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The Comparison of HS-SPME and SPME Arrow Sampling Techniques Utilized to Characterize Volatiles in the Headspace of Wine over an Extended Period of Time

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Introduction

Increased production of wine in a multitude of regions has led to increased competition as well as an upsurge in demand for quality control. Improving grape-quality and identifying overall compounds that are a direct result of grape quality give wine producers a competitive edge in flavor and aroma control. The quality of wine can be measured by flavor/aroma components making the characterization of the volatiles responsible for these constituents an indispensable task. The volatiles documented ranged from alcohols to molecules like fatty acids and esters1. In order to efficiently analyze these volatiles, analysis was performed by GCMS via two sampling methods: headspace solid phase micro extraction (HS-SPME) and SPME Arrow. Both HS-SPME and SPME Arrow samples were collected over a period of time, analyzing the degradation or disappearance of flavor/aroma volatiles in the headspace of wine. In this study, a comparison between the two sampling techniques and their overall ability to extract volatiles from the headspace of wine over a four month period was reported. It was determined that the SPME Arrow2, which can be seen in figure 1 below, proved to be the more effective technique. The sensitivity of the sampling method allowed for more volatile characterization as well as volatile identification over time. This information will give wine producers new insight to how both flavor and aroma are affected by the ever changing headspace of wine.

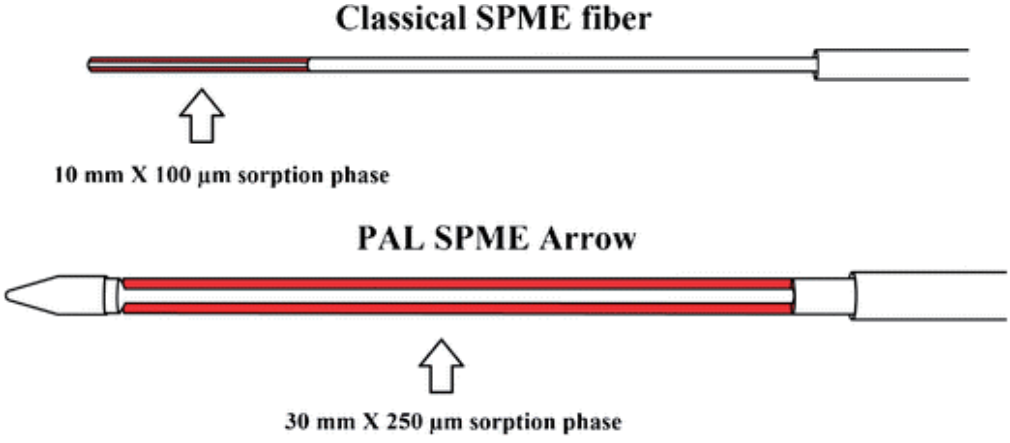

Figure 1: Sorption phase size comparison between classical SPME fiber and PAL SPME Arrow. The original SPME fiber boasts a 100-µm × 10-mm, 0.6-µL sorption phase, whereas the PAL SPME Arrow has a 250-µm × 30-mm, 15.3-µL sorption phase for the 1.5mm diameter model. A 1.1mm diameter is available.

The new SPME Arrow (CTC Analytics) has revolutionized the microextraction sampling technique. The SPME Arrow outlasts the classical SPME fiber with a mechanical robustness that leads to a 2x longer lifetime as well as in increase in sensitivity up to 10x than the original PSME fiber. The design of the SPME Arrow protects the sorptive material minimizing outside factors that could potentially result in loss of analytes.

Experimental

A bottle of Moscato was obtained for the SPME analysis of volatiles in the headspace. Seven milliliter aliquots of the Moscato were transferred to standard 20 mL crimp top vials. The samples were then spiked with 1.5g of sodium chloride to increase ionic strength of the samples, consequently forcing more volatiles into the headspace. The original silicon septa were replace with red high temperature septa to drastically reduce and even eliminate bleed. The two SPME Techniques were both tested utilizing a standard Rxi-5 MS (30m x 0.25mm x 0.25um) column to specifically search for more volatile compounds. The traditional SPME Method was run initially in August when the wine was fresh and unopened. The headspace of the wine was then analyzed again four months later utilizing traditional SPME and SPME Arrow. Qualitative analysis was performed to identify the number of VOCs recovered as well as to compare the relative intensities of the compounds peaks. Table 1 shows the experimental conditions for the GC-MS as well as the autosampler (AOC-6000).

