



Agilent J&W DB-624 Ultra Inert Capillary Column Screens Distilled Spirits by GC/MS Static Headspace

Application Note

Food Testing & Agriculture

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Abstract

This work highlights the utility of using an Agilent J&W DB-624UI column for the screening of select distilled spirits by static headspace GC/MS. The inertness of the column delivers excellent peak shape for active aldehyde analytes in complex distilled spirit matrices. Clear differences are observable in the orange-flavored cognac and bourbon samples investigated. The inertness and selectivity of the DB-624UI column make distilled spirit profiling by static headspace GC straightforward.

Introduction

Small batch distillation of spirits is becoming an increasingly popular means of producing premium spirits that are finding a ready market for consumers with discriminating tastes. Profiling some of the flavor elements found in these beverages can help track completion of the fermentation process, access batch quality, or evaluate the impact new or traditional ingredients have on the bouquet of flavors. In this work, a highly inert Agilent J&W DB-624UI capillary GC column was used to examine the constituents in several select spirits.

Fusel oils and related fermentation products play important roles in defining the aroma and flavor characteristics of alcoholic beverages. Fusel oils or higher alcohols, their esters, vicinal diketones, and aldehydes, all have an effect on the balance of flavor characteristics present in a spirit. Headspace GC/MS profiling can be used to monitor the rise of desired characteristics in a batch, to control off-flavor elements, or as a research and development tool to explore the use of new ingredients that enhance desirable taste elements in a complex matrix.



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A convenient way to analyze a spirit's aromatic profile is by static headspace GC/MS. Spirits typically require 5:1 or higher dilution in the headspace vial due to the high percentage of ethanol present in these beverages and the need to resolve peaks eluting closely with ethanol.

Materials and Methods

An Agilent 7890/5975C GC/MS system equipped with a split/splitless inlet, an MSD triple axis detector, an Agilent 7697A headspace sampler, and MSD ChemStation E.02.02 software was used for this series of experiments.

Conditions

Column:	Agilent J&W DB-624UI, 30 m × 0.32 mm, 1.8 μm (p/n 123-1334UI)
Carrier:	Helium, 2.3 mL/min, constant flow set at 35 °C
Oven:	35 °C (5 min), 10 °C/min to 100 °C (1.5 min), 15 °C/min to 220 °C (3.0 min), 25 °C/min to 250 °C (2.8 min)
Inlet:	Split/splitless, 220 °C, 1 μL, split 20:1
Sample volume:	1 mL
MSD:	Scan mode 30-400 amu, source temp 230 °C, quad temp 150 °C, transfer line temp 260 °C
GC/MS:	Agilent 7890/5975C equipped with MMI and FID
Sampler:	Agilent 7697A headspace with 111 position tray

Flow path supplies

Vials:	Flat bottom crimp cap headspace vials, 20 mL (100 pk, p/n 5182-0837)
Vial caps:	Headspace crimp cap/high performance septa (100 pk, 5190-3987)
Septum:	Non-stick bleed and temperature optimized (50 pk, p/n 5183-4757)
Inlet liner:	Agilent Ultra Inert Liner, 1 mm straight single taper (p/n 5190-4047)
Ferrules:	85/15 Vespel/graphite, 0.5 mm id, short (10 pk, p/n 5062-3514)
Crimper:	Electronic crimper, 20 mm (p/n 5190-3189)
Transfer line:	Deactivated fused silica, 0.53 mm id (5 m, p/n 160-2535-5)
Fitting:	Reducing fitting, 1/6 to 1/32 inch (p/n 0100-2594)
Gold seal:	Gold plated inlet seal with washer (10/pk, p/n 5190-2209)
Magnifier:	20x Magnifier loop (p/n 430-1020)

Sample preparation

Standard fermentation-related alcohols, aldehydes, and acetates were purchased from Sigma Aldrich, St Louis, MO, USA. These standards were made into three stock solutions at a concentration of 1000 μL/L in ethanol (200-proof molecular biology grade purchased from Sigma Aldrich). Subsequent dilutions were made in deionized water.

