Application Note

Spirits Analysis

Analysis of Some Alcohols, Aldehydes, and Esters in Distilled Spirits with the Agilent 8860 Gas Chromatograph

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Abstract

The Agilent 8860 GC configured with a flame ionization detector (FID) provides high sensitivity, good linearity, and stability for the analysis of alcohols, aldehydes, organic acids, and esters in distilled spirits. The highly inert performance of the column ensures excellent peak shapes for most compounds.

Introduction

Distilled spirits constitute a complex mixture of hundreds of flavor compounds in an ethanol-water matrix, including alcohols, aldehydes, organic acids, and esters. The proportion of these trace ingredients determines the flavor and quality of the liquor. It is very important for manufacturers to monitor and test flavor compounds that originate from the original raw materials and the subsequent processes of mashing, fermentation, and distillation.

Chinese liquor is a spirit famous worldwide for its strong flavor and long aftertaste. According to flavor types, Chinese liquor can be divided into Maotai, Luzhou, Fen, and rice flavors, among others. For a long time, the research on liquor focused primarily on the evolution of microorganisms, and the formation of flavor substances during fermentation. The influence of main aroma components such as esters, acids, alcohols, and aldehydes of the typical liquor style was also analyzed. The concentration and proportion of ethyl acetate, ethyl lactate, and ethyl hexanoate play a decisive role in the flavor of liquor. For the sake of the health of the drinkers, the concentration of methanol, isobutyl alcohol, and isoamyl alcohol should be strictly controlled in the production process of liquor. In this Application Note, some real samples were injected into the Agilent 8860 GC system, and certain liquor flavor types were analyzed. The 10 most common compounds in liquor were also quantitatively analyzed.

Experimental

Analyses were performed using an 8860 GC equipped with an FID. Sample introduction was done using an Agilent 7693A automatic liquid sampler with a 5 µL syringe. Table 1 shows the instruments and conditions used.

Sample preparation

Mixed standard stock solutions were prepared by adding defined amounts of each single standard compound with a microliter syringe. A stock solution of 10 compounds, each with a concentration of 1,000 µg/mL was prepared in 60:40 ethanol:water solution (v/v).

To achieve the required levels, six vials were made at each calibration level by spiking varying amounts of stock solution in ethanol aqueous solution. The calibration standards were prepared at standard concentrations of 10, 30, 50, 100, 500, and 1,000 µg/mL. An internal standard (IS) was spiked to each calibration level, corresponding to an IS concentration of 440 µg/mL.

The spirits samples were obtained locally from retail providers in China, and introduced into the GC as neat samples.

Table 1. Agilent J&W DB-FATWAX UI column for spirits method conditions.

Parameter	Value
GC system	8860 GC/FID
Inlet	Split/splitless, 250 °C, split ratio 30:1 Liner: Ultra Inert (p/n 5190-2295)
Column	J&W DB-FATWAX Ultra Inert, 30 m × 0.25 mm, 0.25 µm (p/n G3903-63008)
Carrier	Helium, 1 mL/min, constant flow
Oven	40 °C (4 minutes), then 5 °C/min to 100 °C, then 10 °C/min to 200 °C (10 minutes)
FID	250 °C, Hydrogen: 30 mL/min, Air: 300 mL/min, Make-up gas (N_2): 25 mL/min
Injection	0.5 µL

Results and discussion

To develop a reliable method for monitoring flavor substances in distilled spirits, an 8860 GC configured with automatic injection and an FID was used. Figure 1 shows a typical chromatogram acquired by the system with the 10 standard compounds and one internal standard at a concentration of 100 µg/mL.

Figures 2, 3, and 4 are example chromatograms profiling some of the major components that were found in different flavors of Chinese liquor samples. The system shows great resolution and peak shape for all alcohols, aldehydes, organic acids, and esters. As shown in Figure 2, ethyl acetate, acetaldehyde, and methanol were baseline-separated. Methanol is strongly polar and is prone to tailing, but in this method, a sharp and symmetric peak shape was obtained.

