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Comparison of Three Types of Thin Film-Solid Phase Microextraction Phases for Beverage Extractions

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Keywords

Thin Film Solid Phase Micro-Extraction (TF-SPME), Stir Bar Sorptive Extraction (SBSE) , Gas Chromatography, Mass Spectrometry, Flavor Compounds, Food, Beverages.

Abstract

In this study, Thin Film Solid Phase Micro-Extraction (TF-SPME) devices with carboxen/polydimethylsiloxane (CAR/PDMS), divinylbenzene/polydimethylsiloxane (DVB/PDMS), and hydrophilic lipophilic balanced/polydimethylsiloxane (HLB/PDMS) coatings are investigated for their usefulness for beverage analysis in combination with Stir Bar Sorptive Extraction (SBSE) using the GERSTEL Twister®. A variety of beverages are analyzed including almond milk, black tea, strawberry banana juice, amber lager, and pumpkin ale. The GERSTEL MPS is used in combination with a CIS 4 inlet and thermal desorber for automated thermal desorption of the TF-SPME devices.

Introduction

Alcoholic and non-alcohol beverages are enjoyed by millions of people around the globe. Each product has a unique aroma/flavor profile that is made up of a variety of volatile and semi-volatile compounds. Monitoring these compounds is essential for beverage manufacturers to maintain product quality and minimize off-flavors in order to ensure brand success. The wide range of concentrations, polarities, and functional groups of the compounds found in beverages can make the analysis difficult. Extraction techniques which are simple, use little or no solvent, and are capable of extracting a wide range of analytes are desirable.

Thin Film Solid Phase Micro-Extraction (TF-SPME) is an extension of regular SPME. TF-SPME results in more sensitive analysis than regular SPME due to the increased surface area and phase volume, both of which lead to improved analyte recovery. The TF-SPME device is a 20 mm x 4.8 mm carbon mesh sheet impregnated with a sorptive phase. The available phases contain polydimethylsiloxane (PDMS) with either carboxen (CAR), divinylbenzene (DVB), or hydrophilic lipophilic balanced (HLB) particles. As a result, these mixed phases provide a combination absorptive/adsorptive based extraction. For beverage samples, the TF-SPME devices can be used in headspace or immersion mode. In headspace mode, the TF-SPME device is suspended above the liquid sample. In immersive mode, it is placed directly in the liquid sample. In both cases, the sample is agitated by stirring, in this study using a GERSTEL Twister® which is then desorbed along with the TF-SPME device. The Twister provides additional PDMS phase volume while the TF-SPME device provides enhanced selectivity. The combination of the two devices results in enhanced extraction efficiency. After extraction, the devices are blotted dry and placed in an empty thermal desorption tube for analysis. The devices are analyzed by thermal desorption GC/MS making TF-SPME a simple, efficient, and highly sensitive solvent-less technique for beverage analysis.

Experimental

Instrumentation:
GERSTEL MPS robotic pro sampler
GERSTEL Thermal Desorber 3.5$^+$ (TD 3.5$^+$)
GERSTEL Cooled Injection System (CIS 4) inlet with LN2 option
Agilent 8890/5977B GC/MSD

Analysis Conditions:

TF-SPME:	*CAR/PDMS, DVB/PDMS, and HLB/PDMS*
Stirring:	*1200 rpm, 60 min using GERSTEL Twister, 10 mm x 0.5 mm PDMS.*
TD3.5+:	*Splitless* *40 °C (0.5 min); 400 °C/min; 250 °C (5 min)*
CIS:	*Glass Bead Filled Liner* *Solvent Vent (60 mL/min)* *Splitless; 20 mL/min at 1.2 min* *Split 20:1* *-120 °C (0.25 min); 12 °C/sec; 275 °C (3 min)*
Column:	*30 m Rxi-5MS (Restek) di=0.25 mm, df=0.25 µm*
Pneumatics:	*He, P_i = 7.1 psi* *Constant Flow 1 mL/min*
Oven:	*40°C (2 min); 10°C/min; 300°C (2 min)*
MSD:	*Full scan, 40 – 450 amu*

