LabWorks APPNOTE

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Volatile Organic Compound and Sensory Profiles of Alcoholic versus Non-Alcoholic Wines and a Spirit Using Immersive Twister® and TF-SPME Extraction

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Abstract

Non-alcoholic (NA) wines and spirits are becoming increasingly popular, just like NA beers. Unlike beer, these beverages present greater challenges for alcohol removal due to their higher starting alcohol concentrations. As a result, preserving the volatile organic compounds (VOCs) is more difficult, which contributes to the desired flavors of these beverages. To characterize the VOCs and sensory profiles of alcoholic and NA wines and spirits, this study employs a simultaneous immersion technique with GERSTEL's Twister and thin film-solid phase microextraction (TF-SPME) devices. The GERSTEL Olfactory Detection Port (ODP 4) facilitated sensory-active compound identification, providing a detailed comparison between alcoholic and NA beverages.

Introduction

Non-alcoholic (NA) beverage trends remain a growing market in 2024. New studies for 2024 determined that consumers are prioritizing their physical health, making NA beverages an attractive contender [1]. Because beer is the most consumed alcoholic beverage in the world, more NA varieties are available. However, wine and spirits are also expanding their NA offerings to meet consumers' demands for drinking responsibly and their own health and wellness goals. The caveat to wine and spirits is that they have a higher starting alcohol concentration than beer, thus making the alcohol removal process more complex and flavor preservation more challenging. Dealcoholization techniques for wines and spirits include spinning cone columns, reverse osmosis, and vacuum distillation, with reverse osmosis having fewer issues with flavor loss due to better retention of aroma compounds, such as esters and terpenes [2]. To investigate flavor profile differences between alcoholic and NA beverages, an optimal extraction technique must be considered.

Simultaneous immersion of Twister and thin film-solid phase microextraction (TF-SPME) devices is a proven technique for effectively extracting volatile and semi-volatile compounds. Recently, volatile organic compounds (VOCs) and sensory profile differences in alcoholic and NA beers were determined using these extraction devices [3]. Due to their combined surface area (344 mm^2) and phase volume (33 µL), these high-capacity extraction devices ensure that extremely low detection limits are achievable. The GERSTEL polydimethylsiloxane (PDMS) Twister and PDMS/hydrophilic-lipophilic balanced (HLB) TF-SPME membranes ensure the extraction of polar and non-polar compounds. This makes the Twister/TF-SPME extraction devices ideal for extracting important flavor compounds in alcoholic and non-alcoholic beverages.

In this study, alcoholic and NA wines and lemon liqueur were analyzed. An immersive Twister/TF-SPME approach was utilized to extract and pre-concentrate analytes from beverage matrices. Peak areas and sensory profiles were used to compare VOC and flavor component differences between alcoholic and NA varieties. The GERSTEL Olfactory Detection Port (ODP 4) enables analysts to indicate odor regions of the chromatogram with simultaneous mass spectral data collection for sensory-active compound identification.

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Experimental

Instrumentation

GERSTEL MPS LabWorks Platform with Cryostatic Cooling Device (CCD 2) and ODP 4 on Agilent 8890 GC/5977B Inert plus as shown in Figure 1.

Figure 1: MPS LabWorks Platform equipped with ODP 4 used in this study.

Analysis Conditions LabWorks Platform

TF-SPME	HLB/PDMS
Twister	PDMS
TDU 2	splitless 40 °C; 720 °C/min; 250 °C (5 min)
CIS 4	solvent vent (50 mL/min), split 30:1 -30 °C; 12 °C/sec; 280 °C (3 min)
ODP 4	Transfer Line 250 °C Mixing Chamber 150 °C
Split	2:1 ODP:MSD

Analysis Conditions 8890 GC

Column	30 m HP-5MS UI (Agilent) d_i = 0.25 mm, d_f = 0.25 µm
Pneumatics	He, P_i = 7.07 psi Constant Flow 1.0 mL/min
Oven	40 °C (1 min); 10 °C/min; 280 °C (3 min)

Analysis Conditions 5977B MSD

Full scan	40-350 amu

Sample Preparation

Alcoholic and NA pinot grigio, merlot, and lemon liqueur were purchased from a local liquor store. Each alcoholic and NA wine and liqueur pair was of the same brand and style to ensure the comparison was equivalent.

A 5 mL aliquot of each wine or 1 mL of lemon liqueur and 5 or 9 mL of bottled water were transferred to 10 mL screw-capped vials. A PDMS Twister stir bar was immersed in each sample. A PDMS/HLB TF-SPME membrane was suspended in the vials with a holder. The vials were placed on a GERSTEL Twister 20 position stir plate at room temperature. The samples were stirred at 1100 rpm for 1 hour. After the extraction, the Twister and TF-SPME devices were removed, rinsed with water, and blotted dry before placing each in an empty TD tube. The TD tubes were sealed with a transport adapter and placed in a 40-position tray on the MPS Robotic autosampler for automated analysis.

Sample Introduction

Samples were desorbed in splitless mode with a 50 mL/min helium flow at 250 °C for 5 minutes. Analytes were cold-trapped in the CIS 4 inlet at -30 °C on a Tenax® TA-filled liner. When desorption was complete, analytes were transferred to the column in split mode (30:1) by rapidly heating the inlet to 280 °C.

Olfactometry

GC-O analysis was performed with the column effluent split 2:1 between the ODP 4 and MS, respectively. The ODP transfer line was heated to 250 °C. The mixing chamber was heated to 150 °C and purged with humidified nitrogen to prevent olfactory fatigue and nasal dehydration.