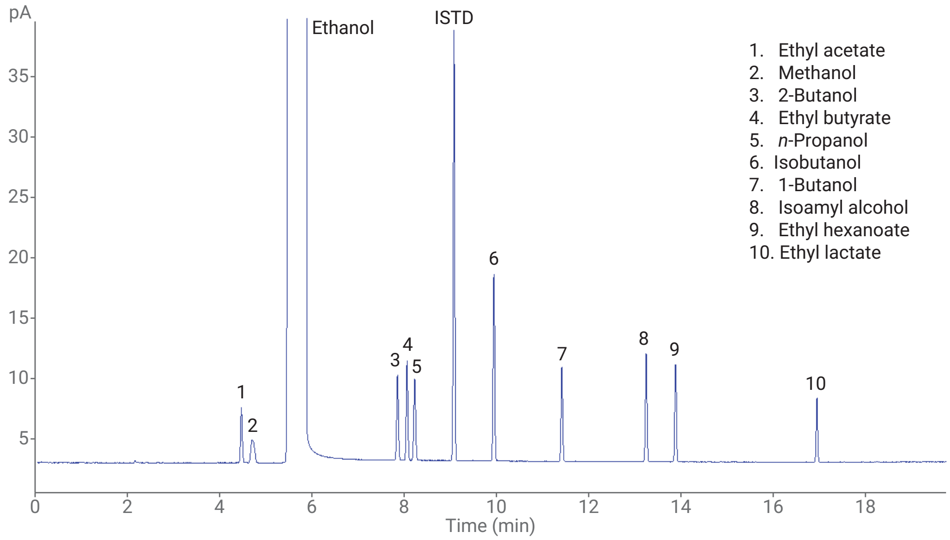

Figure 1. GC/FID chromatogram of 10 target compounds (100 µg/mL) using a J&W DB-FATWAX Ultra Inert column.

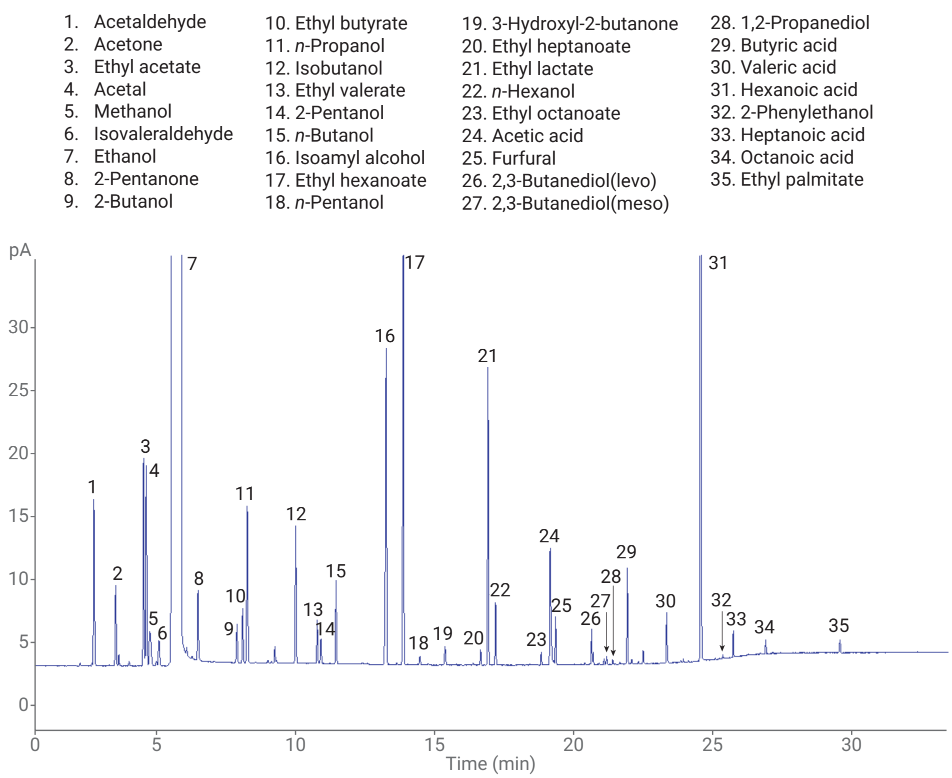

Figure 2. GC/FID chromatogram of a Luzhou flavored Chinese liquor sample.