Sample preparation

Almond milk, black tea, strawberry banana juice, amber lager, and pumpkin ale were purchased at a local store. A 3 mL aliquot of almond milk was diluted with 7 mL of bottled water in a 10 mL screw-capped vial to reduce fat content to ~1%. Three grams of black tea was brewed in 300 mL of water at 80°C for 3 min. A 10 mL aliquot of black tea was added to a 10 mL screw-capped vial. A 1 mL aliquot of strawberry banana juice was diluted with 9 mL of bottled water in a 10 mL screw-capped vial. 10 mL of undiluted amber lager and pumpkin ale were added to 10 mL screw-capped vials. A GERSTEL Twister® stir bar (10 mm x 0.50 mm) was added to each vial. A TF-SPME device was suspended in the vial with a holder and the vial was placed on a GERSTEL Twister 20 position stir plate. The samples were stirred at 1200 rpm for 60 minutes. After extraction, the TF-SPME device and PDMS-Twister were removed from each sample, blotted dry, and placed into an empty TD 3.5$^+$ tube with a glass wool plug at the base. The TD 3.5$^+$ tube was sealed with a transport adapter and placed in a 40 position Twister rack on the MPS robotic pro for automated analysis.

Sample Introduction

Samples were desorbed in splitless mode under a 60 mL/min helium flow at 250 °C for 5 minutes. Analytes were cold trapped in the CIS 4 inlet at -120 °C on a glass bead filled liner. When desorption was complete, analytes were transferred to the column in splitless (almond milk) or split (20:1; black tea, strawberry banana juice, amber lager, pumpkin ale) mode by heating the inlet rapidly to 280 °C.

Results & Discussion

Figure 1 shows the stacked view of the total ion chromatograms (TICs) of almond milk extracted by the CAR/PDMS (top), DVB/PDMS (middle), and HLB/PDMS (bottom) phases. Each phase provides a slightly different chromatographic profile. While all three phases were able to extract a wide variety of compounds including aldehydes, pyrazines, and lactones, analyte peak areas varied across phase types. The low polarity, volatile organic compounds (VOCs) such as 2,5-dimethylpyrazine, benzaldehyde, 2-ethyl-5-methylpyrazine, and 3-ethyl-2,5-dimethylpyrazine show higher response when extracted with the CAR/PDMS and HLB/PDMS phases compared to when using DVB/PDMS. These compounds are all responsible for the nutty/almond aroma of the almond milk. The lactones, responsible for the sweet/creamy/dairy aroma, show higher response when extracted with the DVB/PDMS phase. The late eluting, high log $K_{o/w}$ fatty acids, palmitic and oleic acid, show much higher response when using the HLB/PDMS phase.