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Results and Discussion

Figure 2 shows the stacked view of total ion chromatograms obtained for the alcoholic (top) and NA (bottom) pinot grigio. Table 1 shows the relative peak areas of the compounds identified in alcoholic and NA pinot grigios, normalized to the alcoholic pinot grigio. In the alcoholic pinot grigio, the peak area counts for several esters were significantly higher than in the NA pinot grigio, and some esters, such as ethyl isobutyrate, ethyl isovalerate, and phenethyl acetate, were not detected in the NA pinot grigio. These compounds were likely lost in the dealcoholization process. In the NA pinot grigio, the area counts for butyrolactone, benzaldehyde, and most fatty acids were higher. Newly identified compounds in the NA pinot grigio include sulfur dioxide, acetic acid, propylene glycol, sorbic acid, benzoic acid, terpenes, cis-davanone, and long-chain fatty acids, labeled in blue in Figure 2. Flavors prepared in propylene glycol are added to compensate for volatiles lost after dealcoholization, and preservatives, like sulfur salts, sorbic acid, and benzoic acid, are added to prevent oxidation and spoilage. In the NA pinot grigio, grape juice concentrate, "natural flavors," sodium benzoate, and potassium metabisulfite were listed as ingredients on this variety's nutrition label, thus accounting for the difference in identified compounds.

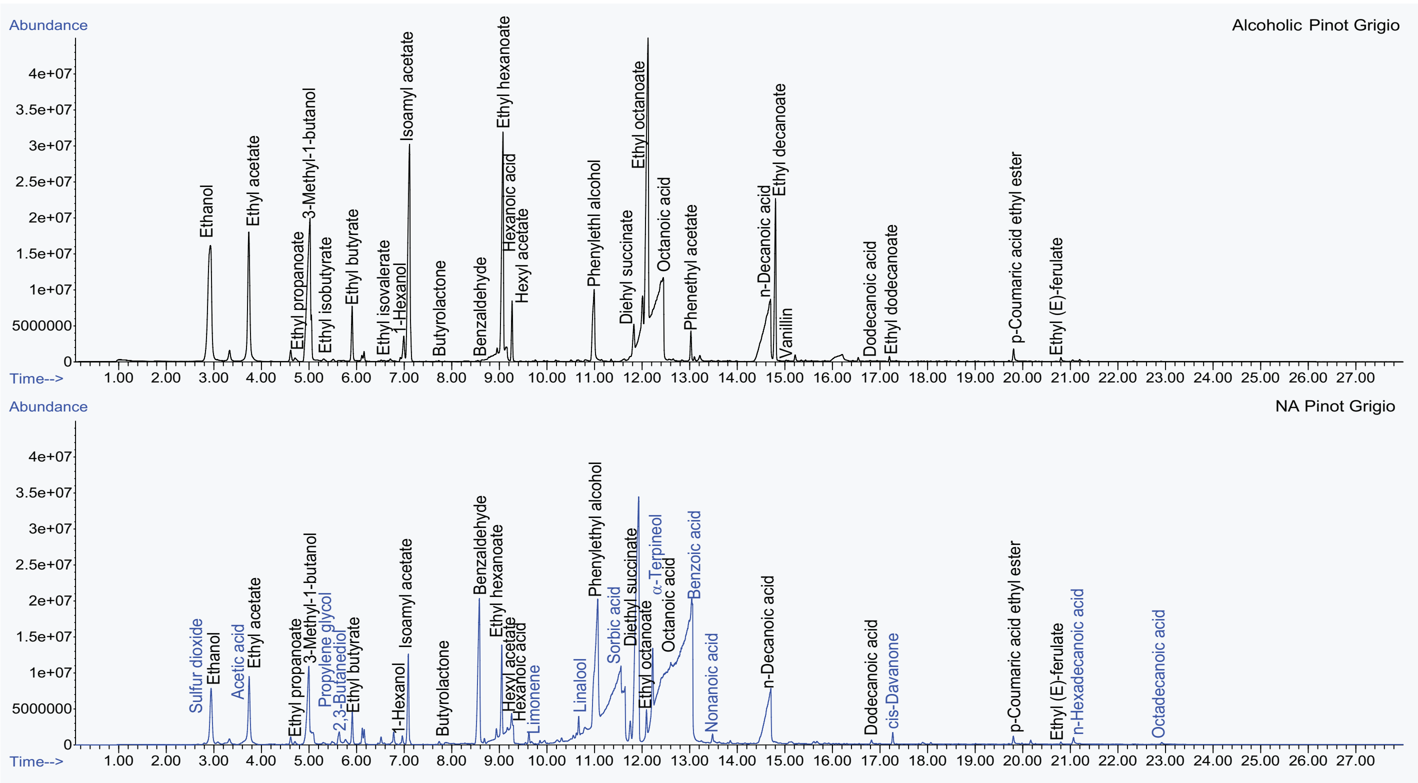

Figure 2: Stacked view of total ion chromatograms obtained for the alcoholic (top) and NA (bottom) pinot grigio.

Table 1: Compounds identified in both alcoholic and NA pinot grigios with relative peak areas.

