the product as well as their concentration. Many esters can be found to be above their sensory threshold level, particular a number of the low boiling point ethyl esters like ethyl 2-methylbutanoate, ethyl hexanoate, and ethyl octanoate, and the acetates like ethyl acetate, isoamyl acetate, isobutyl acetate, hexyl acetate, and 2-phenethyl acetate. These compounds play an important role in the flavor of distilled spirits. Esters are produced as a by-product of biochemical reactions of acetyl coenzyme A with alcohols. Ethyl acetate, is the primary ester found in fermented beverages as well as distilled spirits because ethanol is the alcohol present in highest concentration and is most likely to react with acetic acid. At lower concentrations it can produce a fruity aroma, however at concentrations close to or above 400 ppm it can be perceived as having a solvent-like nail polish off-flavor (Christoph & Bauer-Christoph, 2007; Conner et al., 1994; Nykänen, 1986; Nykänen & Suomalainen, 1983; Verstrepen et al., 2003).

Methanol, 1-butanol, and 2-butanol are not compounds produced during the fermentation process, but are characteristics of the raw material utilized (Christoph & Bauer-Christoph, 2007; Lea & Piggot, 2003). Their detectable threshold values are generally higher and therefore tend to not have a significant impact on the flavor of the product (Heymann & Ebeler, 2017). 1-butanol concentration levels tend to fall below 3 ppm for cherry distillates and as high as 100 ppm for other fruit distillates. Higher alcohols also known as fusel alcohols are by far the largest group of volatile compounds produced from the degradation of amino acids via keto acids. The most important higher alcohols are: 1-propanol, 2-methyl-1-propanol, 2-methylbutnaol, and the aromatic alcohol 2-ethylphenol. Fusel alcohols generally confers a malty/burnt flavor (Nykänen, 1986; Nykänen & Suomalainen, 1983). Excessive amounts of higher alcohols can result in a pungent or “fusel-like” smell, while optimum concentrations can produce a fruity characteristic.

The aim of the present study was to quantify the effectiveness of the BooZi on the chemical aroma profiles of beverages and explore the effect of exposure time on these chemicals. In addition, the effect of the exposure of solutions of isobutanol and 1-butanol (known volatile components of many distilled spirits) to various masses of BooZi material has been performed to quantify the loss of these chemicals. In both cases, the concentration of aroma compounds was expected to decrease following the exposure to the BooZi. In addition, the length of exposure to the BooZi should increase the observed effects. For this purpose, a head-space solid phase micro-extraction (HS-SPME) method coupled with gas chromatography-mass spectroscopy (GC-MS) was adopted and used for the quantitative and semi-quantitative characterization of the volatile and semi-volatile aroma profiles of a wide range of distilled spirits before and after exposure to the BooZi material.

Materials and Methods

Liquor Samples

A list of the type and number of each liquor tested is listed in Table 1. All liquor samples were purchased from a local retailer. The beverages were stored at room temperature and left unopened until prior to analysis. The exposure to the BooZi material was performed in the product container after the initial sample was removed. After the exposure period was completed the BooZi material was removed from the container. The sample volume of the beverage samples ranged from 750 mL to 1.5 L.

BooZi Product

The BooZi products were supplied by the company and delivered in lots of twenty. Each BooZi was individually prepared and activated based on manufacturer’s instructions by soaking the BooZi device in approximately 1 L of distilled water initially at 100 °C. Each BooZi device was soaked in hot water for approximately 3 minutes while continuously stirring the water using a stir bar. The BooZi device was then transferred directly into a newly opened liquor container. All liquor bottles were opened immediately before the introduction of the BooZi device.

Reagents and Standards

Sodium chloride (NaCl) was obtained from EMD Chemicals Inc. (Darmstadt, Germany), 2-heptanol from TCI (Tokyo, Japan), isobutanol, and 1-butanol were obtained from Alfa Aesar (Heysham, England) and were used as supplied. The internal standard for the GC-MS analysis was prepared using 200 mg/L of 2-heptanol in ethanol and used throughout the study. Compounds were compared to the internal standards and reported as relative response values. All solutions were stored in a dark cabinet at room temperature.

Time point sample collection

Approximately 125 mL of the liquor was poured into a storage bottle. The activated device was then placed into the product bottle containing the remaining liquor. At each time point (0, 24, 48, 72, & 96 hours for liquor) a new 125 mL aliquot was removed from the product bottle placed into a new storage bottle. This method was selected to approximate the regular consumption of the beverage by the consumer. All samples were stored at room temperature until analysis was performed, which was following the collection of all timepoints. From the removed aliquot the sample was taken for the following analyses: volatile compounds via GC-MS with SPME extraction, and specific gravity.

