A comparison of Direct Immersion and Headspace SPME Sampling of Whiskey Samples

Application Note

Food and Flavor

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Abstract

Solid Phase Micro Extraction is a non-exhaustive sampling technique in which a coated fiber is exposed to a sample, the analytes of the sample adhere to the fiber and the fiber is then desorbed onto a Gas Chromatograph coupled to a detector for separation and analysis. There are two types of SPME sampling techniques. The first entails bringing a sample to equilibrium and exposing the SPME fiber to the headspace of the sample. The second involves placing the SPME fiber directly into the liquid phase of the sample and allowing the analytes to adhere to the fiber directly from the sample. This application note will examine both SPME sampling techniques using Whiskey samples.

Introduction:

Whiskey is comprised of both volatile and non-volatile flavor components. To fully understand the complexities of a whiskey sample, distilleries often use different sampling techniques. Solid Phase Micro Extraction (SPME) is one of those techniques. Since SPME involves extracting flavors onto a fiber, the fiber extraction coating is integral to separating the analytes of interest out of the matrix. Furthermore, the SPME sampling method plays a role in obtaining an accurate flavor profile.

In order to determine which sampling technique would work best for this analysis, it was essential to choose a SPME fiber coating that would efficiently extract the analytes of interest. There are many fiber coatings in which to choose from, however for this study there were a diverse range of compounds to examine. Ultimately, a 50/30 Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS) fiber was used. This fiber was chosen due to its ability to extract both volatile and semi-volatile flavor compounds.

Headspace SPME entails bringing the sample to equilibrium and exposing the fiber to the headspace of the sample for a period of time. Direct immersion SPME, on the other hand, involves immersing the fiber directly into the sample matrix. During the exposure/immersion time, the SPME fiber extracts the analytes from the matrix. This investigation will examine the advantages and disadvantages of both sampling techniques.

Experimental:

The EST Analytical FLEX Series autosampler was installed on an Agilent 7890A GC and 5975 inert XL MS. A 50/30μm Divinylbenzene/Carboxen/Polydimethylsiloxane (DVB/CAR/PDMS) coated fiber was fitted in the FLEX autosampler for analyte extraction. For analyte separation, a Restek Stabilwax DA 30m X 0.25mm X 0.25μm column was mounted in the GC. The sampling parameters for both the headspace and immersion SPME techniques are listed in Table 1. Table 2 details the GC/MS separation and analysis parameters.

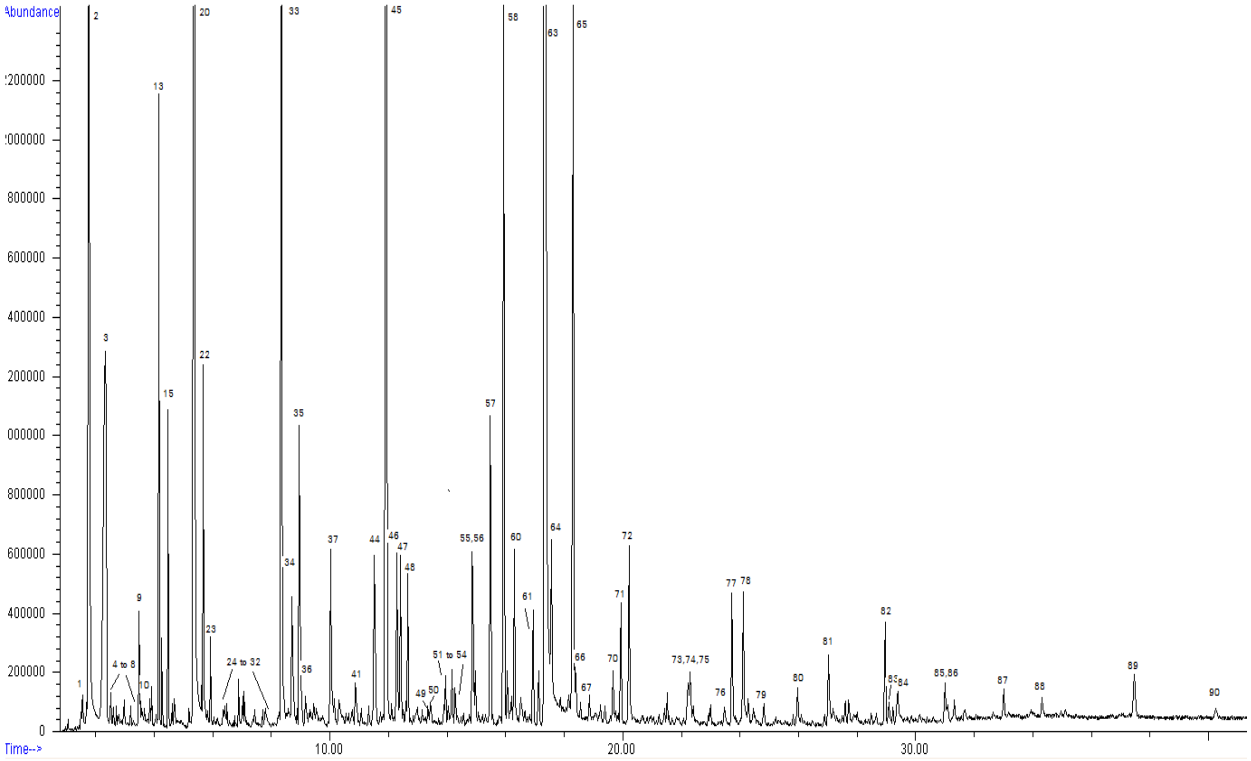
FLEX Autosampler		
General		
Method Type	Immersion SPME	Headspace SPME
GC Ready	Continue	Continue
GC Cycle Time	46min	46min
Constant Heat Mode	Yes	Yes
Incubate Stir		
Incubation Temperature	60°C	60°C
Incubation Time	20min	20min
Stirrer Speed	Off	Medium
Extraction		
Fiber Guide Depth	100%	50%
Sample Vial Fiber Depth	2cm	1cm
Fiber Extraction Time	20min	20min
Wait		
Wait Input	GC Ready	GC Ready
Desorbtion		
Fiber Insertion Depth	1cm	1cm
Fiber Desorbtion Time	2min	2min
Injection Start Input	Start	Start
Condition Fiber		
Fiber Temperature	250°C	250°C
Condition Time	5min	5min