Compound	m/z	Pinot Grigio	NA Pinot Grigio
Ethanol	45	100	30.7
Ethyl acetate	43	100	52.7
Ethyl propanoate	57	100	74.7
3-Methyl-1-butanol	55	100	41.7
Ethyl butyrate	71	100	54.8
1-Hexanol	56	100	24.0
Isoamyl acetate	43	100	28.9
Butyrolactone	42	100	339.6
Benzaldehyde	105	100	22,383.9
Hexanoic acid	60	100	180.6
Ethyl hexanoate	88	100	28.5
Hexyl acetate	43	100	21.9
Phenylethyl alcohol	91	100	253.7
Diethyl succinate	101	100	1,632.8
Ethyl octanoate	88	100	4.6
n-Decanoic acid	73	100	69.8
Ethyl decanoate	88	100	0.4
Dodecanoic acid	73	100	430.5
p-Coumaric acid ethyl ester	147	100	66.5
Ethyl (E)-ferrulate	177	100	58.2
n-Hexadecanoic acid	73	100	482.1

Sensory data was obtained to further investigate differences in alcoholic and NA pinot grigios. First, two panelists tasted the samples side-by-side to determine the sensory characteristics of each. The panelists detected vinegar and cheesy off-notes in the NA pinot grigio, which were not detected in the alcoholic variety. The alcoholic pinot grigio was described as fruitier with pear, apple, orange, and peach notes. The two panelists evaluated the pinot grigios at the ODP 4, and the combined odor descriptors are in Table 2. The tentative compound column indicates compounds that could be identified and eluted during the time window of the odor detected. Without further confirmation, it does not guarantee that the compound is responsible for the odor.

The sensory data are comparable for several retention time regions, including the ethyl esters that correlate with floral and fruity aromas. On the other hand, there were odor regions in the alcoholic pinot grigio where fruity or floral aromas were detected, but not in the NA pinot grigio. Additionally, several odor regions in the NA pinot grigio were described as fecal, vinegar, sweaty, and cheesy, as indicated in the side-by-side tasting. These off-odor regions are labeled in red in Table 2. Some odor regions did not correlate with an identifiable peak at the MS, highlighting the importance of collecting olfactory data when investigating sensory-active compounds. In these cases, coelution prevents analyte identification, or additional analyte mass on column is needed to produce a peak for compound identification. In either case, the ODP 4's trapping capabilities can be used to trap the same region multiple times for increased analyte mass on column or trap and reintroduce onto a column with a dissimilar phase for enhanced separation. Coelution occurred in odor regions with more than one tentatively identified compound. Trapping with the ODP 4 or a selectable ^{1}D/^{2}D-Gas Chromatography-Olfactometry/Mass Spectrometry (^{1}D/^{2}D-GC-O/MS) system with heart cutting can resolve these regions.

Table 2: Combined ODP report from two panelists for alcoholic and NA pinot grigios.

Start RT [min]	Stop RT [min]	Pinot Grigio	NA Pinot Grigio	Tentative Compounds
2.90	2.98	Solvent	Cheesy, sweaty	Sulfur dioxide**, Ethanol
3.58	3.62	Buttery, cocoa	Buttery	
3.70	3.75	n.d.	Sl vinegar	Acetic acid**
4.08	4.13	Sl malty, cocoa	Sl malty, cocoa	
4.22	4.36	n.d.	Sl fatty acid	2,3,4,5-Tetrahydropyridazine**
4.38	4.63	Garlic, onion	Garlic, onion	
4.57	4.63	Waxy, rubber	Rubber	
4.93	5.09	Cocoa, malty	Cocoa, malty	3-Methyl-1-butanol
5.28	5.44	Bubblegum	Bubblegum	Ethyl isobutyrate*
5.67	5.87	Sl cheesy	Cheesy, sweaty	2,3-Butanediol**, Butanoic acid**

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Table 2 (cont.): Combined ODP report from two panelists for alcoholic and NA pinot grigios.

Start RT [min]	Stop RT [min]	Pinot Grigio	NA Pinot Grigio	Tentative Compounds
5.90	5.97	Bubblegum, pineapple	Bubblegum, tropical	Ethyl butyrate
6.55	6.63	Sl cheesy, fruity, fermented, sweaty	Cheesy, sweaty	
6.65	6.85	Apple, pear	Grass, apple, tropical	Ethyl isovalerate*
7.01	7.08	Yeasty, nutty, solvent	Nutty, oxidized, yeasty	1-Hexanol
7.09	7.16	Banana	Banana	Isoamyl acetate
7.60	7.69	Grainy, savory	Baby formula, mushroom, potato	
7.71	7.82	Nutty, waxy, sl smoky	Smoky	Butyrolactone
7.97	8.20	Sl floral	Waxy	
8.39	8.47	Green, oxidized, aldehydic	Sl fecal	
8.51	8.56	Sl fruity	Sl waxy, musty	Benzaldehyde
9.03	9.20	Floral, apple, pineapple	Fruity, orange, tropical	Ethyl hexanoate
9.35	9.40	n.d.	Musty, earwax, sweaty	
9.97	10.03	Peach, honey, floral	Honey, rose, sweaty	
10.34	10.45	Musty, floral, creamy	n.d.	
10.54	10.68	Burnt, minty	Meaty, antiseptic	
10.69	10.72	Floral, syrupy	Fruit loops	Linalool**
11.00	11.20	Honey, rose	Honey, rose	Phenylethyl alcohol
11.21	11.41	Sour, floral, citrus, dusty, green	Smoky, floral, fruity, musty	
11.42	11.46	Soapy, floral, powdery	Grass, swimming pool, aldehydic, sl fatty acid	Sorbic acid**
11.87	11.99	n.d.	Fruity, phenolic, musty, dusty	Diethyl succinate
12.02	12.26	Floral, waxy, soapy, baby lotion	n.d.	Ethyl octanoate
12.40	12.69	n.d.	Sl smoky, waxy, fatty acid, fruity	Octanoic acid
13.06	13.10	Sl waxy, sour, honey	Floral, fruity, powdery	Phenethyl acetate*
13.87	13.92	Herbaceous, anise	Spice, clove	2-Methoxy-4-vinylphenol
14.08	14.26	Spice, waxy, aldehydic	Minty, waxy, sl floral	
14.60	14.81	Floral, musty	Waxy, black currant, smoky, musty	n-Decanoic acid
14.80	14.91	Orange, floral, soapy	Berry, soapy, orange	Ethyl decanoate
15.01	15.25	Vanilla, marshmallow	Vanilla, plastic	Vanillin
16.85	16.98	Sl melon, red fruit, soapy	n.d.	Nerolidol 2*
17.28	17.32	n.d.	Cheesy, fatty acid	cis-Davanone**
17.76	17.85	Sl waxy	Plastic, musty	
18.08	18.18	Perfume, musk, citrus	Floral, spice	
18.55	18.61	Fresh, green, berry	Sl soapy	
20.42	20.49	Sl fruity, fresh, green	n.d.	
20.62	20.72	Sl berry, fresh	n.d.	