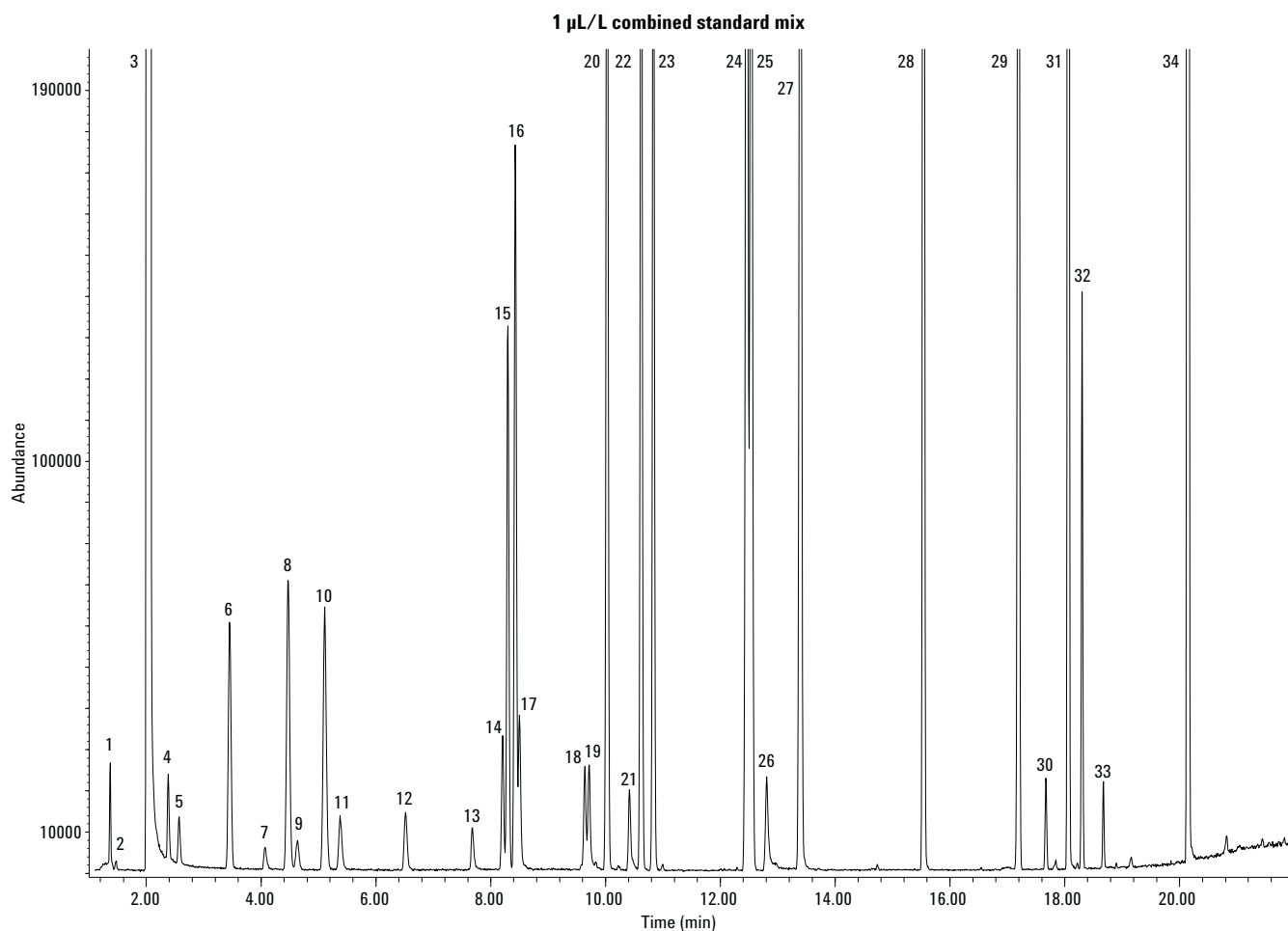
Spirits were bought from a local retailer. A premium orange-flavored cognac, a discount orange-flavored cognac, and a sour mash bourbon were used for profiling. Deionized water (8 mL) was added to 20 mL headspace vials to which 2 mL of spirit was added, to bring the final volume to 10 mL. The effective dilution was 5:1.