Table 1: FLEX Autosampler Experimental Parameters

GC/MS Agilent 7890A/5975 inert XL	
Method Type	**SPME**
Inlet	Split/Splitless
Inlet Temp.	220°C
Inlet Head Pressure	11.809 psi
Mode	Pulsed Splitless
Split Ratio	NA
Purge Flow to Split Vent	10ml/min at 2.01min
Injection Pulse Pressure	20psi until 2min
Inlet Liner	Restek SPME Liner, 0.75mm X 6.35 X 78.5
Column	Restek Stabilwax®-DA, 30m X 0.25mmID X 0.25µm df
Oven Temp. Program	45°C hold for 2 min, ramp 20°C/min to 100°C, hold for 0 min, ramp 5°C/min to 240°C, hold for 10min, 42.2 min. total run time
Column Flow Rate	1.0mL/min
Gas	Helium
Total Flow	14ml/min
Source Temp.	230°C
Quad Temp.	150°C
MS Transfer Line Temp.	220°C
Scan Range	m/z 50-300
Scans	5.5 scans/sec
Solvent Delay	0.7min

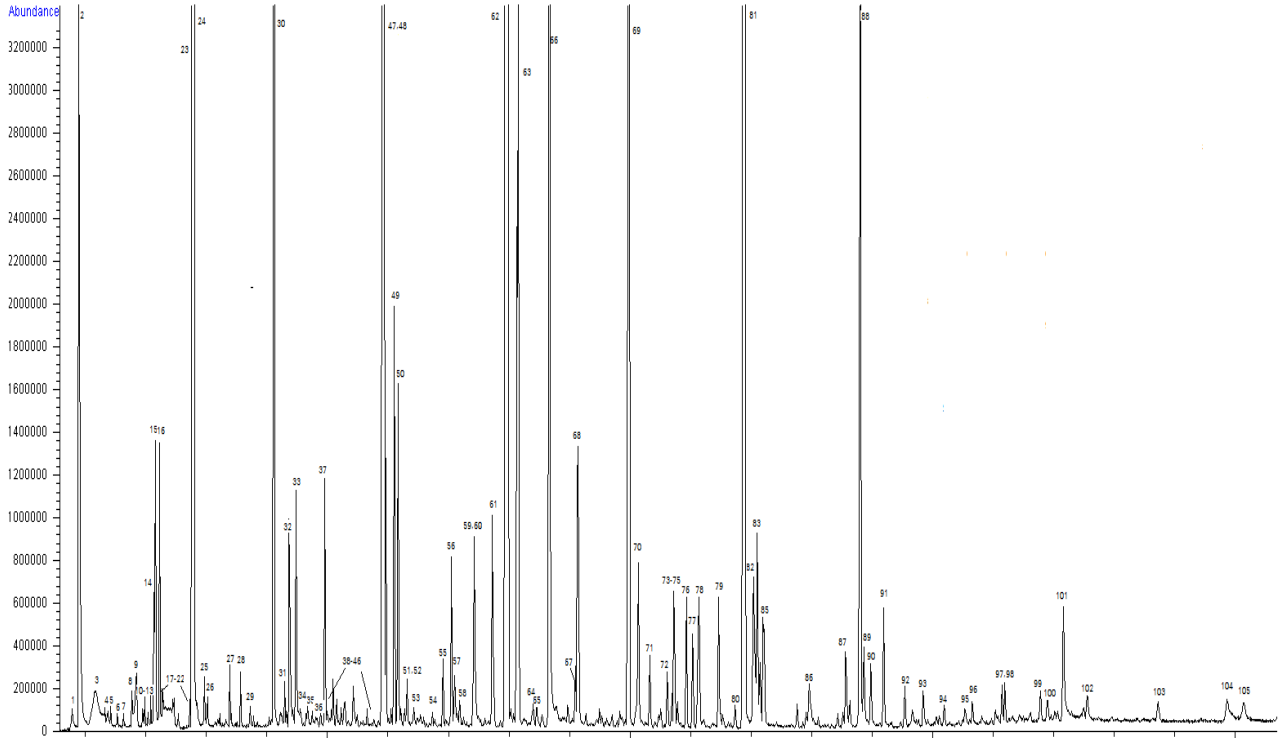
Table 2: GC/MS Experimental Parameters

In order to perform the headspace SPME sampling, 1g of sodium chloride was added to each sample vial along with 5 milliliters of whiskey. The samples were then sealed in a 20ml headspace vial. For the direct immersion SPME, 10 milliliters of whiskey was added to the sample vial and sealed. The FLEX method builder software enabled method development for both types of analyses. Several different fiber coatings were tried in order to establish the best fiber for the application and the optimum fiber for the extraction was decided upon. Finally, once the proper method parameters for each type of extraction were established, the FLEX Series autosampler was set up to perform all of the experiments using the DVB/CAR/PDMS fiber.



1	diethoxymethane	32	nonanal	63	phenyl ethyl alcohol
2	ethylacetate	33	octanoic acid ethyl ester	64	unknown
3	boric acid, triethyl ester	34	carbonyl sulfide	65	5-butyldihydro-4-methyl cis 2(3H)furanone
4	propanoic acid ethyl ester	35	2-furancarboxaldehyde	66	1-dodecanol
5	propanoic acid, 2-methylethyl ester	36	2-ethyl-1-hexanol	67	cyclododecane