Table 1: Experimental conditions for the instrument acquisition method

SPME Method	**: AOC-6000**
Fiber	: DVB/CAR/PDMS 23ga. Supelco Fiber
Sample Prep (Incubation/Agitation)	: 40 °C 20 minutes 500 rpm
Sample Extraction	: 40 °C 40 minutes
Sample Desorption	: 260 °C 3 minutes
Post Conditioning	: 260 °C 2 minutes
Gas Chromatogram	**: GC-2010 Plus**
Injection	: Splitless Injection at 260 °C 1 minute sampling time
Column	: Rxi-5 MS 30.0m x 0.25 mm x 0.25 µm Helium carrier gas Constant linear velocity, 36.1 cm/sec Column Flow 1.00 mL/min Purge Flow 3.0 ml/min
Oven Program	: 40 °C, hold 2.0 min 3 °C /min to 250 °C, hold 15.0 min Total GC run time 87.00 min
Detector	**: GCMS-QP2020**
Operating mode	: SCAN
Ion Source	: 200 °C, EI mode, 70eV
Interface Temp	: 250 °C
Solvent Cut Time	: 2 min
Start Time – End Time (min)	: 2.5 – 87.00
Event Time	: 0.200 sec
Start m/z – End m/z	: 50.00 – 350.00

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Results and Discussion

In figure 2, the chromatogram for the traditional SPME acquisition of the headspace of the newly opened wine. Overall 48 peaks were detected.

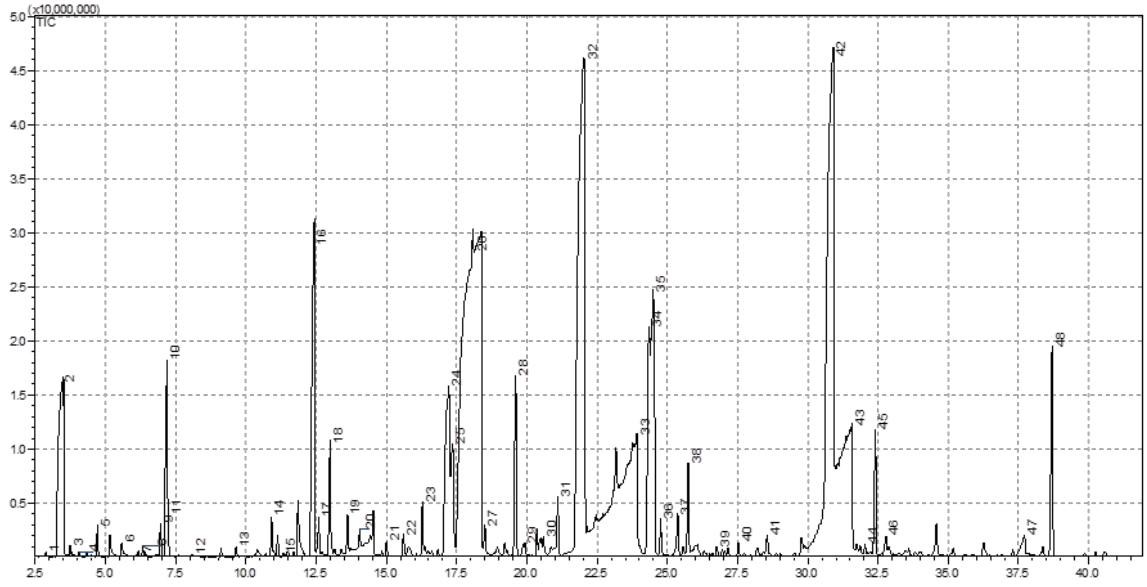

Figure 2: TIC of Moscato using traditional SPME

Figure 3 Shows the chromatogram of the Moscato after a four month period, which was acquired by the standard SPME Method. Overall, 26 peaks were detected ranging from alcohols to fatty acids.

