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.

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.

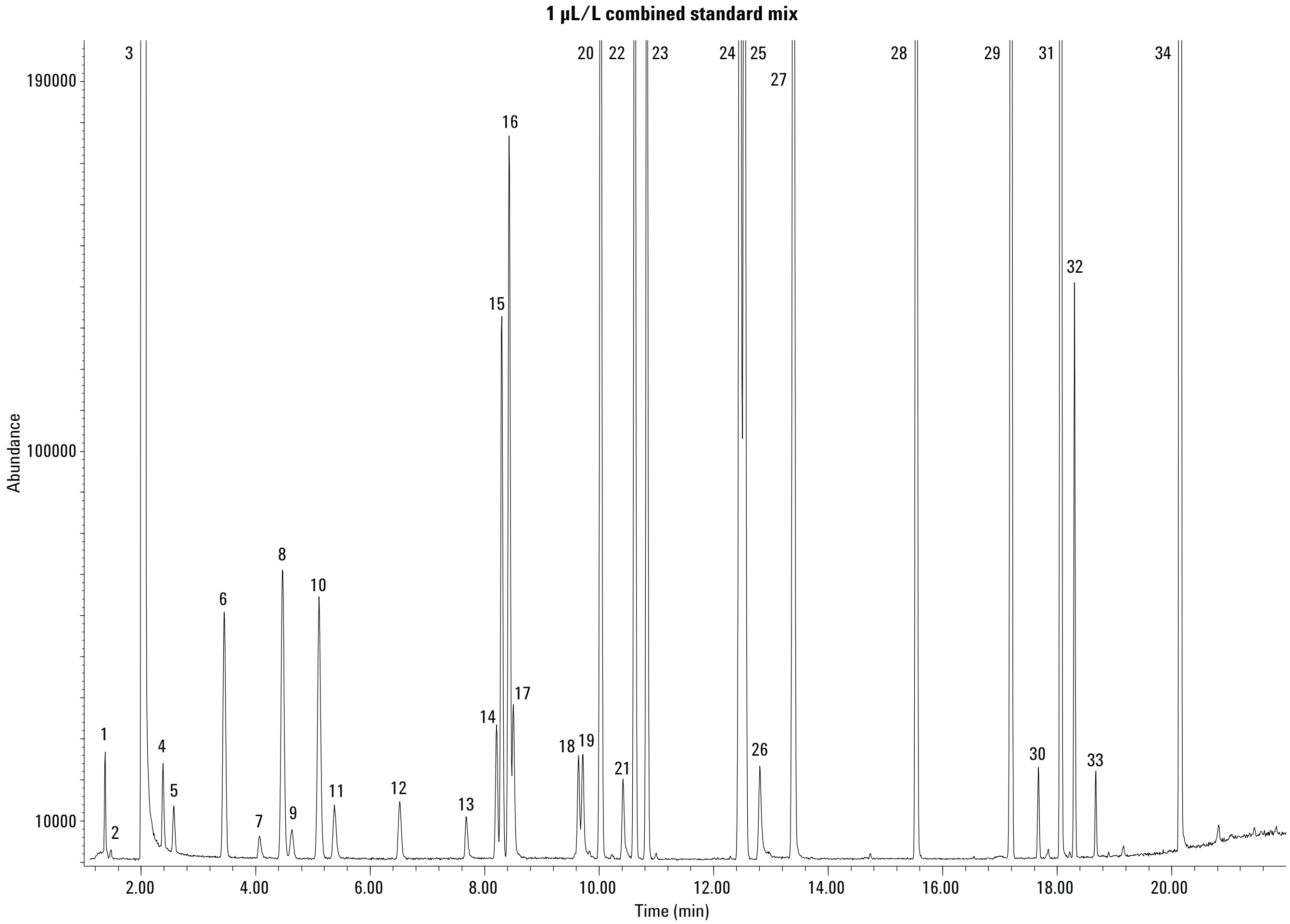
Spirits were bought from a local retailer. A premium orange-flavored cognac, a discount orange-flavored cognac, and a sour mash bourbon were used for profiling. Deionized water (8 mL) was added to 20 mL headspace vials to which 2 mL of spirit was added, to bring the final volume to 10 mL. The effective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

