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# Utilizing SPME Arrow and GC-MS to Characterize the Aroma profile of Leading Seltzers Brands

Alan Owens, Jonathan Soffer, Eberhardt Kuhn, Shimadzu Scientific Instruments, Columbia, MD, USA

## Introduction

Whether it's a warm day at the beach or just a weekend afternoon spent at home, an alcoholic or hard seltzer is usually close by. The explosion of the hard seltzer segment has caught the attention of many companies eager to get in on the success. Early in 2018, only 10 hard seltzer brands were on the market. This increased to 26 brands by the beginning of 2019, and now more than 65 brands are fighting for consumers' attention and purchase.

But what sets the industry leading seltzers apart? In this study, two seltzer brands were analyzed via GC-MS. The headspace was sampled via SPME Arrow to extract the major fragrance and aroma inducing compounds. The analytes identified ranged from the major mono and sesquiterpenes to the additional ketones and ethyl esters. By characterizing the headspace of several flavors including: cherry, lime, berry and grapefruit, a side by side comparison was created showing the individuality between the two brands.

Regardless of the flavor variety, compounds such as beta-myrcene, geraniol, D-limonene, linalool, isoamyl acetate and ethyl butyrate were identified at varying concentrations. The use of SPME Arrow in addition to GCMS proves to be a useful advantage not only in the quality control of these beverages, but the R&D for new flavors or even the knowledge of competing flavor profiles.

**Figure 1**: Shimadzu GCMS-QP2020 NX with AOC-6000Plus

## Instrumental Conditions

| GC | | | MS | |
|---|---|---|---|---|
| Inlet | 250C | | Transfer Line | 250C |
| Column | Stabilwax-MS | | Ion source | 200C |
| Carrier Gas | Helium | | Scan | 40-500 m/z |
| Linear velocity | 41.3 cm/s | | | |
| Split ratio | 20 | | | |
| | | | | |
| **AOC -6000Plus** | | | | |
| SPME Arrow | DVB/CAR/PDMS | Incubation Time | 10min | |
| Incubation Temp | 60C | Sampling time | 10min | |

**Table 1**: Analytical conditions

## Experimental Approach

Two major seltzer brands were sampled via HS-SPME Arrow and analyzed on the QP2020 NX single quad. Across the two brands, nine unique flavors were run: black cherry, blueberry acai, grapefruit, lemon, lime, orange, raspberry lime, wild berry, and raspberry. Each of these flavors were run according to the parameters established in table 1.

For each flavor a TIC was acquired and was processed qualitatively in order to characterize the aroma profile from each beverage. Common terpenes and prominent volatile compounds usually found in beverages were identified. A chromatogram for Lemon Seltzer 1 can be found below in Figure 2. The corresponding compounds of interest and their area counts were collated in to table 2.

After all flavors were characterized, three common flavors between two brands were compared qualitatively: lime, grapefruit, and black cherry. The chromatograms were overlaid to distinguish the chromatography and overall display the differences in peak area and height.