Controlled Experiments

Isobutanol and 1-butanol solutions were prepared at three different concentration levels shown in Table 2. These solutions were then placed into a 250 mL storage container with varying masses of the BooZi material (Table 2). A 10 mL aliquot was taken from each sample solutions and analyzed using SPME-GC-MS analysis every 24 hours for a total of three days.

Method for Volatile Compounds in Liquor

Sample preparation

A 10 mL aliquot sample of each liquor sample was added to a 20 mL headspace analysis vial. For the analysis of the liquor, because of a high percentage of ethanol, three mL of liquor were added to seven mL of water. In order to force as much of the semi-volatiles out of solution, three grams of sodium chloride were also added to the vial. All sample vials were spiked with 50 µL of an internal standard, containing 200 mg/L of 2-heptanol. The vial was then transferred to the GC-MS for analysis.

SPME extraction

A divinylbenzene-carboxen-polydimethylsiloxane 50/30 µm (DVB/CAR/PDMS) fiber was selected for the analysis because it has been shown in the literature to provide reasonably high extraction efficiencies for a wide range of chemical compounds (Rodrigues et al., 2008; Staffolo, Bertola, Martino, & Bevilacqua, 2004). The fiber was conditioned according to the manufacturer’s instructions by inserting it directly into the GC-MS injector at 250 °C for 30 minutes. The sample was agitated and allowed to equilibrate at 40 °C for 10 minutes prior to exposure of the fiber. The fiber was exposed to the headspace of the vial for 30 minutes while being agitated (250 rpm). The fiber was then inserted into the GC-MS injector and deabsorbed for a total of 2 minutes at 250°C to allow for sample analysis.

GC-MS

Gas chromatography – mass spectroscopy (GC-MS) was carried out using a Shimadzu GC-2010 coupled to a QP2010 SE quadrupole mass spectrometer. A Rxi-5Sil MS column (30 m X 0.25 µm I.D.) with a film thickness of 0.25 µm was used. The GC was equipped with a split-splitless injector which was held at 250 °C. The analysis was performed with a splitless injection over the two-minute desorption time. The GC oven was initially set to 30 °C with a two minutes hold and then was raised in three steps: 30-70 °C at 10 °C/min and held for one minute; 70-220°C at 4°C/min and 220-270 °C at 20 °C/min and finally held at 270 °C for 6 minutes. The response of the mass spectrometer was monitored in TIC mode from 35-280 m/z. Compounds were identified via match to the NIST Mass spectra library.

Statistical Analysis Methods

The relative response relative to the internal standard, 2-heptanol was calculated because response factors are not available for all compounds determined. Compounds were correlated for the initial and 96-hour time points using a combination of retention time and spectral matched compound name. At no point was the BooZi device not completely submerged in the liquor.

Identifying Compounds with Significant Changes

Compounds that were found to have six or more occurrences within the data set were selected for further statistical analysis. Compounds, which met the occurrence requirement, were tested using a Wilcoxon signed rank test to compare the distribution of concentrations at the initial time and 96 hours after introduction of BooZi. The Wilcoxon signed rank test is the nonparametric equivalent to the paired t-test. The Wilcoxon signed rank test is appropriate for smaller data sets where there is uncertainty in

Table 1: A list of the type and number of each type of liquor tested. When multiple liquors of one type were tested, a difference in retail price was used to infer quality. In addition, some liquor types include a variety that has added flavor indicated by the *. The sampling frequency is also included.

Number	Liquor Type	Untreated	24 hour exposure	48 hours exposure	96 hour exposure
1	Vodka 1	X	X	X	X
2	Vodka 2	X	X	X	X
3	Vodka 3	X	X	X	X
4	Vodka 4*	X	X	X	X
5	Gin 1	X	X	X	X
6	Gin 2	X	X	X	X
7	Scotch1	X	X	X	X
8	Scotch 2	X	X	X	X
9	Whisky 1	X	X	X	X
10	Whisky 2	X	X	X	X
11	Bourbon	X	X	X	X
12	Cognac	X	X	X	X
13	Tequila 1	X	X	X	X
14	Tequila 2	X	X	X	X
15	Rum 1	X	X	X	X
16	Rum 2	X	X	X	X
17	Rum 3*	X	X	X	X
18	Kahlua	X	X	X	X
19	Fireball	X	X	X	X
20	Jagermeirter	X	X	X	X

Table 2: A) Shows the effect of BooZi loading (0.1, 0.5, 1.0 grams) as a percent decrease from the initial concentration of the 1-butanol (10, 50, and 100 mg/L). B) Shows the effect of BooZi loading (0.1, 0.5, 1.0 grams) as a percent decrease from the initial concentration of the isobutanol (100, 500, and 1000 mg/L).