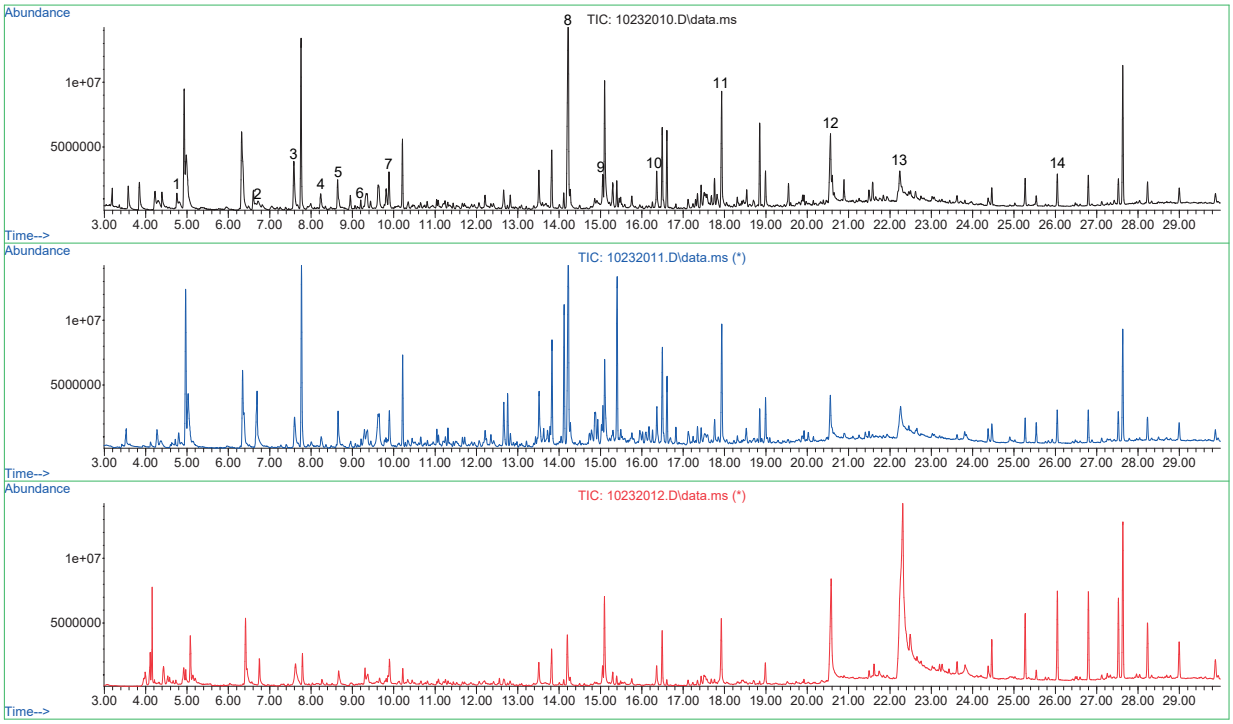

Figure 1: Stacked view of TICs for almond milk using CAR/PDMS (top), DVB/PDMS (middle), and HLB/PDMS (bottom) TF-SPME devices in combination with a PDMS-Twister® (SBSE).

Peak #	Compound	m/z	CAR	DVB	HLB	Log $K_{o/w}$
1	Hexanal	56	1.05	0.79	1.00	1.78
2	2,5-Dimethylpyrazine	108	1.25	0.73	1.00	0.63
3	Benzaldehyde	77	1.28	0.97	1.00	1.48
4	2-Ethyl-5-methylpyrazine	121	1.14	0.87	1.00	1.00
5	2-Ethyl-1-hexanol	57	1.54	1.89	1.00	2.73
6	3-Ethyl-2,5-dimethylpyrazine	135	1.50	1.35	1.00	1.50
7	Nonanal	57	1.38	1.48	1.00	3.27
8	Vanillin	151	4.63	4.05	1.00	1.21
9	gamma-Decalactone	85	1.33	1.86	1.00	2.72
10	gamma-Undecalactone	85	1.61	1.73	1.00	3.30
11	delta-Dodecalactone	99	1.49	1.59	1.00	3.60
12	Palmitic acid	60	0.62	0.40	1.00	7.17
13	Oleic acid	55	0.14	0.17	1.00	7.64
14	Hexacosane	57	0.37	0.39	1.00	13.11

Table 1. List of compounds for figure 1 with area counts normalized to HLB.

Figure 2 shows a stacked view of total ion chromatograms (TICs) of black tea extracted by the CAR/PDMS (top), DVB/PDMS (middle), and HLB/PDMS (bottom) phases. Several classes of compounds were identified including terpenes, aldehydes, and ketones. Many of the very volatile compounds (VVOCs), such as 2-methylfuran, 2-ethylfuran, and furfural, are maillard reaction products responsible for the roasted aroma of black tea. These compounds were only found when using the CAR/PDMS and HLB/PDMS phases. However, DVB/PDMS was effective at extracting VOCs and semi-volatile compounds (SVOCs) including caffeine. For the SVOCs, DVB/PDMS extraction results in higher recovery of compounds with a lower log $K_{o/w}$ whereas only HLB/PDMS was able to extract 1-nonadecanol whose log $K_{o/w}$ = 8.9