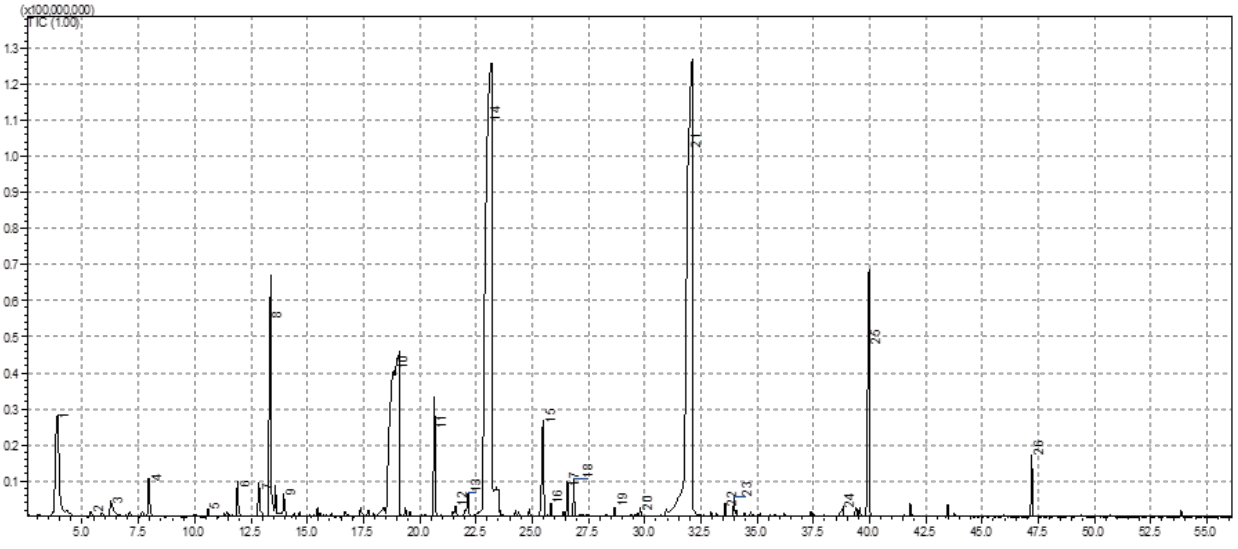

Figure 3: TIC of Moscato after 4 months utilizing traditional SPME

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Figure 4 shows the chromatogram recorded utilizing the SPME Arrow. This data was acquired after a four month period as well. All qualitative and quantitative parameters were kept consistent throughout the three runs. Overall, 25 peaks were detected.