Note: n.d. = not detected; sl = slight; */** = only present in alcoholic/NA

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Figure 3 shows the stacked view of total ion chromatograms obtained for the alcoholic (top) and NA (bottom) merlot. Table 3 shows the relative peak areas of the compounds identified in the alcoholic and NA merlot, normalized to the alcoholic merlot. Most of the compounds identified in the alcoholic and NA merlots, including esters, ketones, aldehydes, alcohols, and fatty acids, are the same. However, in the alcoholic merlot, the peak area counts for several ethyl esters were significantly higher than in the NA merlot, and several compounds like ethyl propanoate, ethyl isobutyrate, ethyl-2-hexenoate, and ethyl decanoate were likely lost in the NA merlot due to the dealcoholization process. Furthermore, newly identified compounds in the NA merlot include sorbic acid, benzoic acid, isovaleric acid, 2-heptanone, diethyl fumarate, and triethyl citrate, labeled in blue in Figure 3. Sorbic acid, benzoic acid, diethyl fumarate, and triethyl citrate are food additives that preserve flavor and extend shelf life, especially when alcohol is absent from the product. Diethyl fumarate is a metabolite of fumaric acid, which helps stabilize wine [4]. In the NA merlot, alcohol was removed using a spinning cone column as a gentle means of preserving aroma compounds and preventing oxidation. Even with a gentle alcohol removal process, important aroma compounds are still lost, affecting flavor preservation in the NA product.

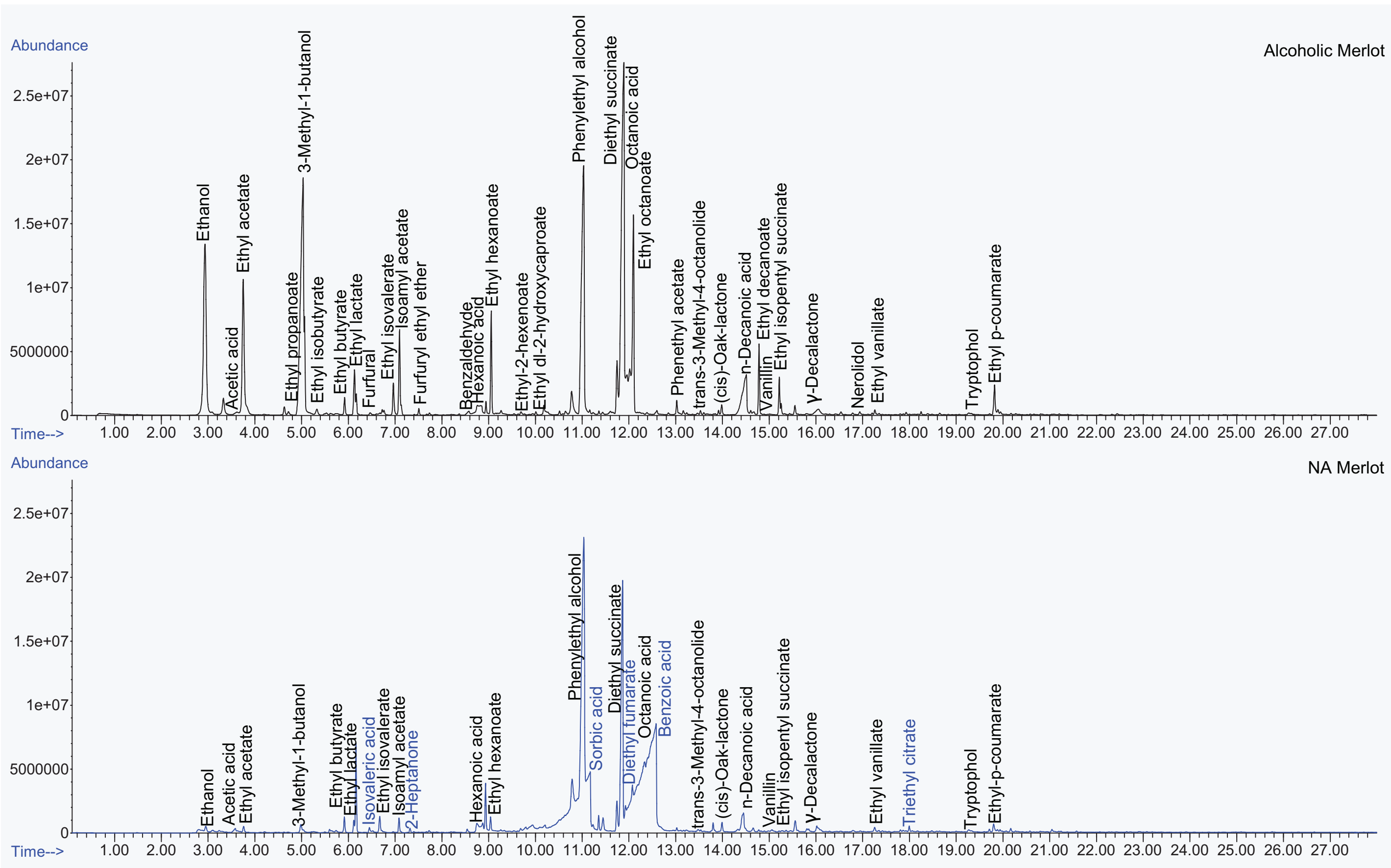

Figure 3: Stacked view of total ion chromatograms obtained for the alcoholic (top) and NA (bottom) merlot.