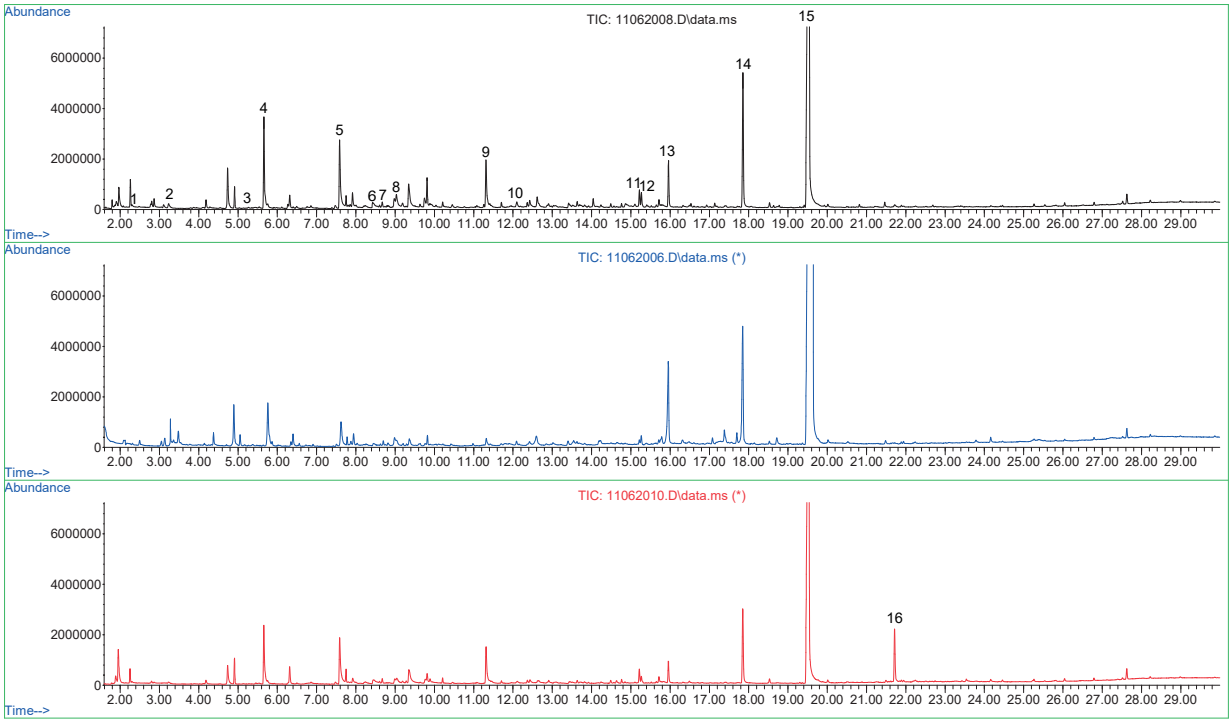

Figure 2: Stacked view of TICs for black tea using CAR/PDMS (top), DVB/PDMS (middle), and HLB/PDMS (bottom) TF-SPME devices in combination with a PDMS-Twister (SBSE).

Peak #	Compound	m/z	CAR	DVB	HLB	Log $K_{o/w}$
1	2-Methylfuran	82	0.91	-	1.00	2.30
2	2-Ethylfuran	81	1.37	-	1.00	3.23
3	Furfural	96	2.06	-	1.00	0.41
4	2E-Hexenal	41	1.36	0.96	1.00	1.50
5	Benzaldehyde	106	1.25	0.59	1.00	1.48
6	2E,4E-Heptadienal	81	0.90	0.35	1.00	1.60
7	Limonene	68	1.18	1.31	1.00	4.57
8	1-Ethyl-1H-pyrrole-2-carboxaldehyde	123	2.64	1.46	1.00	0.80
9	Methyl salicylate	120	1.14	0.16	1.00	2.55
10	Geraniol	69	2.46	1.73	1.00	3.56
11	E-beta-Ionone	177	1.20	0.32	1.00	2.90
12	5,6-epoxy-beta-Ionone	123	2.11	1.53	1.00	2.00
13	Dihydroactinidiolide	111	2.01	5.38	1.00	2.20
14	1-Hydroxycyclohexyl phenyl ketone	99	1.67	1.91	1.00	2.60
15	Caffeine	194	1.09	3.05	1.00	-0.07
16	1-Nonadecanol	83	-	-	1.00	8.90

Table 2. List of compounds for figure 2 with area counts normalized to HLB.

Figure 3 shows a stacked view of total ion chromatograms (TICs) of strawberry banana juice extracted by the CAR/PDMS (top), DVB/PDMS (middle), and HLB/PDMS (bottom) phases. For this sample type, the DVB/PDMS phase provides a higher response than the other two phases. The chromatographic profile is dominated by esters and terpenes, which impart the fruity flavors of the juice.