## Results

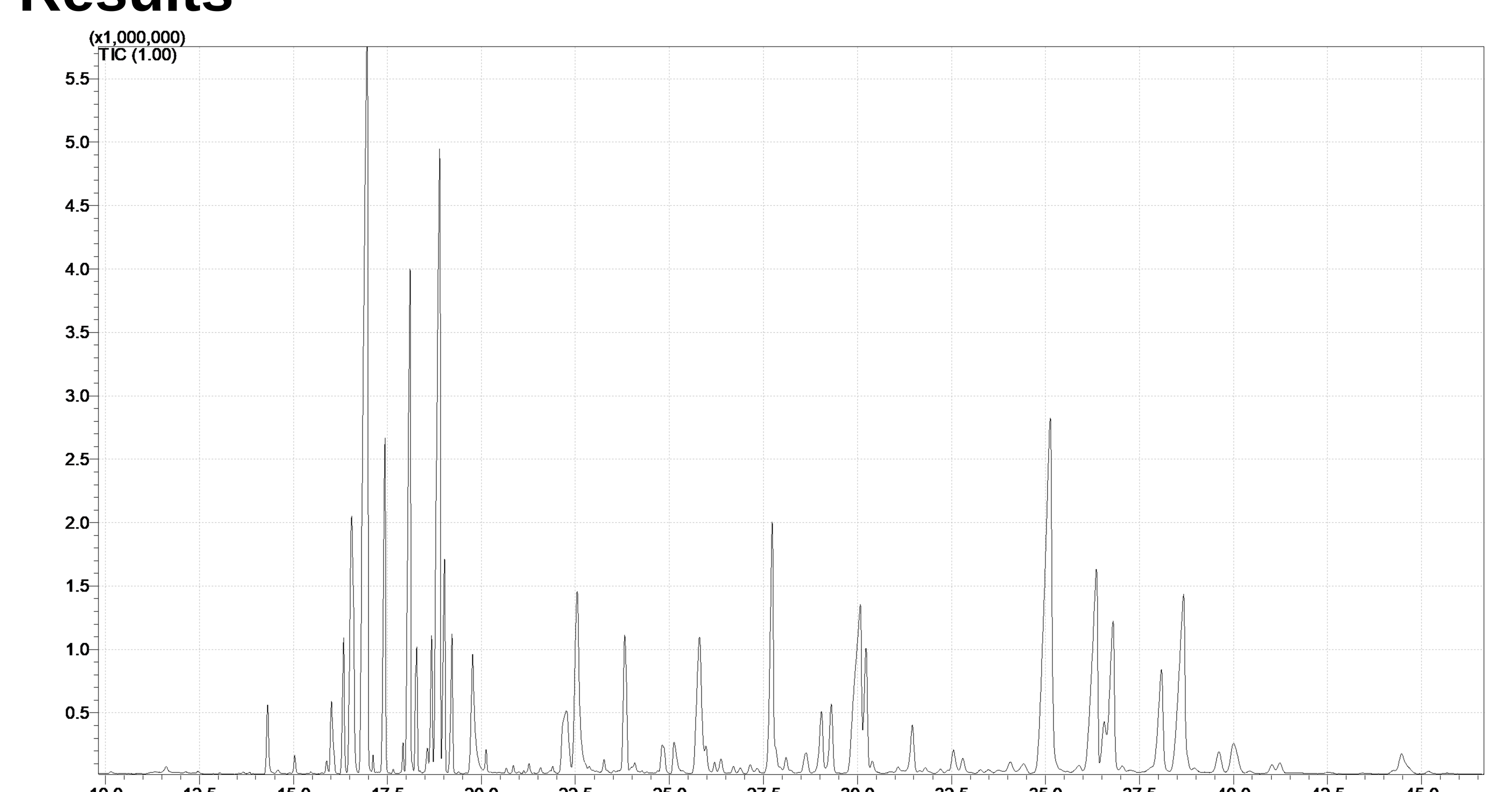


**Figure 2(above) Table 2(below)**: Chromatogram for Lemon seltzer 1 and compound table

| Compound | RT | Area | Height | SI |
|---|---|---|---|---|
| Ethyl Acetate | 5.501 | 608719 | 129869 | 99 |
| Ethanol | 7.085 | 15065536 | 1219638 | 99 |
| Ethyl Butyrate | 11.622 | 48547 | 9677 | 98 |
| Camphene | 12.46 | 15655 | 3592 | 97 |
| Isobutanol | 14.586 | 68133 | 11900 | 97 |
| Isoamyl acetate | 15.035 | 179410 | 48585 | 99 |
| .beta.-Myrcene | 16.011 | 648210 | 135541 | 100 |
| D-Limonene | 16.96 | 8275299 | 1057102 | 99 |
| Eucalyptol | 17.436 | 1172227 | 297366 | 100 |
| .gamma.-Terpinene | 18.102 | 4578834 | 937079 | 100 |
| Acetic acid, hexyl ester | 19.217 | 1239481 | 340769 | 100 |
| Octanal | 19.764 | 788478 | 113458 | 100 |
| Linalool | 20.124 | 79812 | 28363 | 99 |
| Sulcatone | 21.263 | 56211 | 17322 | 98 |
| Nonanal | 22.546 | 1451799 | 168746 | 99 |
| Acetic acid | 25.127 | 593169 | 83530 | 99 |
| Decanal | 25.799 | 913491 | 95016 | 100 |
| (+)-2-Bornanone | 26.878 | 30265 | 5581 | 97 |
| Benzaldehyde | 27.331 | 42307 | 7104 | 96 |
| Linalool | 27.732 | 1656491 | 283383 | 99 |
| 1-Octanol | 28.096 | 77701 | 14376 | 96 |
| Fenchol | 29.304 | 531096 | 91238 | 100 |
| Propylene Glycol | 30.076 | 10420485 | 931807 | 97 |
| .alpha.-Cyclogeraniol acetate | 31.799 | 43475 | 7245 | 95 |
| Isoborneol | 33.261 | 54109 | 7581 | 97 |
| trans-Ocimenol | 33.734 | 13957 | 2257 | 86 |
| .alpha.-Terpineol | 35.123 | 5430672 | 425966 | 99 |
| (-)-Carvone | 37.047 | 87010 | 11569 | 95 |
| .alpha.-Terpinyl acetate | 37.323 | 16441 | 2390 | 95 |
| Geranyl acetate | 38.67 | 3636766 | 330716 | 100 |
| Citronellol | 38.952 | 22276 | 3410 | 94 |
| Geraniol | 44.463 | 392819 | 40038 | 98 |
| Phenylethyl Alcohol | 49.206 | 439799 | 34510 | 99 |
| Caryophyllenyl alcohol | 59.007 | 47683 | 7474 | 98 |

SPME Arrow was extremely effective at recovering several prominent terpenes and aromatics from the lemon seltzer. Limonene and linalool have a clear presence as expected as well as geraniol. Some unexpected detections appeared later in the run with fenchol and caryophyllenyl alcohol. Below are the comparison TICs of seltzer 1 (black) and seltzer 2 (pink). Figures 3,4,and 5show the TICs for grapefruit, black cherry, and lime respectively. Base shift was applied to highlight differences in the chromatograms.