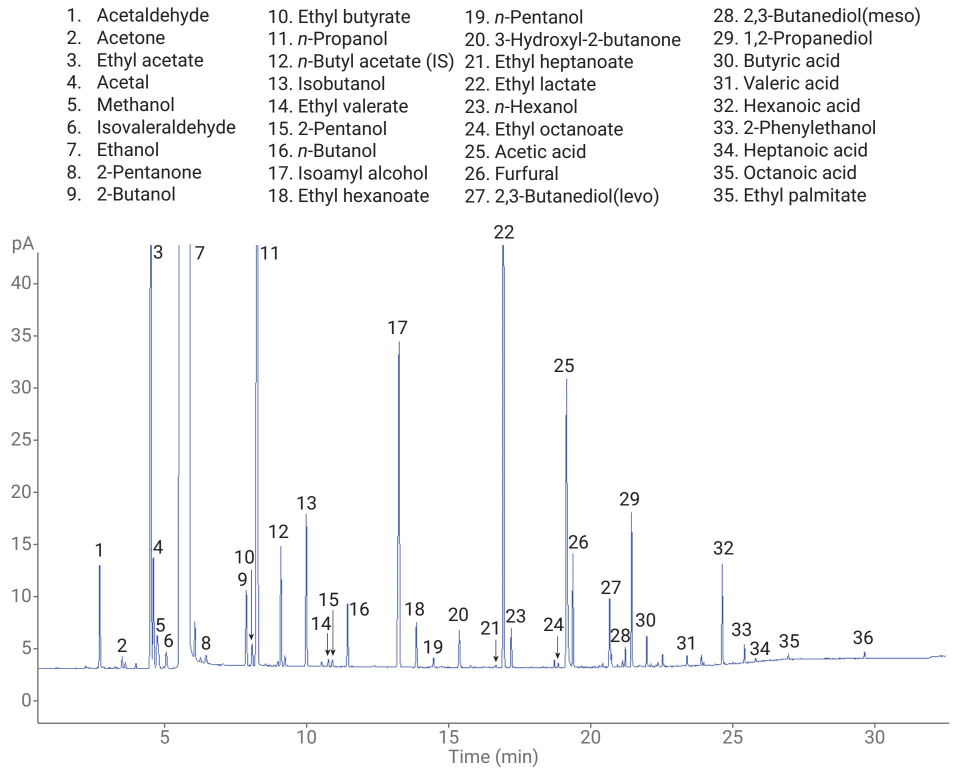

Figure 3. GC/FID chromatogram of a Maotai flavored Chinese liquor sample.

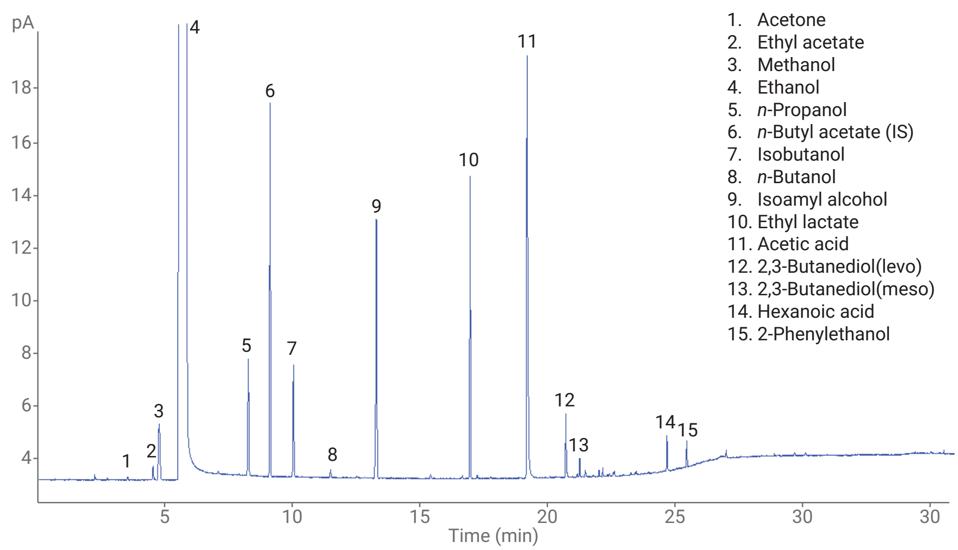

Figure 4. GC/FID chromatogram of a Fen flavored Chinese liquor sample.

The correlation coefficients (R^2) for all 10 compounds were ≥0.9992 for the range of 10 to 1,000 µg/mL. Table 2 shows detailed calibration information, and Figures 5, 6, and 7 show the calibration curves of methanol, isobutanol, and ethyl lactate.

Table 2. R^2, RSDs, and LODs for 10 target compounds.

