Optimization of Solid Phase Micro Extraction of Aroma Compounds in Wine

Application Note

Food/Flavor

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Abstract:

The analysis of wine aromas is a complex process. A reference to the aroma of a wine is indicative of the scents associated with the grapes used to make the wine. The bouquet, on the other hand, aids in the determination of the aging process. There are hundreds of compounds that can contribute to the overall aroma of wine. In order to determine the aroma compounds, analysts can use static headspace, dynamic headspace, Solid Phase Micro Extraction (SPME), liquid-liquid extraction, etc… This analysis will compare three different SPME fibers and their efficiency in discerning aroma compounds.

Introduction:

Solid Phase Micro Extraction (SPME) is considered a non-exhaustive sampling technique, meaning the analytes are not completely removed from the matrix being tested. SPME involves exposing an extraction phase into a sample's headspace or into the sample itself for a defined time. The efficiency of SPME sampling is dependent on several things. The sample matrix, agitation of the sample, the time and temperature of the extraction, the SPME fiber coating (extraction phase), and the thickness of the fiber coating are all examples of variables that can affect the efficiency of the analyte extraction.

This application will explore how the coating on a SPME fiber can affect analyte recoveries. The three different fibers compared in this study were a 100μm Polydimethylsiloxane (PDMS) fiber, a 65μm Divinyl Benzene (DVB)/PDMS fiber and a 50/30μm DVB/Carboxen (CAR)/PDMS fiber. The sampling technique was headspace SPME extraction.

Experimental:

The sampling system used for this study was the FLEX Autosampler. The FLEX was coupled to an Agilent 7890 GC and 5975 MS analytical system while the GC was configured with a Restek Rxi-624 Sil MS 30m x 0.250mm x 1.4μm column. The SPME fibers were procured from Supelco and Chardonnay was chosen for the type of wine to be tested.

Using the FLEX drag and drop method development software, the sampling parameters of the wine were enhanced in order to finalize the most efficient sampling and analysis parameters. Ultimately, it was found that one gram of sodium chloride and five milliliters of wine sealed in 20ml headspace vials along with the sampling and analysis parameters listed in Table 1 and 2 worked best for this analysis.

Autosampler	FLEX
General	
Method Type	SPME
GC Ready	Continue
GC Cycle Time	25min
Constant Heat Mode	Yes
Sample Incubate Agitate	
Incubation Temp.	40ºC
Incubation Time	5.1min
Agitation Speed	100%
Agitation Delay	0.1min
Agitation Duration	5.0min
Extraction	
Fiber Guide Depth	50%
Sample Vial Fiber Depth	1cm
Extraction Time	60min
Agitate	No
Wait	
Wait on Input	Yes
Wait Input	GC Ready
Desorbtion	
Injection Port	A
Fiber Guide Speed	20%
Fiber Guide Depth	60%
Fiber Insertion Speed	50
Fiber Insertion Depth	1cm
Fiber Desorbtion Time	3min
Injection Start Output	Start

Table 1: Flex Autosampler Experimental Parameters

GC/MS	Agilent 7890/5975
Inlet	Split/Splitless
Inlet Temp.	290ºC
Inlet Head Pressure	11.905 psi
Mode	Pulsed Splitless
Injection Pulse Pressure	30psi until 3.0min
Purge Flow to Split Vent	10ml/min at 3.01min
Desorbtion	3min at 290°C
Column	Rxi-624 Sil MS 30m x 0.25mm I.D. 1.4μm film thickness
Oven Temp. Program	40ºC hold for 2.0 min., ramp 10ºC/min to 220ºC, hold for 1min, total run time 21 min
Column Flow Rate	1.0ml/min
Gas	Helium
Total Flow	14.0ml/min
Source Temp.	230ºC
Quad Temp.	150ºC
MS Transfer Line Temp.	180ºC
Scan Range	m/z 31-265
Scans	3.07 scans/sec
Solvent Delay	0.7 min.