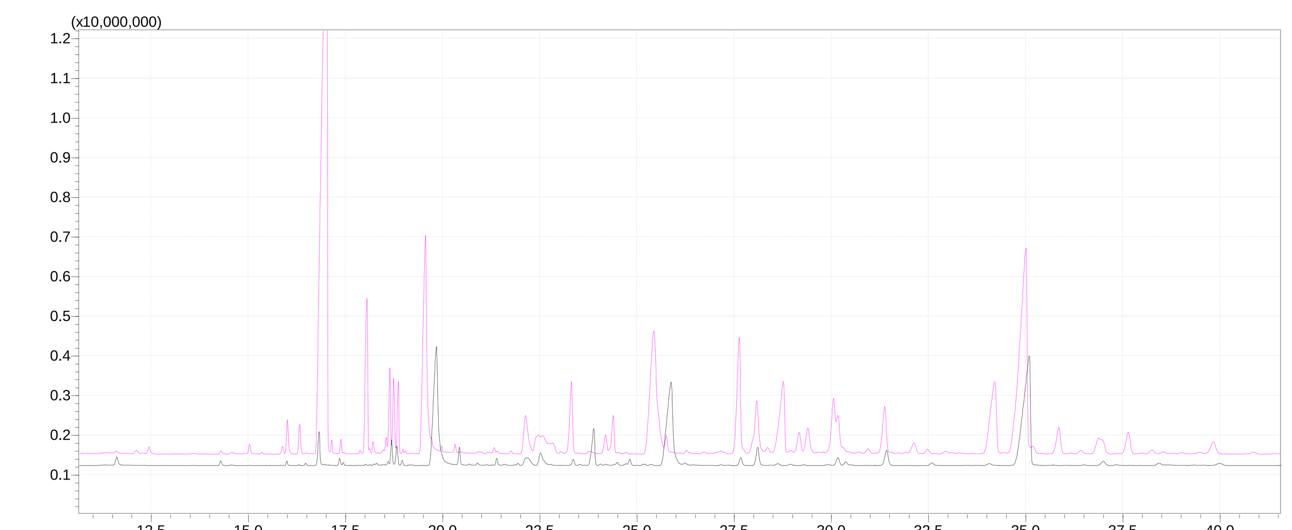


**Figure 3.** Grapefruit chromatogram


**Figure 4.** Black cherry chromatogram

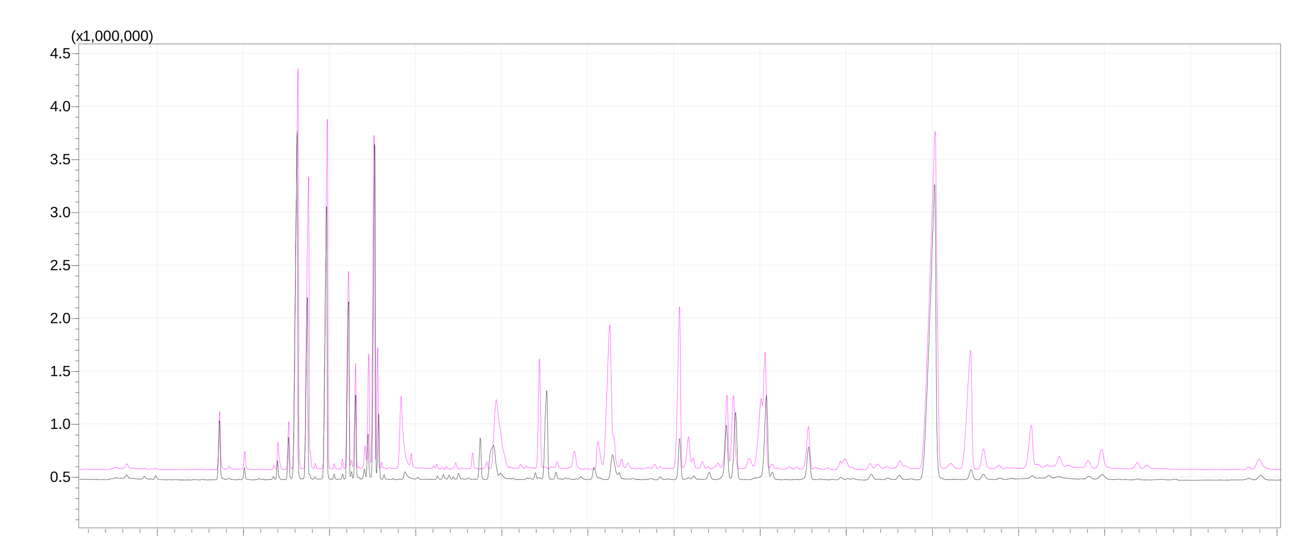


**Figure 5.** Lime chromatogram

## Conclusion

HS-SPME Arrow paired with GCMS proves more than efficient for the characterization of the headspace and aroma profiles of seltzers. The detection of several expected terpenes and additional volatiles that have an affect on taste and aroma, is easily obtainable. The methodology used here also proved useful in comparing multiple brands of seltzers unlocking the potential for quality control and quality assurance capabilities. Further quantitative work is expected to determine overall linearity and effectiveness of the method.