Results and Discussion

Figure 1 shows the combined total ion chromatogram for aldehyde, fusel alcohol, and fusel acetate standard mixes at 1 μL/L. At this level, using SCAN mode, each of the standards gave high quality matches versus the National Institute of Standards and Technology (NIST) spectral library. Peaks were well resolved on the Agilent J&W DB-624UI column. Peak shapes for aldehydes were sharp and well defined, indicative of the highly inert character of the column.

Selectivity for the analytes of interest in the standard mix was excellent. The column delivered clear separation between the positional isomeric pair, isoamyl alcohol, and active amyl alcohol, and also their esters. To achieve this level of separation, a 60 m column is often used, which results in additional run time. Here, the entire run was complete in 28 minutes.

Screening for fermentation and distillation-related flavor components was straightforward at the 1 μL/L level using SCAN mode. Compounds of interest eluting close to ethanol were resolvable and easily identified through NIST library matching. Lower level detection using either simultaneous SIM/SCAN or SIM modes is a very reasonable expectation for a defined set of target components with known fragmentation patterns to specify qualifying and quantifying ions.

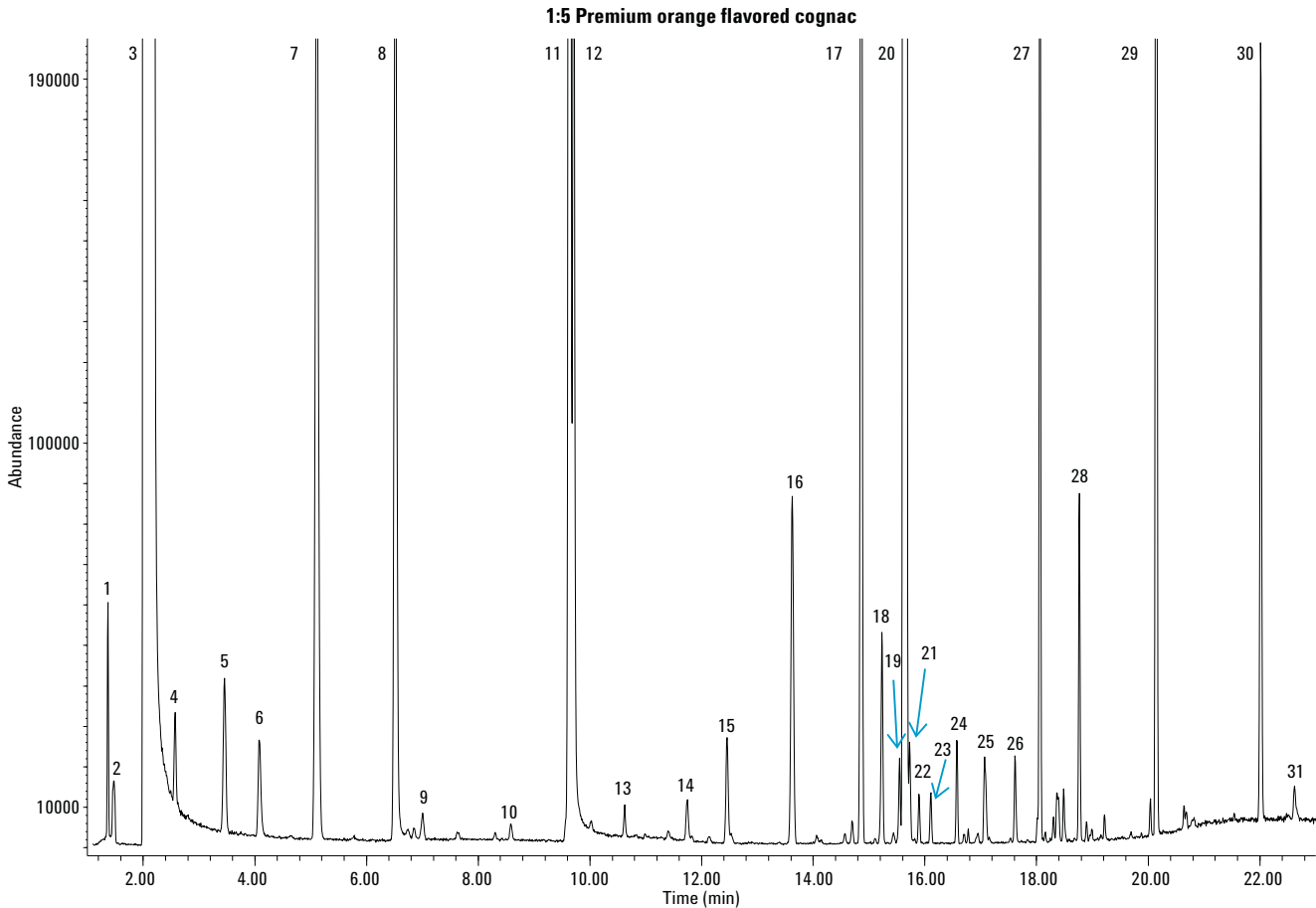


Peak ID		
1.	Acetyl aldehyde	12. Isobutyl alcohol