Name	RT	R^2	RSD (n = 6)		
			100 µg/mL	Chinese liquor	MDL (µg/mL)
Ethyl acetate	4.51	0.9992	3	2.8	3
Methanol	4.75	0.9998	1.3	1.2	5
2-Butanol	7.88	0.9998	1.3	1.4	2
Ethyl butyrate	8.09	0.9995	2.5	2.2	2
n-Propanol	8.26	0.9998	1.1	1.1	2
Isobutanol	9.96	0.9998	1.1	1.2	2
1-Butanol	11.43	0.9998	1.4	1.2	2
Isoamyl alcohol	13.25	0.9998	1.2	1.3	2
Ethyl hexanoate	13.88	0.9998	1.6	1.1	2
Ethyl lactate	16.93	0.9999	1.1	1.2	3

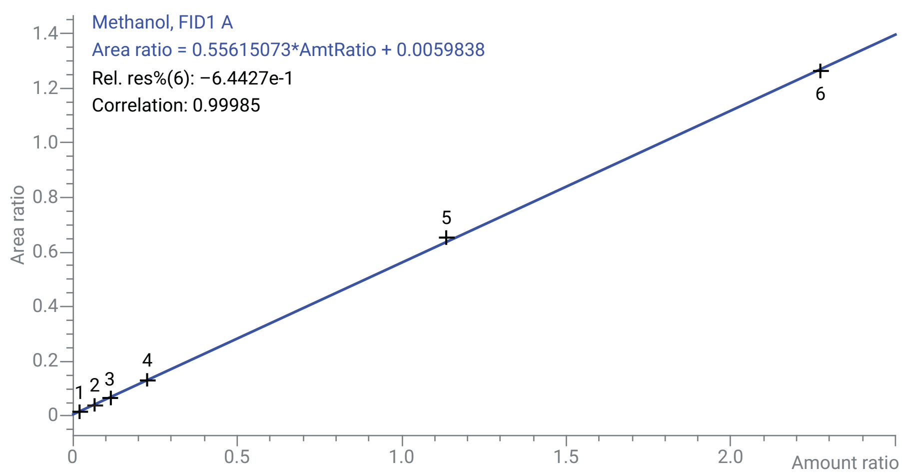

Figure 5. Methanol calibration curve (R^2 = 0.99985).

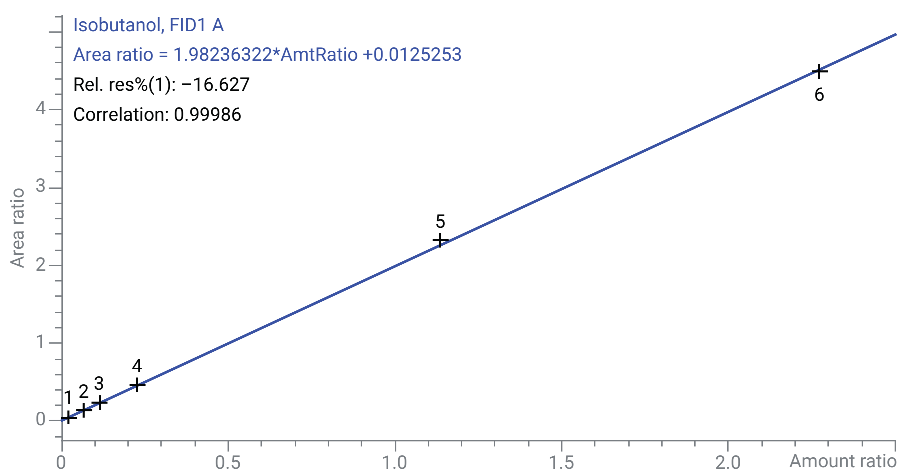

Figure 6. Isobutanol calibration curve (R^2 = 0.99986).

To verify the integrity of the system, repeatability was determined. Repeatability tests were performed on both the standard and the real samples. Table 2 illustrates that for most compounds, the area %RSD is well below 3 %. Figure 8 is an overlay of six replicates of the Chinese liquor injections. As the figure illustrates, the retention time and area stability were excellent.

Signal-to-noise ratio (S/N) was used for method detection limit (MDL) calculation. A concentration of 5 µg/mL standard solution was used to test the MDL, and Table 2 lists the values for all compounds. For all compounds, the MDLs were ≤5 µg/mL.

Conclusion

In this Application Note, the 8860 GC configured with automatic injection and an FID provides a reliable and economical solution for the analysis of alcohols, aldehydes, organic acids, and esters in liquor. The EPC control and J&W DB-FATWAX UI column provides excellent peak shape, resolution, and great repeatability.