Table 3: Compounds identified in both alcoholic and NA merlots with relative peak areas.

Compound	m/z	Merlot	NA Merlot
Ethanol	45	100	2.4
Acetic acid	43	100	109.7
Ethyl acetate	43	100	10.7
3-Methyl-1-butanol	55	100	2.1
Ethyl butyrate	71	100	84.0
Ethyl lactate	45	100	24.6
Ethyl isovalerate	88	100	38.9
Isoamyl acetate	43	100	16.1
Hexanoic acid	60	100	80.3
Ethyl hexanoate	88	100	2.0
Phenylethyl alcohol	91	100	98.7
Diethyl succinate	101	100	55.6
trans-3-Methyl-4-octanolide	99	100	49.4
(cis)-Oak-lactone	99	100	95.0
n-Decanoic acid	73	100	25.6
Vanillin	151	100	70.7
Ethyl isopentyl succinate	101	100	2.1
γ-Decalactone	85	100	609.1
Ethyl vanillate	151	100	74.5
Tryptophol	130	100	107.4
Ethyl-p-coumarate	147	100	26.4

After a side-by-side tasting, the two panelists detected sour, sweaty, rancid, and earthy off-notes in the NA Merlot, which were not present in the alcoholic variety. The alcoholic merlot was described as having jammy, brown spice, phenolic, and cocoa notes, which are more typical red wine characteristics. The combined ODP data from both panelists and tentatively identified compounds are in Table 4. Several regions in the NA merlot were described as sweaty, cheesy, butyric, earthy, rotten, mushroom, or sour, which all coincide with the side-by-side tasting. These off-odor regions are labeled in red in Table 4. Several of these odor regions correlated with the tentatively identified compounds acetic acid, isovaleric acid, and 5-methylfurfural. On the other hand, there were several odor regions in the alcoholic merlot, which were described as berry, cotton candy, woody, floral, etc., but were not detected in the NA merlot. This exemplifies the loss of fruity and floral notes important to the alcoholic merlot.

Table 4: Combined ODP report from two panelists for alcoholic and NA merlots.

Start RT [min]	Stop RT [min]	Merlot	NA Merlot	Tentative Compounds
2.83	2.88	Sour, buttery, dairy	Fecal, musty	
2.94	3.05	Solvent	Sl fishy	Ethanol
3.52	3.67	Buttery, popcorn	Apple cider vinegar	Acetic acid
4.16	4.20	Cocoa, malty	Sl cocoa, malty	
5.27	5.41	Fruity, bubblegum	Sl fruity, bubblegum	Ethyl isobutyrate*
5.90	6.02	Green, fermented	Green, bubblegum	Ethyl butyrate
6.49	6.64	Sweaty, cheesy	Sweaty, parmesan	Isovaleric acid**
6.68	6.81	Strawberry, pineapple, sweaty	Red fruit, candy	Ethyl isovalerate
7.00	7.20	Nutty, yeasty, banana	Solvent	Isoamyl acetate
7.50	7.57	Pungent, marker	Solvent	Furfuryl ethyl ether*
7.70	7.78	Pungent, burnt	Skunky	Butyrolactone
8.48	8.50	n.d.	Sl vegetal, earthy, rotten	Benzaldehyde, 5-Methylfurfural**
8.78	8.91	Sl fruity, green, waxy	Musty, mushroom	Hexanoic acid
9.05	9.18	Berry	Sl fruity	Ethyl hexanoate
9.51	9.57	Sl nutty	Yeasty, bready	2-Ethyl-1-hexanol

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Table 4 (cont.): Combined ODP report from two panelists for alcoholic and NA merlots.

Start RT [min]	Stop RT [min]	Merlot	NA Merlot	Tentative Compounds
9.74	9.87	Artificial grape, berry	Sl cotton candy	Ethyl-2-hexenoate*
9.99	10.05	Cotton candy, berry, floral	n.d	Ethyl dl-2-hydroxycaproate*
10.35	10.47	Waxy, floral	Metallic, mushroom	
10.57	10.82	Sl vanilla, musky	Smoky, waxy, rose	Linalool
10.91	10.93	Musty, herbal	n.d.	
10.96	11.14	Rose, maple	Sour, maple, herbal rose	Phenylethyl alcohol
11.4	11.48	Swimming pool, floral	Swimming pool, floral	
11.72	11.77	Waxy, sl phenolic	Waxy, musty, dusty	Diethyl succinate
11.92	12.08	Sl band-aids	Sl Phenolic	Ethyl hydrogen succinate
12.08	12.15	Celery	n.d.	Ethyl heptanoate
12.13	12.19	Sl maple, brown fruit	n.d.	
12.30	12.37	Floral, diaper cream	n.d.	
12.75	12.81	Waxy, swimming pool	Waxy, swimming pool	
13.56	13.64	Cinnamon, dates	Dusty	γ-Heptalactone*
13.91	13.95	Brown spice	Sl peppermint	(cis)-Oak-lactone
14.30	14.62	Fruity, vanilla, frankincense	Fruity, floral, cinnamon	Eugenol, n-Decanoic acid
14.66	14.74	n.d.	Pungent, musty, dusty	
14.8	14.95	Fruity, floral, soapy	Berries, mothballs	Ethyl decanoate*
15.05	15.15	Vanilla	Vanilla	Vanillin
15.62	15.74	Soapy, shaving cream	Herbaceous, soapy	
15.87	16.00	Sl peach	Creamy, floral	γ-Decalactone
16.81	16.97	Grape, vanilla	Artificial grape	Nerolidol 2
17.78	17.87	Burnt rubber, machine oil	Smoky, fruity, machine oil	
18.64	18.86	Musky	n.d.	Atraric acid*
18.96	19.07	Sl cologne	n.d.	
20.26	20.37	Woody, sl clove	Sl brown spice	