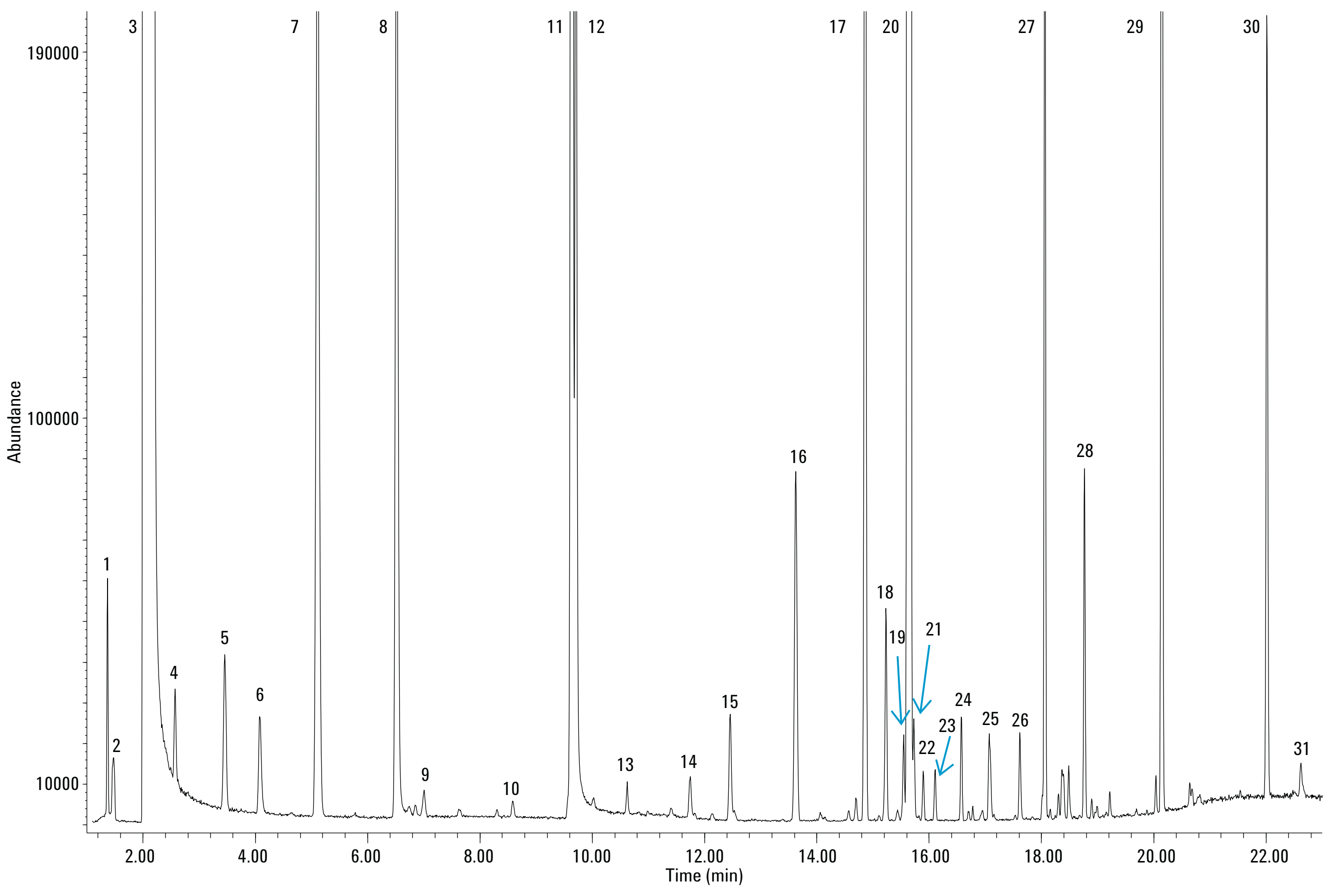


Peak ID
1. Acetyl aldehyde
2. Methanol
3. Ethanol
4. Acetone
5. Isopropanol
6. Isobutyl aldehyde
7. 1-Propanol
8. Butyl aldehyde
9. 2,3 Butanedione (vicinal diketone)
10. Ethyl acetate
11. 2-Butanol
12. Isobutyl alcohol
13. 1-Butanol
14. 2,3 Pentanedione (vicinal diketone)
15. Ethyl propanoate
16. Propyl acetate
17. 3-Pentanol
18. Isoamyl alcohol
19. Active amyl alcohol
20. Isobutyl acetate
21. 1-Pentanol
22. Ethyl butanonate
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 impourity
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 µm 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 (C_{16}).