A) 1-butanol

Concentration (mg/L)	100			50			10		
Mass BooZi (g)	1	0.5	0.1	1	0.5	0.1	1	0.5	0.1
Day 1	57%	42%	33%	61%	51%	25%	63%	47%	19%
Day 2	70%	40%	32%	71%	56%	36%	71%	60%	14%
Day 3	67%	54%	44%	71%	55%	36%	71%	61%	14%

B) Isobutanol

Concentration (mg/L)	1000			500			100		
Mass BooZi (g)	1	0.5	0.1	1	0.5	0.1	1	0.5	0.1
Day 1	65%	49%	35%	71%	55%	28%	67%	54%	22%
Day 2	75%	54%	31%	82%	63%	32%	84%	75%	29%
Day 3	76%	58%	38%	82%	65%	30%	92%	83%	27%

meeting the Normality assumption. Adjusting *p*-values according to the Benjamini-Hochberg method controlled inflation of the Type I Error rate in multiple testing. This method controls the false discovery rate, which allows for more power than the conventual approach of controlling family-wise error rate.

Results and Discussion

Controlled experiments

Most distilled spirits contain small amounts of compounds other than alcohol. Congeners are complex organic molecules that have been shown to have some toxic effects. Acetone, acetaldehyde, furfural, and higher alcohols or fusel alcohols (2-methyl-1-butanol, isoamyl alcohol, isobutyl alcohol (isobutanol) and n-propyl alcohol) are all examples of commonly found congeners in distilled spirts (Cai, Rice, Koziel, Jenks, & van Leeuwen, 2016). There was a distinct reduction in both isobutanol and 1-butanol (shown as a % reduction in Table 2). The greatest decrease occurred within the first 24 hours. The concentration of both compounds (isobutanol and 1-butanol) in some cases continued to decrease over the entire testing period. There appeared to be a small decrease in the concentration of both compounds following 120 hours of exposure to the BooZi device (not shown). However, there was not a significant difference in isobutanol and 1-butanol in the relative size or shape.

There is an apparent relationship between the amount of BooZi material added to the sample matrix and the observed reduction. The greatest reduction in the concentration of the two selected congeners occurred when the largest amount of BooZi material was added to the sample matrix. In all cases the overall percent reduction was largest at the higher BooZi load and approached 90% compared to approximately 30% for the lowest BooZi load. The amount of BooZi material appears to be more important than the initial concentration of the selected compound

(1-butanol or isobutanol). The smallest reduction of both congeners was observed when the lowest amount of the BooZi material was placed in the lowest concentration of the compounds. This observation is not unexpected in that the BooZi device is a molecular sieve and the reduction of the compounds is based upon the interaction of the liquid sample with the porous material. When probability of the compound interacting with the material is small, which would exist when the concentration of compound is relatively low and the amount of material is small, the effect of the product is the smallest.

Analysis of Liquor

Specific gravity and general properties

The specific gravity of each of the distilled spirits was measured every time a sample was collected for analysis. The BooZi device did not have an effect on the specific gravity of any of the distilled spirit samples. Although one might expect to see a change in the specific gravity following a significant change in the overall chemical composition of the sample matrix. However, the chemical compounds (congeners) in question are present in such low concentrations (ppb/ppm) that their removal from the sample matrix would have little to no effect on the overall specific gravity in comparison to ethanol.(Lea & Piggot, 2003) Ethanol is considered a primary flavor compound in a number of fermented beverages like distilled spirits, wine, and beer (Pires, Teixeira, Brányik, & Vicente, 2014).

Volatile and semi volatile compounds

The SPME fiber selected will play a role in the extraction of target compounds of interest within the food or beverage analyzed (Roberts, Pollien, & Milo, 2000). The number of compounds detected is in small part a function of the fiber's polarity and the volatility characteristics will determine what compounds make it into the headspace that will then be extracted for analysis. SPME fiber extraction is based on the interaction between the coating and the vapor molecules, which allows for preferential extractions of specific compounds. The extraction efficiency of both the specific compounds and the internal standard is affected by the composition of the headspace in which the fiber is exposed. To account for these variations the ratio between the compound and the internal standard was used (Rodrigues et al., 2008). The CAR/ PDMS/DVB fiber was selected for this project because of its ability to extract the broadest spectrum of volatile and semi-volatile compounds.

A total of 784 different compounds were identified in the 20 different distilled spirit samples analyzed. As expected, each distilled spirit contained a different number of aroma compounds. This includes differences found in different commercial brands within a specific category of distilled spirit. For almost all distilled spirit types there were more compounds detected in the lower quality brand/version than in the higher tier or quality product. In almost all cases the number of compounds changed between before and after the use of the BooZi device. The changes can be attributed primarily to the exposure to the BooZi device and not loss from evaporation because the initial time point (0 hr) was stored at room temperature until all sampling was completed. If compounds were lost either through evaporation or with reaction with air, it would be expected that the initial sample would be accounted for by this delay in sampling.