References

1. Kenneth L.; Zhou, Y. Analysis of Distilled Spirits Using an Agilent J&W DB-WAX Ultra Inert Capillary GC Column, *Agilent Technologies Application Note*, publication number 5991-6638EN, **2016**.
2. Cai, X. Y.; Yin, J. J.; Hu, G. D. Determination of Minor Flavor Components in Chinese Spirits by Direct Injection Technique with Capillary Columns. *Chin. J. Chromatogr*. **1997**, *15(5)*.

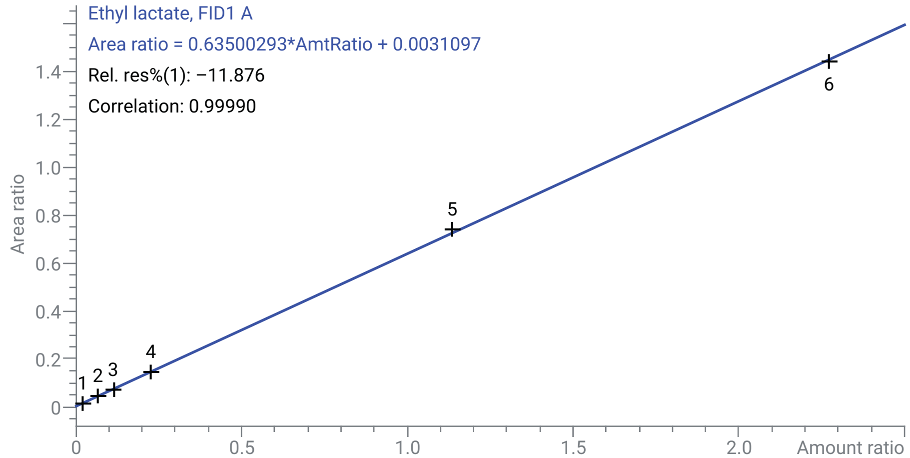

Figure 7. Ethyl lactate calibration curve (R^2 = 0.99985).

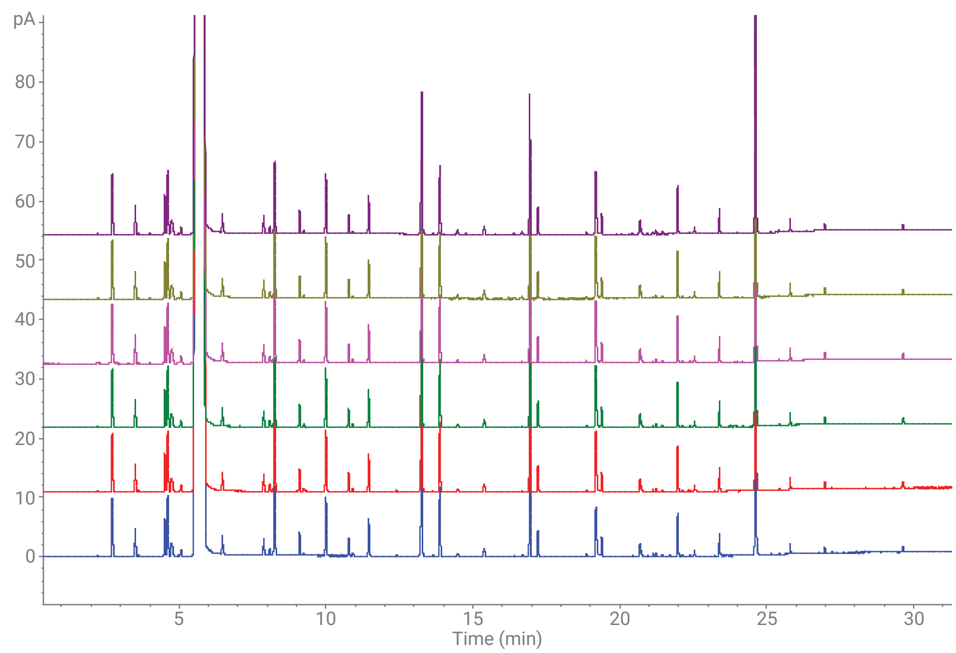

Figure 8. Overlaid GC/FID chromatograms of six repeat injections of the same Chinese liquor.

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Printed in the USA, January 2, 2019
5994-0490EN

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