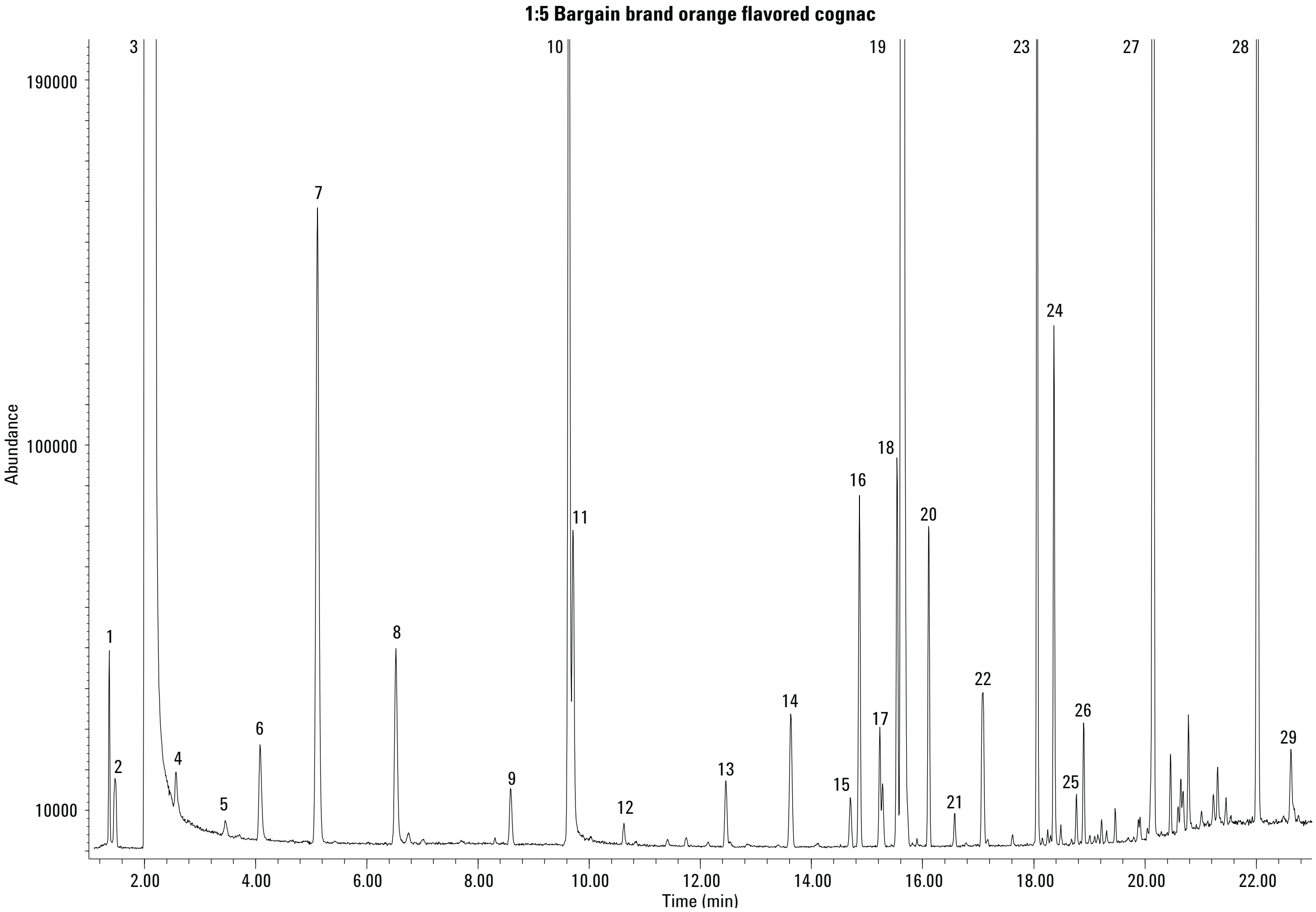
Note the excellent peak shapes for the aldehydes in the chromatogram peaks 1, 5, 10, 14, and 19. Aldehydes can be challenging to chromatograph due to their reactivity. In this case, there was no evidence of peak tailing, which is often observed when analyzing these reactive compounds.



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

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 × 0.32 mm, 1.8 µm 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.