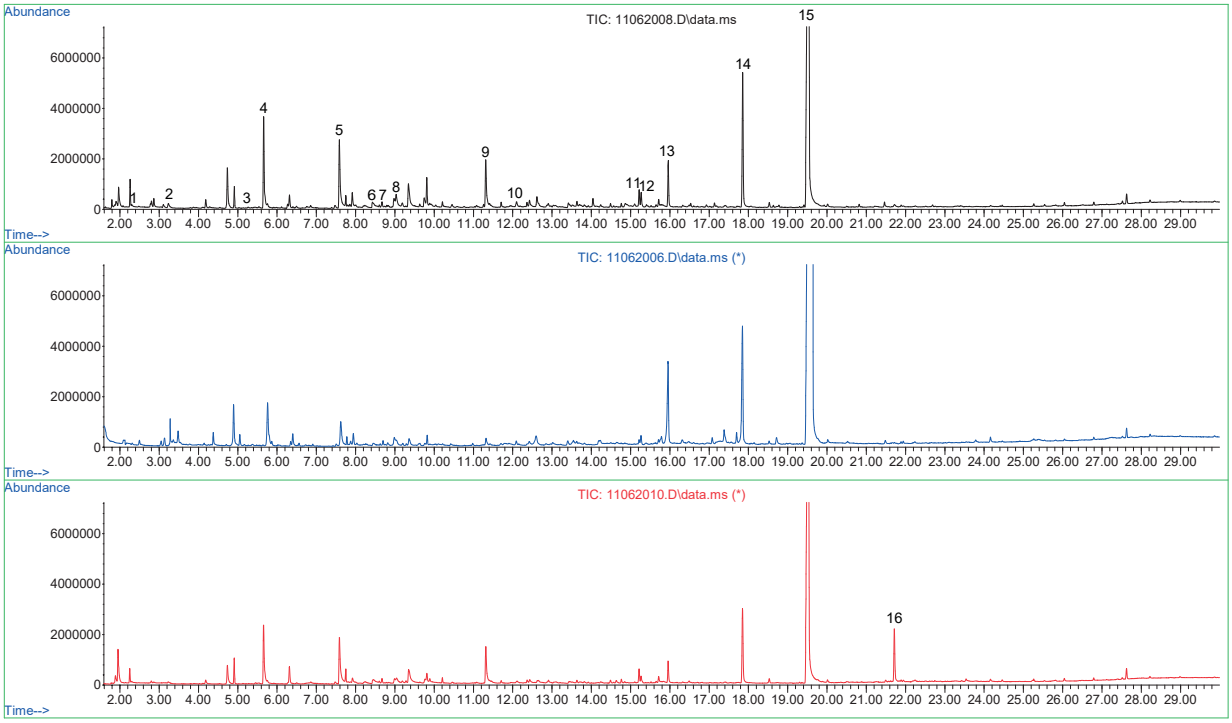

Figure 3: Stacked view of TICs for strawberry banana juice using CAR/PDMS (top), DVB/PDMS (middle), and HLB/PDMS (bottom) TF-SPME devices in combination with a PDMS-Twister (SBSE).

Peak #	Compound	m/z	CAR	DVB	HLB	Log $K_{O/W}$
1	Dimethyl sulfide	62	0.83	0.71	1.00	0.92
2	Ethyl acetate	43	0.30	1.06	1.00	0.73
3	Ethyl butyrate	71	0.72	2.59	1.00	1.85
4	Butyl acetate	43	0.70	3.39	1.00	1.78
5	Furfural	96	0.92	0.32	1.00	0.41
6	3Z-Hexen-1-ol	67	0.82	5.17	1.00	1.61
7	Isoamyl acetate	43	1.16	4.50	1.00	2.25
8	Ethyl hexanoate	88	0.93	1.80	1.00	2.40
9	3Z-Hexenyl acetate	67	0.90	1.77	1.00	1.90
10	Limonene	68	1.28	1.38	1.00	4.57
11	Isoamyl butyrate	70	1.11	2.16	1.00	2.60
12	Isoamyl isovalerate	70	1.21	1.85	1.00	3.10
13	alpha-Terpineol	59	0.68	10.89	1.00	2.98
14	Decanal	43	1.09	1.85	1.00	3.76
15	Eugenol	164	1.71	6.04	1.00	2.27
16	Methyl Cinnamate	131	1.12	1.60	1.00	2.62
17	Dimethyl anthranilate	165	1.31	1.98	1.00	2.30
18	gamma-Decalactone	85	0.87	2.68	1.00	2.72
19	gamma-Bisabolene	93	2.76	2.55	1.00	4.70
20	Isocoumarin	164	1.14	4.97	1.00	2.40

Table 3. List of compounds for figure 3 with area counts normalized to HLB.