Table 2: GC/MS Experimental Parameters

Four replicate samples were done for each fiber in order to determine the consistency of the sampling technique. The compound responses were then averaged thus providing a more comprehensive representation of the experimental results. Figure 1 shows chromatograms of the SPME extracted aroma profiles while Figure 2 displays a Fiber Comparison Graphic. Table 3 lists the compound response summary.

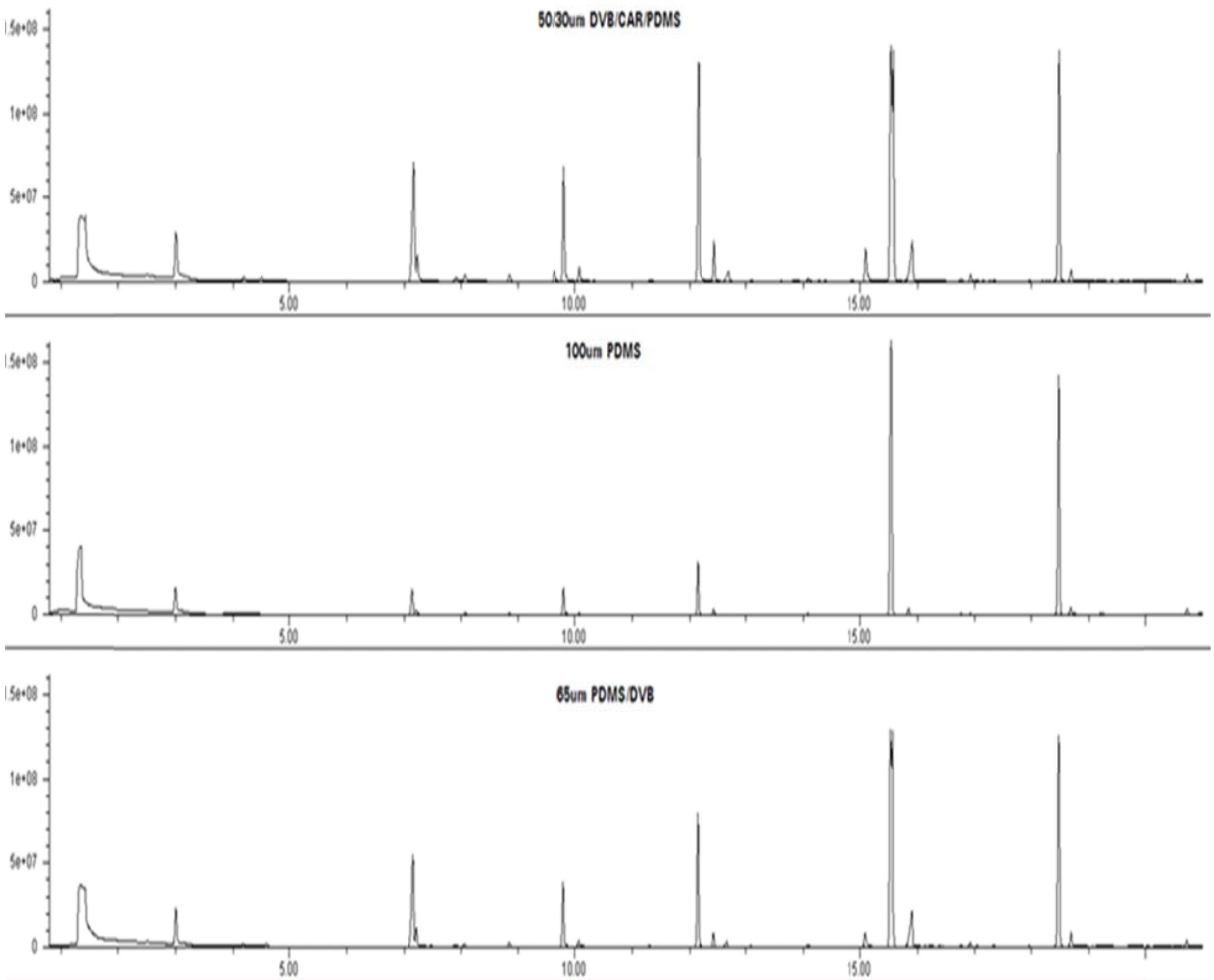

Figure 1: Chromatograms of the Wine Aroma Profiles Using the Three Fibers

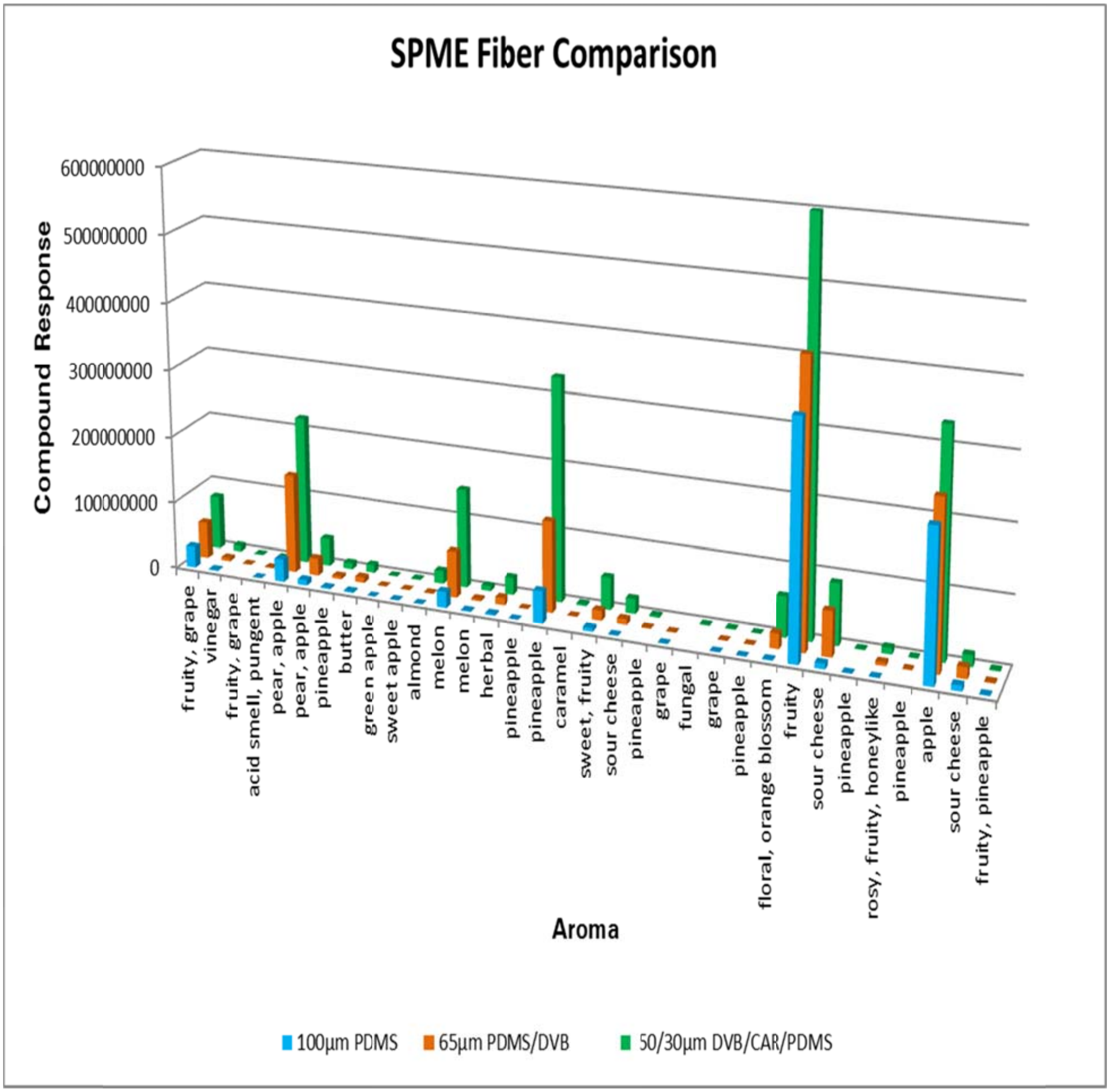

Figure 2: Fiber Comparison Results Summary

Compound	Aroma	Compound Response		
		100μm PDMS	65μm PDMS/DVB	50/30μm DVB/CAR/PDMS
Ethyl Acetate	fruity, grape	31258107	53904215	79839130
acetic acid	vinegar	1628922	4687871	8770418
Ethyl Propionate	fruity, grape		354863	695502
Isobutyric Acid	acid smell, pungent	288481	480709	847682
Isoamyl alcohol (fusel oil)	pear, apple	33850591	145952948	219902286
amyl alcohol (fusel oil)	pear, apple	8132232	25571385	40687560
ethyl butyrate	pineapple	2078046	4196941	9053230
ethyl lactate	butter	1935494	7912028	11749922
ethyl-2-methyl butyrate	green apple	84106	143886	311868
ethyl isovalerate	sweet apple	257874	360209	917756