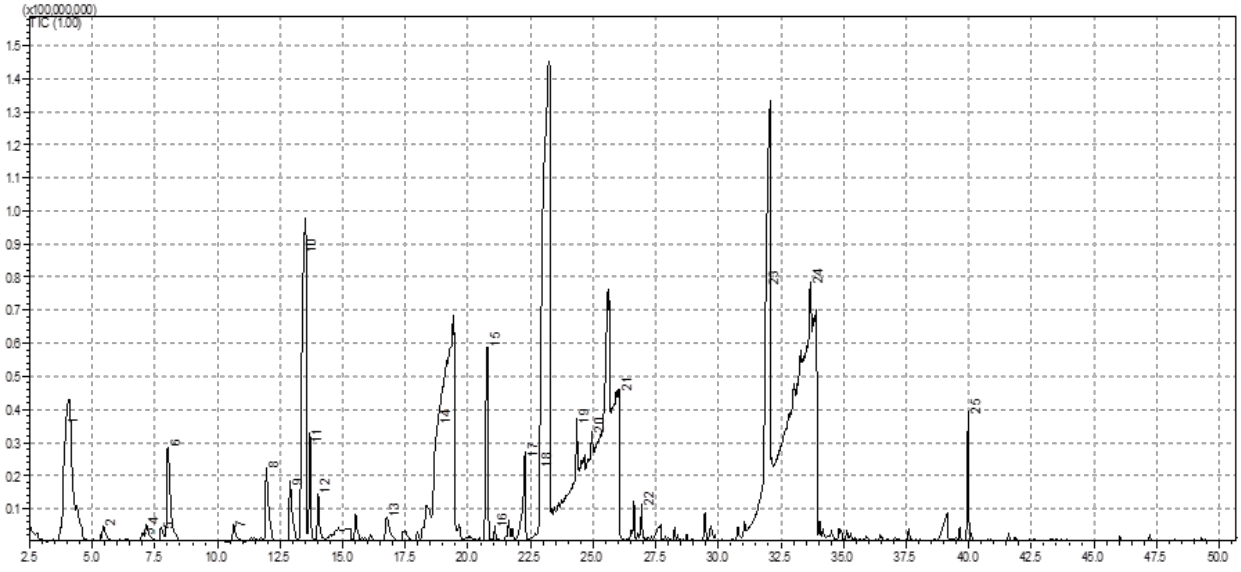

Figure 4: TIC of Moscato after 4 months utilizing SPME Arrow

A list of the major compounds that were found in the headspace of wine was compiled to compare area counts. Not all compounds were selected, only the major components that we expected to see. The table with the components and their respective area counts can be seen below.

Table 2: List of major components found in the headspace of wine and their respective area counts

Compound Name	SPME	SPME after 4months	SPME Arrow after 4 months
1-Pentanol	109505892	97954731	69586324
Butanoic acid, ethyl ester	1661914	3327537	15556171
3-Furaldehyde	2602589	19175005	
Butanoic acid, 2-methyl-, ethyl ester	459608	--	4498357
Butanoic acid, 3-methyl-, ethyl ester	481065	23535537	8992544
1-Hexanol	4981709	--	18040944
1-Butanol, 3-methyl-, acetate	32792834		98554627
3-Oxatricyclo[4.1.1.0(2,4)]octane, 2,7,7-trimethyl-	571183	2051940	8113552
2H-Pyran, 2-ethenyltetrahydro-2,6,6-trimethyl-	1171544	5104035	16508930
Hexanoic acid, ethyl ester	25979767	66126904	104326013
Acetic acid, hexyl ester	12118128	5923500	19160101
D-Limonene	2116078	--	--
Phenylethyl Alcohol	147118189	234855296	3366222
Octanoic acid, ethyl ester	44005522	164438395	188048185
Octanoic acid	4483080		2397269
Geranyl ethyl ether 1	1212001	1589674	6753665
Naphthalene, 1,2-dihydro-1,1,6-trimethyl-	1597961	2330652	--
Dodecanoic acid	63116778	2795102	118257597
Ethyl tridecanoate	9303435	58279582	--

Summary and Conclusions

Overall both techniques were extremely effective at identifying volatile organic compound. The saturated wine samples contained ample VOCs in the headspace even after four months of being opened. The SPME Arrow method was a much more sensitive method recovering almost twice as many VOCs as well as some additional compounds not found on the list. However, with this sensitivity, the SPME Arrow method is more susceptible to column bleed as well as phthalates from septum bleed. Due to its increased sensitivity, the SPME Arrow can be used for applications where low detection limits are necessary, but it could also be used for applications with long sample prep periods. The increased size of the stationary would allow the Arrow fiber to produce the same sensitivity as the traditional fiber in less time.

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References

1. Khio, S.-W.; Cheong, M.-W.; Zhou, W.; Curran, P.; Yu, B. Characterization of theVolatility of Flavor Compounds in Alcoholic Beverages through Headspace Solid-Phase Microextraction (HS-SPME) and Mathematical Modeling. Journal of Food Science 2011, 77 (1), C61–C70.
2. Kremser, A., Jochmann, M.A. & Schmidt, T.C. Anal Bioanal Chem (2016) 408: 943. doi:10.1007/s00216-015-9187-z

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