6	propane, 1,1-diethoxy-2-methyl	37	nonanoic acid ethyl ester	68	phenol
7	1-butoxy-1-ethoxyethane	38	5-nonanol	69	unknown
8	acetic acid, 2-methyl propyl ester	39	butyl caprylate	70	d\ihydro-5-pentyl- 2(3H)furanone
9	unknown	40	1-octanol	71	tetradecanoic acid ethyl ester
10	butanoic acid, 2-methylethyl ester	41	5-methyl-2-furancarboxaldehyde	72	octanoic acid
11	butanoic acid, 3-methylethyl ester	42	hexadecane	73	eugenol
12	butane, 1,1-diethoxy-3-methyl	43	octamethyl trisiloxane	74	unknown
13	2-methyl-1-propanol	44	benzonitrile	75	4-ethyl phenol
14	1,1-ethoxy ethoxy pentane	45	decanoic acid ethyl ester	76	1,1-dimethylethyl-methyl benzene
15	3-methyl acetate-1-butanol	46	3-methylbutyl ester octanoic acid	77	hexanoic acid ethyl ester
16	ethyl ester pentanoic acid	47	ethyl cis-4-decanoate	78	decanoic acid
17	benzene ethanamine, N-pentafluorophenyl methylene (?)	48	butanedioic acid diethyl ester	79	2,6-bis(1,1-dimethylethyl)-phenol
18	1-butanol	49	tetradecanal	80	Cyclotetradecane
19	Dodecane	50	4-ethyl benzaldehyde	81	benzoic acid
20	3-methyl-1-butanol	51	undecanoic acid ethyl ester	82	unknown
21	1,1-diethyoxy hexane	52	3-methyl 2-butanoic acid	83	vanillin
22	hexanoic acid ethyl ester	53	acetone dimethyl hydrozone	84	1-octadecene
23	1,1-diethoxy-2-methyl propane	54	trans-1-butyl-2-methylcyclopropane	85	benzamide
24	tridecane	55	9-decen-1-ol	86	dibutyl phthalate
25	septum bleed	56	1,9-nonanediol	87	hexanoic acid bis(2-ethylhexyl ester)
26	1,1,3-triethoxy propane	57	acetic acid 2-phenyl ethyl ester	88	hexadecanoic acid
27	heptanolc acid ethyl ester	58	dodecanoic ethyl ester	89	2,6,10-dodecatrien-1-ol, 3,7,11 trimethyl
28	trimethyl silanol (?)	59	hexanoic acid	90	di-n-octyl phthalate
29	1-hexanol	60	3-methylbutyl decanoate		
30	3-ethoxy-1-propanol	61	trans-4-hydroxy-3-methyl cotanoic acid lactone		
31	tetradecane	62	butanedioic acid diethyl ester		