2.	Methanol	13. 1-Butanol
3.	Ethanol	14. 2,3 Pentanedione (vicinal diketone)
4.	Acetone	15. Ethyl propanoate
5.	Isopropanol	16. Propyl acetate
6.	Isobutyl aldehyde	17. 3-Pentanol
7.	1-Propanol	18. Isoamyl alcohol
8.	Butyl aldehyde	19. Active amyl alcohol
9.	2,3 Butanedione (vicinal diketone)	20. Isobutyl acetate
10.	Ethyl acetate	21. 1-Pentanol
11.	2-Butanol	22. Ethyl butanolate
		23. Hexanal
		24. Isoamyl acetate
		25. Active amyl acetate
		26. 1-Hexanol
		27. Heptanal
		28. Octanal
		29. 1,3,5-Trioxane impurity
		30. 1,3,5-Trioxane impurity
		31. Ethyl caprylate
		32. 1-Phenyl ethyl acetate
		33. Benzaldehyde, 3 methoxy
		34. Ethyl caprate

Figure 1. Total ion chromatogram of aldehyde, fusel alcohol, and fusel acetate combined standard on an Agilent J&W DB-624UI, 30 m x 0.32 mm, 1.8 μ m column.

The total ion chromatogram of the premium orange-flavored cognac displayed a good screening profile for the spirit in Figure 2. A fair number of components contained in the standard mix were present in the sample as were some additional peaks, most notably the ethyl acetates of long chain organic acids up to ethyl myristate (C₁₆).

Note the excellent peak shapes for the aldehydes in the chromatogram peaks 1, 5, 10, 14, and 19. Aldehydes can be challenging to chromatograph due to their reactivity. In this case, there was no evidence of peak tailing, which is often observed when analyzing these reactive compounds.