Figure 4 shows a stacked view of total ion chromatograms (TICs) of amber lager extracted by the CAR/PDMS (top), DVB/PDMS (middle), and HLB/PDMS (bottom) phases. Compounds such as 2-furanmethanol and 2-acetylpyrrole impart sweet, bready, caramel notes whereas phenyl ethyl alcohol, isoamyl acetate, and linalool provide fruity and floral aromas, all of which are characteristic of an amber lager. While the ethanol response is higher when using DVB/PDMS, other VVOCs such as dimethyl sulfide and ethyl acetate generate higher responses with CAR/PDMS and HLB/PDMS. The DVB/PDMS device shows the greatest extraction efficiency for VOCs and SVOCs, many of which have a log $K_{O/W}$ value in the range 1-4, but lower concentration compounds like 2-acetylpyrrole and linalool are not detected due to coelution with large fatty acid peaks and other high concentration compound peaks such as phenyl ethyl alcohol.

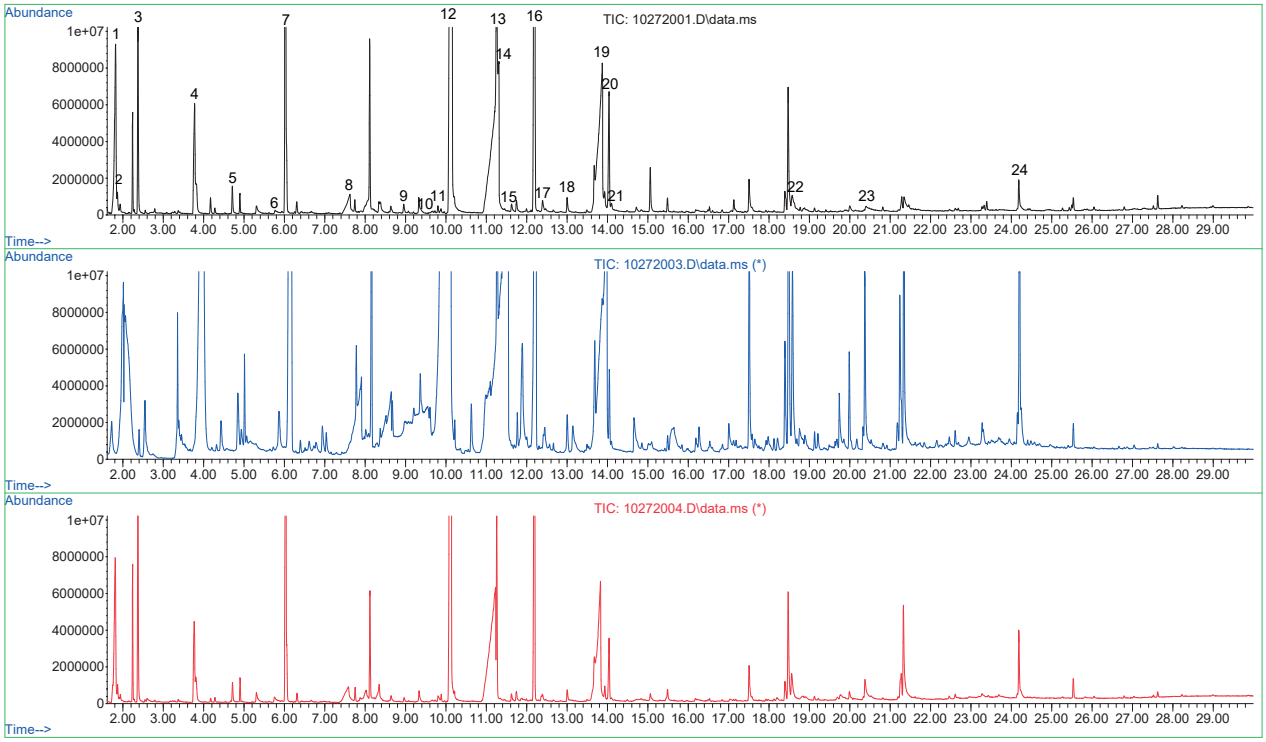

Figure 4: Stacked view of TICs for amber lager using CAR/PDMS (top), DVB/PDMS (middle), and HLB/PDMS (bottom) TF-SPME devices in combination with a PDMS-Twister (SBSE).