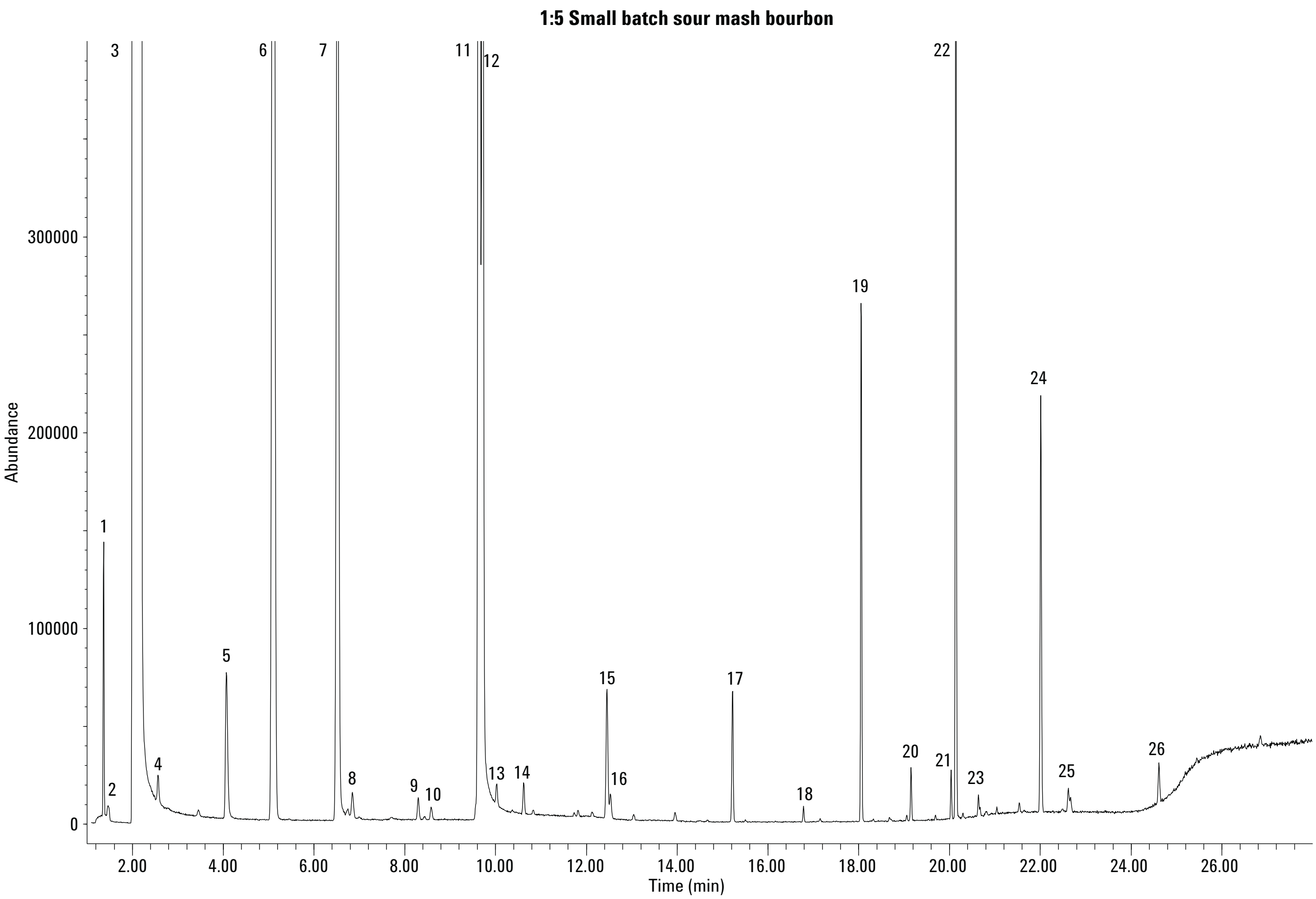


Peak ID

1. Acetyl aldehyde
2. Methanol
3. Ethanol
4. Ethyl formate
5. Isobutyl aldehyde
6. 1-Propanol
7. Ethyl acetate
8. Isobutyl alcohol
9. Acetyl aldehyde
10. Isoamyl alcohol
11. Active amyl alcohol
12. Ethyl butanonate
13. Isoamyl acetate
14. α-Pinene
15. β-Pinene
16. β-Myrene
17. Ethyl caproate
18. 3 Carene
19. Octanal
20. D-Limonene
21. γ-Terpinene
22. (+) 4 Carene
23. β-Linalool
24. Ethyl caprylate
25. Decanal
26. Octanal diethyl acetal
27. Ethyl caprate
28. Ethyl laurate
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 × 0.32 mm, 1.8 µm 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

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

For More Information

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