Note: n.d. = not detected; sl = slight; */** = only present in alcoholic/NA

Like the pinot grigios findings, some odor regions contained more than one tentatively identified compound. For instance, in the alcoholic merlot, the odor region between 10.96 and 11.14 minutes was described as rose and maple. In contrast, this region was characterized similarly but with a new "sour" note in the NA merlot.

Phenylethyl alcohol was identified in this odor region in both the alcoholic and NA merlots, but sorbic acid coelutes with phenylethyl alcohol in the NA, as shown in Figure 4. While phenylethyl alcohol is known for its rose-like aroma, sorbic acid has a faint, acrid odor. Given these characteristics, it is unlikely that either of these compounds is responsible for the "sour" off-odor detected in the NA merlot. There is likely a compound coeluting with phenylethyl alcohol and sorbic acid, thus requiring separation via the ODP 4's trapping capabilities or a selectable ^{1}D/^{2}D-GC-O/MS. If the compound has a low odor threshold, additional analyte mass on column would be needed to produce a peak for identification.

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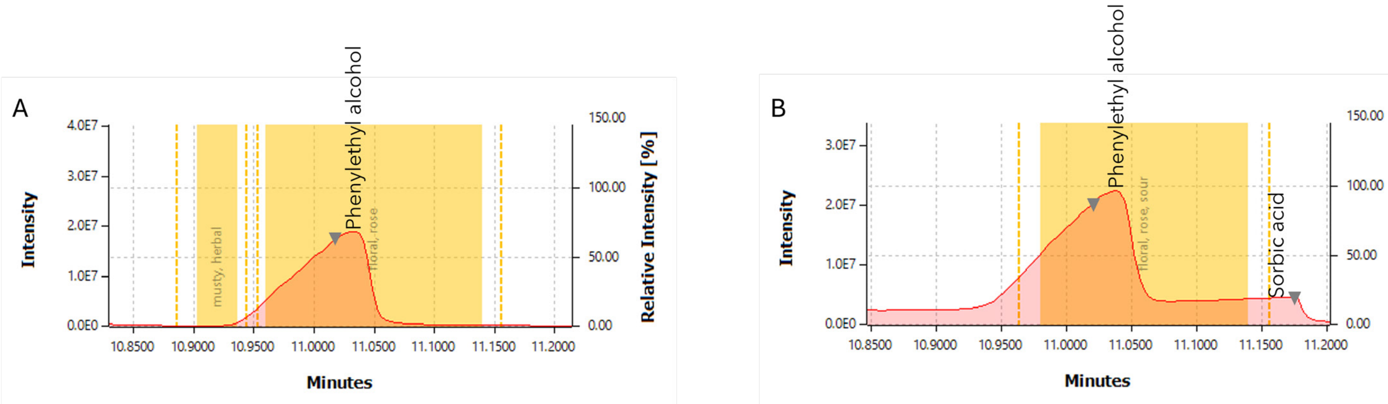

Figure 4: Chromatograms of odor region of interest from 10.96 to 11.14 minutes in the alcoholic (A) and NA (B) merlot.

Figure 5 shows the stacked view of total ion chromatograms obtained from the alcoholic (top) and NA (bottom) lemon liqueur. The compounds identified in both alcoholic and NA lemon liqueurs included aldehydes and several terpenes. Like the wine samples, newly identified compounds in the NA lemon liqueur are labeled in blue. The NA lemon liqueur contained several newly identified mono- and sesquiterpenes and food preservatives like sorbic and benzoic acid. Table 5 shows the relative peak areas of the compounds identified in the alcoholic and NA lemon liqueur, normalized to the alcoholic lemon liqueur. Peak area counts for o-cymene, limonene, eucalyptol, γ-terpinene, phenylethyl alcohol, and α-terpineol were higher in the NA lemon liqueur than in the alcoholic. Peak area counts for nerol acetate and geranyl acetate decreased significantly in the NA lemon liqueur.