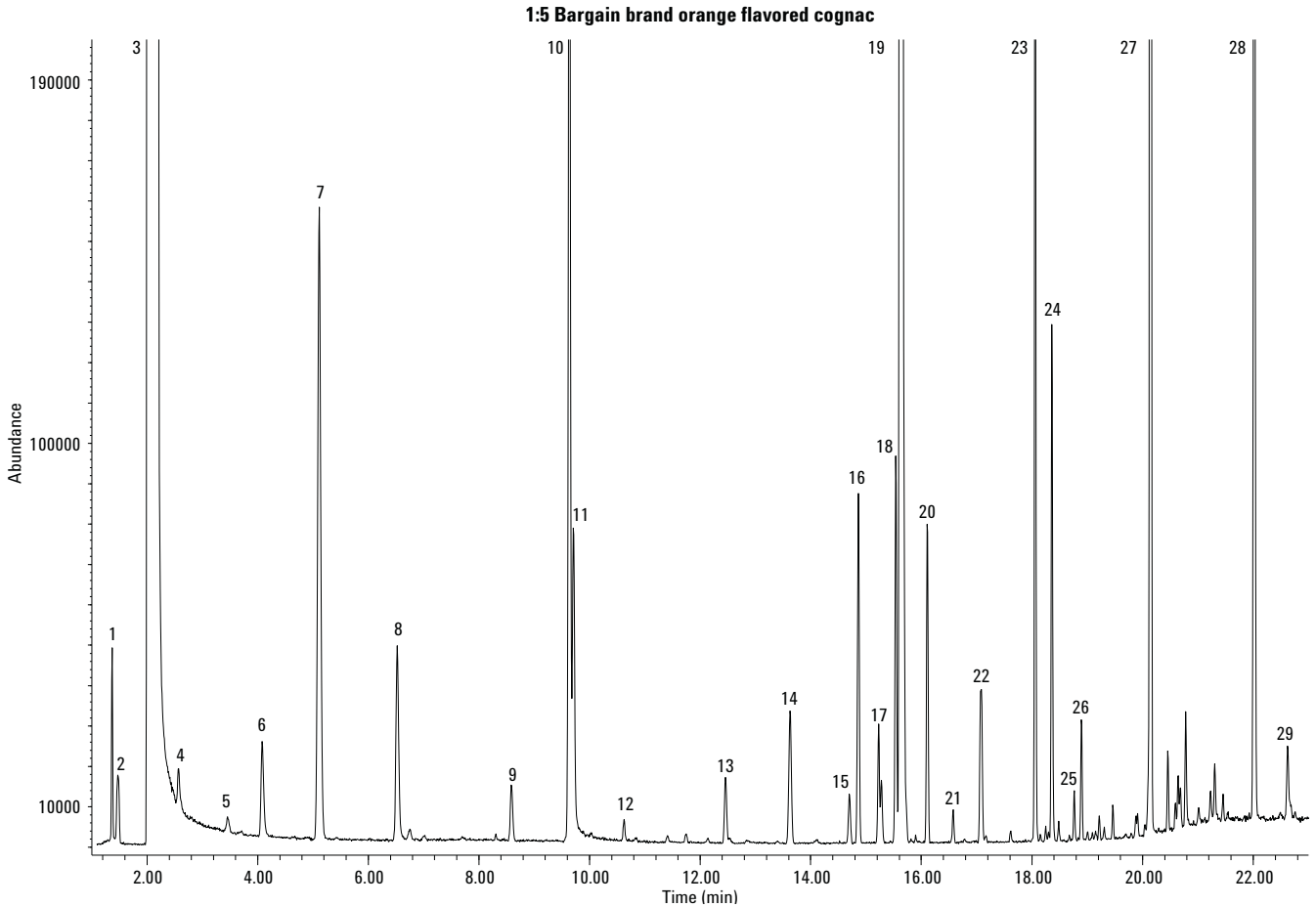


Peak ID	11. Isoamyl alcohol	22. β -Ocimene
1. Acetyl aldehyde	12. Active amyl alcohol	23. γ -Terpinene
2. Methanol	13. Ethyl butanonate	24. (+) 4 Carene
3. Ethanol	14. Isobutyl aldehyde	25. β -Linalool
4. Ethyl formate	15. Isoamyl acetate	26. <i>trans</i> -2-pinanol
5. Isobutyl aldehyde	16. α -Pinene	27. Ethyl caprylate
6. 1-Propanol	17. β -Pinene	28. α -Terpeneol
7. Ethyl acetate	18. Ethyl caproate	29. Ethyl caprate
8. Isobutyl alcohol	19. Octanal	30. Ethyl laurate
9. Allyl ethyl ether	20. D-Limonene	31. Ethyl myristate
10. Acetyl aldehyde	21. β -Phellandrene	

Figure 2. Total ion chromatogram of a premium orange-flavored cognac diluted 1 to 5 with distilled water in the headspace vial on an Agilent J&W DB-624UI, 30 m \times 0.32 mm, 1.8 μ m column.