Peak #	Compound	m/z	CAR	DVB	HLB	Log $K_{o/w}$
1	Ethanol	45	1.08	4.81	1.00	-0.31
2	Dimethyl sulfide	62	1.18	-	1.00	0.92
3	Ethyl acetate	43	0.96	0.71	1.00	0.73
4	Isoamyl alcohol	55	1.43	13.12	1.00	1.16
5	Ethyl butyrate	71	1.39	4.92	1.00	1.85
6	2-Furanmethanol	98	0.76	6.77	1.00	0.28
7	Isoamyl acetate	73	1.04	5.05	1.00	2.25
8	4-Methylpentanoic acid	57	1.04	5.27	1.00	1.40
9	Benzeneacetaldehyde	91	1.84	1.59	1.00	1.78
10	2-Acetylpyrrole	94	1.22	-	1.00	1.93
11	Linalool	71	1.30	-	1.00	2.97
12	Phenyl ethyl alcohol	91	1.46	4.14	1.00	1.36
13	Ethyl octanoate	88	1.37	1.74	1.00	3.50
14	Octanoic acid	60	1.47	3.99	1.00	3.05
15	Ethyl nicotinate	106	1.08	0.71	1.00	1.30
16	Phenylethyl acetate	104	1.45	2.36	1.00	2.30
17	Nonanoic acid	60	1.38	7.29	1.00	3.42
18	2-Methoxy-4-vinylphenol	150	1.26	3.37	1.00	2.40
19	Decanoic acid	60	1.53	3.26	1.00	4.09
20	Ethyl decanoate	88	1.97	1.41	1.00	4.60
21	Skatole	130	2.05	1.79	1.00	2.60
22	Tryptophol	130	0.76	4.44	1.00	1.80
23	Dehydro-cohumulinic acid	219	0.37	4.73	1.00	3.10
24	Oleamide	59	0.51	3.89	1.00	6.60

Table 4. List of compounds for figure 4 with area counts normalized to HLB.

Figure 5 shows a stacked view of total ion chromatograms (TICs) of pumpkin ale extracted by the CAR/PDMS (top), DVB/PDMS (middle), and HLB/PDMS (bottom) phases. Many of the compounds responsible for the pumpkin spice flavor were extracted including cinnamaldehyde (cinnamon), eugenol (clove), and myristicin (nutmeg). While the ethanol response is higher when using DVB/PDMS, other VVOCs such as isoprene and dimethyl sulfide generate higher responses with CAR/PDMS and HLB/PDMS. The DVB/PDMS device shows the greatest extraction efficiency for the VOCs. For the SVOCs, DVB/PDMS generates a higher response for compounds with log $K_{O/W}$ < 3 whereas HLB/PDMS is more efficient for compounds with log $K_{O/W}$ > 3.