Figure 1: Static Headspace SPME Results



1	diethoxymethane	36	octahydro-4-methy-8-methylen-1,4-methano-1H-indene	71	9-hexadecenoic acid
2	ethylacetate	37	nonanoic acid ethyl ester	72	nonadecanoic acid ethyl ester
3	boric acid, triethyl ester	38	benzaldehyde	73	6,10,14-trimethyl-2-pentadecanone
4	2-methyl propanoic acid ethyl ester	39	ethyl-di-2-hydrozxycaproate	74	octamethyl trisiloxane
5	1,1-diethoxy-2-methyl propane	40	butyl caprylate	75	hexadecanal
6	unknown	41	unknown	76	pentadecanoic acid ethyl ester
7	2-methylpropyl ester acetic acid	42	decahydro naphthalene	77	ethyl cis-4-decenoate
8	butanoic acid ethyl ester	43	1H-3a,7-methanoazulene, 2,3,4,77,8,8a-hexahydro-3,6,8,8-tetrameth…	78	propanoic acid 2 phenylethyl ester
9	2-fluoro-1-propene	44	5-methyl-2-furancarboxaldehyde	79	ethylidene cyclohexane
10	3-methyl butanoic acid ethyl ester	45	triacontane	80	isopropyl palmitate
11	1,1-diethyoxy-3-methyl butane	46	octamethyl trisiloxane	81	hexadecanoic acid ethyl ester
12	3,4-dimethyl heptane	47	decanoic acid ethyl ester	82	ethyl-9-hexadecanoate
13	2-propyl-1,3-dioxolane	48	decanoic acid ethyl ester	83	ethyl-9-hexadecanoate
14	unknown	49	octanoic acid 3-methyl butyl ester	84	oleic acid
15	2-methyl-1-propanol	50	ethyl cis-4-decenoate	85	octamethyl trisiloxane
16	1-butanol, 3-methyl-acetate	51	benzoic acid ethyl ester	86	1-hexadecanol
17	trimethylsilylester benzoic acid-2-trimethylsilyloxy	52	butanedioic acid diethyl ester	87	bis(trimethylsilyl)mercapto acetic acid
18	pentanoic acid ethyl ester	53	ethyl 9-decanoate	88	14-pentadecenoic acid
19	3-methyl decane	54	propyl decanoate	89	oleic acid
20	trans-2,3-bis-(1-methylethyl)-oxirane	55	undecanoic acid ethyl ester	90	10-octadecenoic acid methyl ester
21	limonene	56	butyl caprate	91	9,17-octadecadienal (Z)
22	1,1-diethoxy-hexane	57	3-methyl butyl decanoate	92	vanillin
23	2-methyl-1-butanol	58	ethanone, 1-(1,3-dimethyl-3-cyclohexen-1-yl)-	93	tetrasilaoctane…
24	3-methyl-1-butanol	59	9-decen-1-ol	94	9,12-octadecadienoic acid (ZZ)
25	diethoxy acetic acid ethyl ester	60	bis(trimethylsilyl)-mercaptoacetic acid	95	tetradecanoic acid
26	tridecane	61	acetic acid-2-phenylethyl ester	96	hexyl-diethyl ester propanedioic acid
27	heptanoic acid ethyl ester	62	dodecanoic acid ethyl ester	97	unknown
28	1-hexanol	63	3-methylbutyl decanoate	98	fluorenamine
29	tetradecane	64	1,1-dimethoxy-octadecane	99	6(methylthio)-1(H)-purin=-2-amine
30	octanoic acid ethyl ester	65	trans-3methyl-4-octanolide	100	unknown
31	hexanoic acid-2-methylbutyl ester	66	phenylethyl alcohol	101	hexadecanoic acid
32	carbonyl sulfide	67	1-ethenyloxy-butane	102	4-hydroxy-3,5-dimethoxy benzaldehyde
33	2-furancarboxaldehyde	68	trans-4-hydroxy-3-methyloctanoic acid lactone	103	decahydro carotene
34	pentadecane	69	tetradecanoic acid ethyl ester	104	15-tetracosenoic acid methyl ester
35	decanal	70	isoamyl laurate	105	bis(e-ethylhexyl)phthalate