The total ion chromatogram of the bargain-brand orange-flavored cognac displayed a good screening profile for the spirit in Figure 3, with observable distinctions from the premium cognac shown in Figure 2. The isobutyl aldehyde, ethyl acetate, and isoamyl alcohol levels appeared to be lower

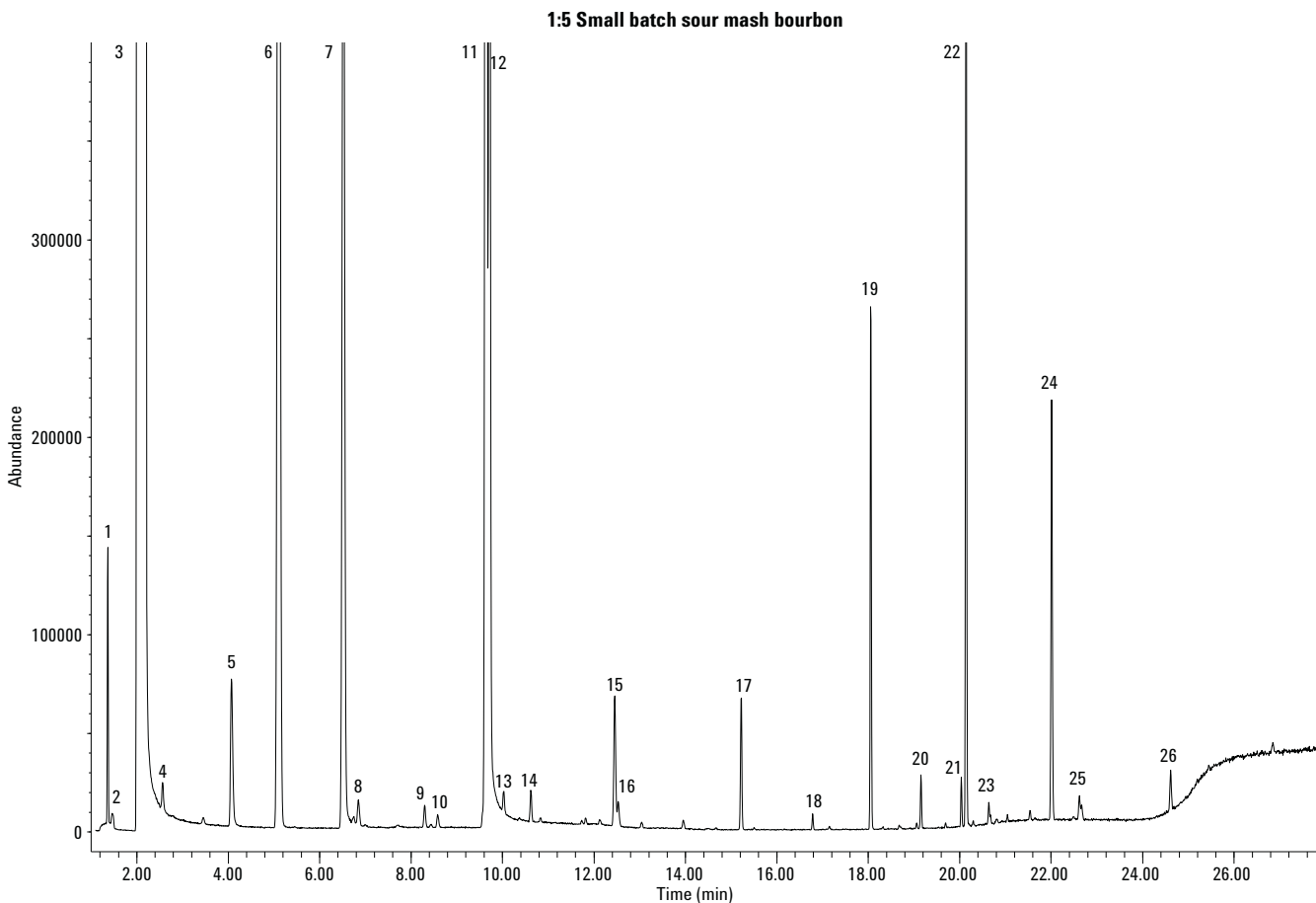
than that observed in the premium brand sample. The difference in β -pinene levels was quite striking, with a much lower level in the bargain brand. The terpenoid profiles were also quite different in the 14 to 22 minute elution range.