furfural	almond	119390	655436	18897072
isoamyl acetate	melon	23972749	68424564	145967747
amyl acetate	melon	1316636	3055747	7140538
1-hexanol	herbal	2407359	10653817	25540743
methyl hexanoate	pineapple	38820	66304	
ethyl caproate	pineapple	47647217	134176149	330034112
5-methyl furfural	caramel		284317	2575859
acetic acid, hexyl ester	sweet, fruity	5290351	14817461	48082731
carproic acid	sour cheese	485991	7981897	22002155
ethyl hexanoate	pineapple		918574	2634351
ethyl heptanoate	grape	147931	534362	
methyl 2-furoate	fungal			806279
ethyl caprylate	grape	167192	427297	1126258
butyl caproate	pineapple	62070	206868	277747
phenylethyl alcohol	floral, orange blossom	1166516	22337840	59820072
ethyl caprylate	fruity	346158872	416898825	599725741
caprylic acid	sour cheese	8112405	66154421	89957822
pentyl caproate	pineapple	422955		1037477
2-phenethyl-acetate	rosy, fruity, honeylike	725031	5019328	9222550
ethyl-3hydroxyhexanoate	pineapple		982184	1315743
capric acid ethylester	apple	221666584	246664455	332482209
capric acid	sour cheese	8503036	16856301	17186893
isoamyloctanoate	fruity, pineapple	1101269	1736849	1663384

Table 3: Compound Response Summary

Conclusions:

Overall, the non-polar 100μm PDMS fiber was the least successful in extracting the aroma compounds from the wine samples. The PDMS fiber was recommended for volatile compounds but did not remove the less volatile analytes in the matrix as well as the other fibers. The 65μm PDMS/DVB fiber performed substantially better. This fiber was recommended for volatiles and amines and produced better analyte recoveries than PDMS alone. However, the 50/30μm DVB/CAR/PDMS fiber was by far the most effective coating for the aroma analysis of wine. This fiber extracted more aroma compounds and saw much better compound response than the two others.

Headspace SPME was an efficient method for removing aroma compounds from the wine samples for separation and analysis. Furthermore, with the correct fiber selection, the aroma profiles can be discerned and used for quality control or research. The FLEX autosampler was the perfect selection for this analysis as the process was easily automated and, once the optimum parameters were developed, the FLEX did all of the work.

References:

1. Pawliszyn, Janusz. *Handbook of Solid Phase Microextraction.* P.R. China: Chemical Industry Press of China, 2009
2. Cannavan, Tom. *Wine-pages*, 21 Aug. 2014, http://www.wine-pages.com/

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