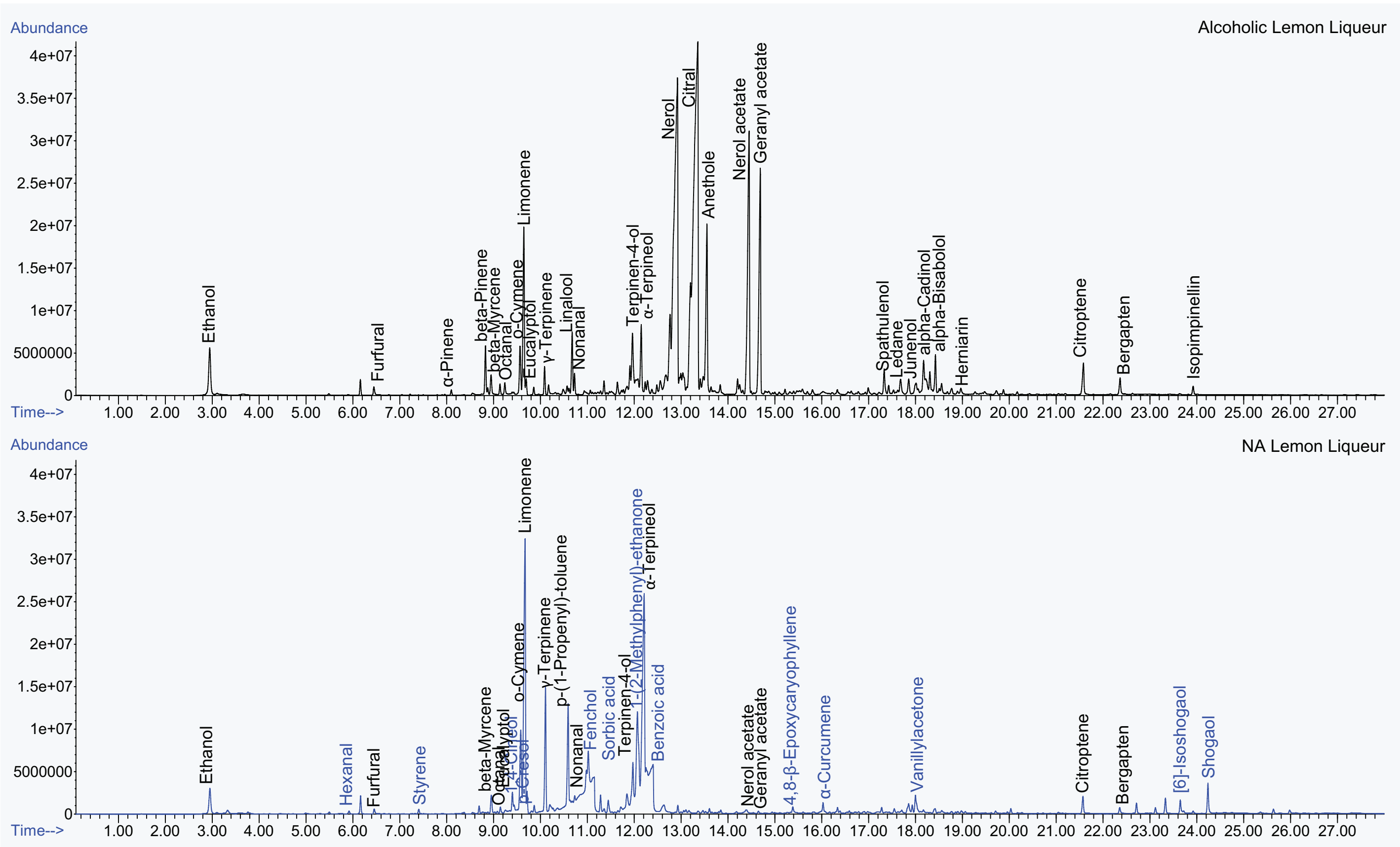

Figure 5: Stacked view of total ion chromatograms obtained for the alcoholic (top) and NA (bottom) lemon liqueur.

Table 5: Compounds identified in both alcoholic and NA lemon liqueurs with relative peak areas.

Compound	m/z	Lemon liqueur	NA Lemon liqueur
Ethanol	45	100	10.6
Furfural	96	100	57.1
β-Myrcene	93	100	21.6
Octanal	43	100	55.2
o-Cymene	119	100	226.2
Limonene	68	100	109.0
Eucalyptol	43	100	138.1
γ-Terpinene	93	100	475.3
Phenylethyl alcohol	91	100	403.7
Terpinen-4-ol	71	100	60.5
α-Terpineol	59	100	423.2
Nerol acetate	69	100	0.7
Geranyl acetate	69	100	0.5
Citropetene	206	100	48.0
Bergapten	216	100	35.7

Unlike the NA wines, the NA lemon liqueur did not exhibit a distinct off-odor(s); however, its aroma profile differed significantly from that of its alcoholic counterpart. After a side-by-side tasting, the two panelists described the alcoholic lemon liqueur as syrupy, fresh lemon, powdered sugar, and candy. But in the NA lemon liqueur, the notes were described as lemon-lime, lemonade, artificial, pine, and cleaner.

The combined ODP data from both panelists are in Table 6. There were twelve instances where citrus, lemon, or orange notes were detected by each panelist at the ODP for the alcoholic lemon liqueur but not in the NA lemon liqueur. In Table 6, these odor regions are labeled in red. Traditionally, this beverage is crafted using a simple recipe: lemon peels are soaked in pure alcohol, and sugar is added. The alcohol efficiently extracts natural oils from the lemon peels, producing an authentic lemon flavor. Nerol and citral were tentatively identified and correlated with the odor regions from 12.75 to 13.06 and 13.10 to 13.43 minutes, respectively. These odor regions were only detected in the alcoholic lemon liqueur. Nerol and citral are the most prevalent compounds concentrated in lemon peels [6]. Yet, they could not be identified in the NA lemon liqueur in Figure 5, ultimately affecting the perceived flavor and aroma of the final NA product.

The NA lemon liqueur's nutrition label listed a "lemon peel infusion" as one of the ingredients. However, when creating non-alcoholic versions of such infused beverages, distilleries often add "natural flavors," which consist of esters, aldehydes, ketones, and terpenes derived from natural sources. "Natural flavors" were also listed as an ingredient in the NA lemon liqueur. In the alcoholic lemon liqueur, the detected odors were not described as artificial; instead, they were attributed to parts of a citrus fruit: peel, pulp, rind, or oil. In Table 6, there were three instances where an "artificial" odor was detected in the NA lemon liqueur, and these regions are labeled in blue. From 9.66 to 9.72 minutes, the odor region was described as artificial, lemon-lime, and correlated with the tentatively identified compound limonene. From 10.25 to 10.30 minutes, the odor region was described as artificial and powdery. While it correlates with p-cresol in the chromatogram, this compound is known to have a phenolic, animalic aroma and is likely not the cause of the odor. This is why it is essential to label such compounds as tentatively identified. All sensory-active compounds should be confirmed with a reference standard to ensure that retention time, mass spectrum, and odor match those found in the sample. Finally, from 10.76 to 10.81 minutes, the odor region was described as smoky, lemon, and artificial and correlated with a few coeluting peaks, two of which were identified as nonanal and sorbic acid. Again, where there is coelution, the ODP 4's trapping capabilities or a selectable $^{1}D/^{2}D$-GC-O/MS system should be employed for enhanced separation.