Peak ID	10. Isoamyl alcohol	20. D-Limonene
1. Acetyl aldehyde	11. Active amyl alcohol	21. γ -Terpinene
2. Methanol	12. Ethyl butanonate	22. (+) 4 Carene
3. Ethanol	13. Isoamyl acetate	23. β -Linalool
4. Ethyl formate	14. α -Pinene	24. Ethyl caprylate
5. Isobutyl aldehyde	15. β -Pinene	25. Decanal
6. 1-Propanol	16. β -Myrene	26. Octanal diethyl acetal
7. Ethyl acetate	17. Ethyl caproate	27. Ethyl caprate
8. Isobutyl alcohol	18. 3 Carene	28. Ethyl laurate
9. Acetyl aldehyde	19. Octanal	29. Ethyl myristate

Figure 3. Total ion chromatogram of a bargain-brand orange-flavored cognac diluted 1 to 5 with distilled water in the headspace vial on an Agilent J&W DB-624UI, 30 m \times 0.32 mm, 1.8 μ m column.

Figure 4 shows the total ion chromatogram of a small batch, sour mash bourbon. The bourbon screening profile presented a somewhat simpler profile than the orange cognac samples shown in Figures 2 and 3. In the bourbon sample, some of the key characteristics appeared to be high levels of ethyl acetate, isobutyl alcohol, isoamyl alcohol, active amyl alcohol, and ethyl caprate (C12).



Peak ID	9. Ethyl propanoate	18. Heptanoic acid, ethyl ester
1. Acetyl aldehyde	10. Diethyl acetal	19. Ethyl caprylate
2. Methanol	11. Isoamyl alcohol	20. Ethyl nonanoate
3. Ethanol	12. Active amyl alcohol	21. Ethyl <i>trans</i> -4-decanoate
4. Ethyl formate	13. Isobutyl acetate	22. Ethyl caprate
5. 1-Propanol	14. Ethyl butanonate	23. Isoamyl octanoate
6. Ethyl acetate	15. Isoamyl acetate	24. Ethyl laurate
7. Isobutyl alcohol	16. Active amyl acetate	25. Isoamyl n-decanoate
8. Diethylformal	17. Ethyl caproate	26. Ethyl myristate

Figure 4. Total ion chromatogram of a small batch sour mash bourbon diluted 1 to 5 with distilled water in the headspace vial on an Agilent J&W DB-624UI, 30 m × 0.32 mm, 1.8 μm column.

Conclusions

The Agilent J&W DB-624UI 30 m × 0.32 mm, 1.8 µm column delivers excellent inertness and selectivity for analytes related to fermentation and distillation in complex spirit matrices. The column's inertness is clearly demonstrated by the sharp symmetrical peaks for aldehyde components in both the 1 µL/L standard and the orange-flavored cognac samples. This application demonstrates the utility of the highly inert and selective J&W DB-624 UI column for static headspace GC/ MS profiling of complex spirit matrices.

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