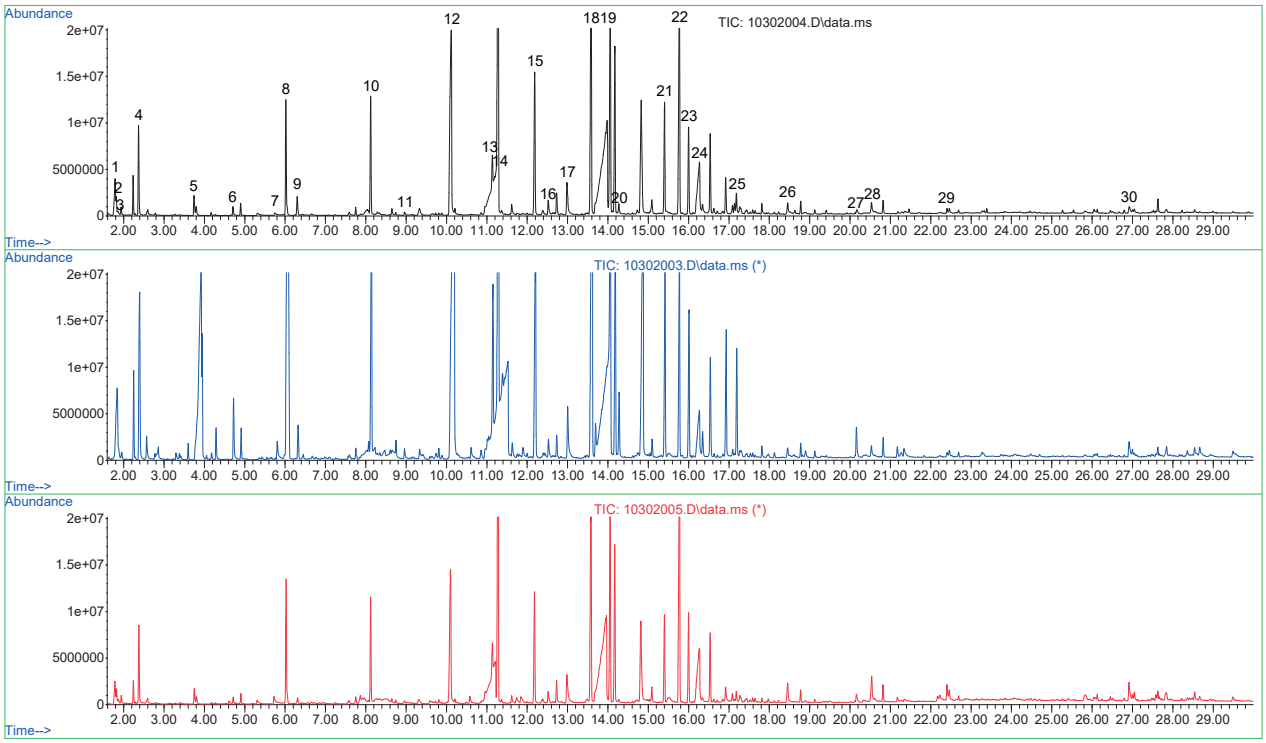

Figure 5: Stacked view of TICs for pumpkin ale using CAR/PDMS (top), DVB/PDMS (middle), and HLB/PDMS (bottom) TF-SPME devices in combination with a PDMS-Twister (SBSE).

Peak #	Compound	m/z	CAR	DVB	HLB	Log $K_{O/W}$
1	Ethanol	45	1.39	3.45	1.00	-0.60
2	Isoprene	67	1.25	-	1.00	2.42
3	Dimethyl sulfide	62	0.10	0.28	1.00	0.92
4	Ethyl acetate	43	1.11	2.81	1.00	0.73
5	Isoamyl alcohol	55	1.26	24.12	1.00	1.16
6	Ethyl butyrate	71	1.40	8.41	1.00	1.85
7	2-Furanmethanol	98	0.29	1.37	1.00	0.28
8	Isoamyl acetate	73	0.89	6.51	1.00	2.25
9	Styrene	104	5.63	8.54	1.00	2.95
10	Ethyl hexanoate	88	1.16	2.83	1.00	2.40
11	Benzeneacetaldehyde	91	1.97	5.79	1.00	1.78
12	Phenylethyl alcohol	91	1.69	4.02	1.00	1.36
13	Terpinen-4-ol	71	0.93	4.55	1.00	3.26
14	Octanoic acid	60	1.03	1.95	1.00	3.05
15	Phenylethyl acetate	104	1.33	2.27	1.00	2.30
16	Cinnamaldehyde	131	1.26	1.45	1.00	1.90
17	Cinnamyl alcohol	92	1.19	1.63	1.00	1.90
18	Eugenol	164	1.16	2.15	1.00	2.27
19	Methyl eugenol	178	1.04	1.52	1.00	3.03
20	Isoeugenol	164	3.34	21.97	1.00	3.04
21	Methyl isoeugenol	178	1.28	2.49	1.00	2.50
22	Myristicin	192	0.96	0.76	1.00	3.53
23	Elemicin	208	1.00	1.79	1.00	2.50
24	Dodecanoic acid	73	0.90	0.76	1.00	4.60
25	Isoelemicin	208	2.11	11.57	1.00	2.50
26	Tetradecanoic acid	73	0.54	0.57	1.00	6.11
27	Ethyl-(E)-ferrulate	222	0.60	3.37	1.00	2.20
28	Hexadecanoic acid	73	0.47	0.43	1.00	7.17
29	Ethyl linolate	67	0.25	0.11	1.00	7.30
30	Licarin A	326	0.30	0.79	1.00	4.40

Table 5. List of compounds for figure 5 with area counts normalized to HLB.

Conclusions

This study has demonstrated the usefulness of different TF-SPME phases for beverage extractions. While the extraction efficiency is matrix dependent, in general CAR/PDMS is well suited for VVOCs, DVB/PDMS is well suited for VOCs and SVOCs, and HLB/PDMS covers the widest range and is well suited for VVOCs, VOCs, and SVOCs. All three phases were able to extract compounds from a very wide polarity range (log $K_{O/W}$ -0.60 – 13.1). TF-SPME provides a simple, solvent-less extraction technique that can be readily used for quality control and for troubleshooting off-flavors in these sample types. In each case, a GERSTEL Twister® was used for stirring the sample and was desorbed along with the TF-SPME device. The Twister provides additional PDMS phase volume while the TF-SPME devices provide enhanced selectivity. The combination of the two devices results in enhanced extraction efficiency.

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