Table 6: Combined ODP report from two panelists for alcoholic and NA lemon liqueurs.

Start RT [min]	Stop RT [min]	Lemon Liqueur	NA Lemon Liqueur	Tentative Compounds
2.81	2.95	Sulfur, pungent, fecal	Fecal	Ethanol
3.59	3.70	Malty, cocoa, buttery	Buttery	
4.30	4.47	Onion, garlic	Onion, garlic	
4.84	4.91	Malty, grainy	n.d.	
5.44	5.45	Sl smoky	Musty	
5.60	5.67	Sl rubbery	Rubbery, waxy	
6.03	6.07	n.d.	Sl sweaty	
6.30	6.36	Skunky	Skunky	
6.42	6.51	Red fruit, sweaty	Cheesy, butyric	Furfural
6.69	6.75	Fruity	Red fruit	2-Furanmethanol
6.98	7.10	Bready, yeasty	Grainy, bready	
8.12	8.16	Sl citrus	n.d.	α-Pinene*
8.33	8.38	Sl citrus, juicy	n.d.	Camphene*
8.89	9.06	Rubbery, skunky, herbaceous	Waxy, solvent	β-Myrcene
9.14	9.24	Citrus, floral	Swimming pool	Octanal, Carveol
9.29	9.50	Sl cleaner	Solvent, lemon	1,4-Cineole**
9.66	9.72	Sl anise	Artificial, lemon-lime	Limonene
9.72	9.82	Pepper, pungent	Mint, eucalyptus	Eucalyptol
9.83	9.95	Floral, powdery, fruity	Floral, rose	β-Ocimene
10.04	10.08	Cotton candy, rose	n.d.	γ-Terpinene
10.25	10.30	n.d.	Artificial, powdery	p-Cresol**
10.52	10.62	Juicy, fruity, candy	Musty, earthy, roasted	Fenchone
10.63	10.75	Smoky, pine, fatty acid	Sl pine, waxy	
10.76	10.81	Citrus, rind, waxy	Smoky, lemon, artificial	Nonanal, Sorbic acid**
10.99	11.06	Floral	Floral, rose	Phenylethyl alcohol
11.33	11.49	Lemon peel	n.d.	trans-Pinocarveole
11.66	11.78	Plastic, woody, oily	Musty, dusty	
11.91	11.94	Oily, citrus	n.d.	Isoneral
12.06	12.17	Orange, pulp	Floral, waxy, pine	Terpinen-4-ol
12.20	12.28	Earthy, dusty	Herbal, aldehydic	(-)-trans-Isopiperitenol
12.64	12.76	Musty, soapy	n.d.	
12.75	13.06	Lemon oil, peel, pungent	n.d.	Nerol*
13.06	13.43	Pepper, powdered sugar, lemon, soapy	Rose, cleaner, sl brown spice	Citral*
13.54	13.65	Sour, citrus, floral	Citrus, burnt	Anethole
14.42	14.53	Brown spice, potpourri	Brown spice, clove, violet	Nerol acetate
14.67	14.81	Waxy, citrus, woody	Musty, dusty	Geranyl acetate
15.22	15.35	Sl pepper, soapy	Waxy, smoky	Chrysanthenone*
16.42	16.56	Sulfur, machine oil	Lubricating oil	
17.11	17.15	Fruity	n.d.	
17.29	17.45	Waxy, pine, soapy, musty	n.d.	Spathulenol*
17.87	18.01	Incense, citrus	Lubricating oil	Junenol*

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Table 6 (cont.): Combined ODP report from two panelists for alcoholic and NA lemon liqueurs.

Start RT [min]	Stop RT [min]	Lemon Liqueur	NA Lemon Liqueur	Tentative Compounds
18.15	18.21	Sl burnt, orange	Floral, soapy	α-Cadinol*
18.30	18.39	Citrus	n.d.	α-Bisabolol*
18.87	18.98	Peppery, spice	n.d.	Herniarin
18.98	19.08	Creamy, coconut	Floral, creamy	
19.30	19.50	Creamy, men's cologne	n.d.	
19.90	19.98	Citrus, waxy, peel	n.d.	Nootkatone*
20.76	20.84	Cologne, musky, woody	n.d.	
21.57	21.69	Sl orange	Sl floral	Citroptene
22.32	22.38	Sl hay	Floral, creamy, lactone	Bergapten
23.04	23.11	n.d.	Sl rotten meat	

Note: n.d. = not detected; sl = slight; */** = only present in alcoholic/NA

Conclusion

This study has demonstrated the ability of immersive Twister/TF-SPME to extract the broadest range of analytes and obtain detailed flavor profiles in alcoholic and NA beverages. The data provided depicts peak area differences, loss of compounds, and the presence of new compounds within NA counterparts. These distinctions are attributed to the dealcoholization technique and added ingredients listed on nutrition labels. The ODP 4 is used to effectively correlate detectable peaks with sensory-active regions, which is imperative to NA beverage product development and consumer satisfaction.

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