As expected with a molecular sieve (BooZi), there was a larger decrease in amount from the large molecular size, regardless of molecular type. And this reduction increases with increasing exposure time. In most cases the lowest relative amount for each compound was observed at the 96-hour sample.

The type of fiber selected has a poor affinity for extracting aldehydes, so a relatively small number of aldehydes were identified. The few aldehydes that were detected all showed a decrease in the concentration amount over the length of the exposure; most showed significant decreases. For example: nonanal ($C_9H_{18}O$), decanal ($C_{10}H_{20}O$), and tridecanal ($C_{13}H_{26}O$) all showed a decrease in amount with exposure to BooZi.

Ethers and carboxylic acids had varied response; very little to no change in small molecules with larger and more significant reduction in larger molecules. For example: N-propyl acetate ($C_5H_{10}O_2$) did not decrease in amount while acetyl octyl ester ($C_{10}H_{20}O$) did. And large carboxylic acids such as octanoic acid ($C_8H_{16}O_2$) and decanoic acid ($C_{10}H_{20}O_2$) both showed a reduction.

The smaller alcohols showed no reduction in the concentration; however, large (fusel) alcohols showed a decrease with increasing length of exposure. For example: 1-decanol ($C_{10}H_{22}O$) and 2-methyl-1-propanol ($C_4H_{10}O$) show no decrease with exposure to BooZi but 1-octen-3-ol ($C_8H_{16}O$) and 1-dodecanol ($C_{12}H_{26}O$) showed a decrease with exposure to the BooZi material.

Statistical analysis

There were a total of 784 compounds identified in the 20 different liquor samples. However, 678 compounds had less than six occurrences. Compounds below the threshold number of occurrences were not subjected to the statistical analysis. The remaining 106 compounds occurred within at least six times over the samples tested. Statistical analysis was performed to determine which compounds within this subset of 106 showed a significant change following 96 hours exposure to the BooZi. The resulting analysis showed there were 23 compounds for which the change was statistically significant. These compounds are shown in Table 3.

The majority of the compounds that showed a significant difference were esters. Since esters are one of the primary groups of flavor compounds which contribute numerous pleasant properties the significant changes in these types of compounds may have resulted in significant changes in perceived flavor and aroma. Esters tend to play an important role in the flavor and aroma profile of distilled spirits due to the number of compounds found within the product as well as their higher concentration. For example, ethyl butanoate, isoamyl caproate, and ethyl heptanoate all contribute fruity aromas and would be considered positive attributes. However, isoamyl decanoate has a waxy aroma and flavor and maybe unwanted. The significant changes observed in these esters could decrease the concentration below their sensory threshold levels.

The one aldehyde that was found to be significantly different following the exposure to the BooZi was 3-methylbutanal. The 3-methylbutanal is a metabolite produced from the yeast and is a positive addition to the aroma. Like the esters a significant change in this compound could result in the concentration falling below the sensory threshold levels.

Conclusions

It has been shown through targeted and non-targeted analysis of distilled spirits that the BooZi effectively removes a wide variety of chemical compounds over the length of the exposure. The BooZi has been shown to be effective in removing chemical compounds in distilled spirits, which will affect not only the flavor but also the quality of the beverage. The impact of the change is a function of the compound concentration as well as the amount of BooZi material involved. It should be noted that while the work showed significant changes in a large number of aroma compounds, the relationship between these changes and any claims made by BooZi, LLC were not investigated and were beyond the scope of this study. While there are wide ranges of compounds that changed in concentration following the 96-hour BooZi exposure, there has not been a complementary sensory study to examine if these changes affect the perceived flavor or aroma.

Author Contributions

Drew Budner collected and analyzed the data, and drafted the manuscript. Lindsey Bell ran all included statistics and gave final approval of manuscript. Katherine Thompson-Witrick assisted with interpretation of the results and drafting of the manuscript.

Table 3: List of compounds based on library identification to be statistically different after 96 hours of exposure to BooZi and the associated corrected *p*-values.

Compound	*p*-Value
Isoamyl acetate	0.0035
1-Dodecanol	0.0027
2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)	0.0004
Octyl ethanoate	0.0039
Ethyl pentadecanoate	0.0017
Anethole	0.0025
3-methyl-butanal	0.0021
Ethyl butanoate	0.0021
Butylated Hydroxytoluene	0.0015
Ethyl decanoate	0.0009
Ethyl laurate	0.0092
Ethyl orthoformate	0.0059
Isoamyl caproate	0.0092
Isopropyl myristate	0.0092
3-methylbutyl octanoate	0.0014
Ethyl heptanoate	0.0092
trans-2-Pinanol	0.0029
Ethyl nonanoate	0.0011
Ethyl octanoate	0.0039
Isoamyl decanoate	0.0105
Guaiacol	0.0021
Phenylethyl Alcohol	0.0059
Ethyl propanoate	0.0059

Notes and References

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