Figure 2: Direct Immersion SPME Results

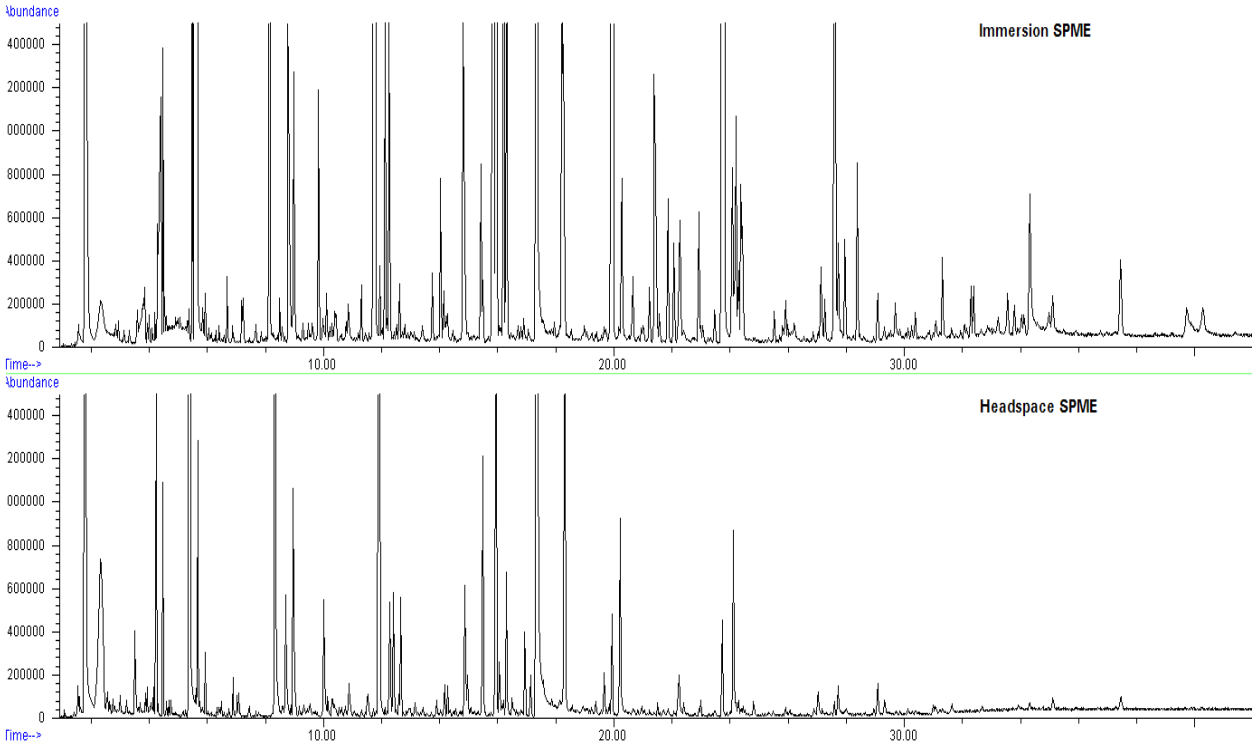


Figure 3: SPME Technique Comparison Chromatogram Overlay

Conclusions:

The FLEX Series Autosampler with the SPME option provided an excellent platform to automate both of the SPME extraction techniques. SPME provided an impressive amount of information on the analytes in the whiskey samples whether using headspace or immersion extraction. Although the same SPME fiber was used for both techniques, the direct immersion SPME was able to extract the heavier compounds in the matrix much more readily than the headspace SPME. Since, the heavier compounds do not separate out into the headspace as readily as the lighter analytes, this was expected. On the other hand, headspace SPME extraction is not as hard on the fiber as direct immersion SPME, thus, the number of extractions that can be done with one fiber is much greater when using headspace SPME. In conclusion, the technique for sampling the whiskey sample would be dependent upon the analytes of interest in the sample and the number of extractions required of the fiber.

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