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Application News

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Food and Beverages / GC-2010

A Comparison Study of Different Capillary Columns for Analysis of Alcohol Congeners in Alcoholic Beverages

❑ Introduction

Alcoholic beverages contain a wide range of volatile components, primary of which are alcohols and short-chain aldehydes. To ensure consistency in the quality and flavour of the finished products, distilleries and alcoholic beverage manufacturers monitor the presence and relative levels of these compounds. Gas chromatography (GC) is usually the preferred technique in analysing these compounds. Fifteen components as listed in Table 1 are monitored by ethanol distilleries and alcoholic beverage manufacturers in the Philippines. The Association of Official Analytical Chemists (AOAC) and the Commission of the European communities have published methods for the analysis of fusel oils, methanol, ethanol, aldehydes and higher alcohols by GC in spirit drinks and distilled liquors [1~3]. The conventional GC methods for alcoholic beverage analysis are based on packed column, because glass tubing material for the packed column is inert, rarely causes tailing or decomposition of samples and minimizes interaction between the target component and the walls of the tube. However, packed glass columns are prone to breakage and may cause adsorption of the more reactive components present in alcoholic beverages. Most modern GC instruments are configured for capillary column use for the inherent advantages over packed columns such as more efficient separation, narrower peaks and consequently, lower limits of detection. This motivates an investigation into the potential of using capillary column in separating alcohols, aldehydes and other congeners typically found in alcoholic beverages. In this study, four capillary columns are selected and their performance are compared with packed column in terms of separation of all key components found in alcoholic beverages.

❑ Experimental

Methods and Standard Preparation

Standard solutions containing varying amounts of alcohol congeners were prepared in accordance with in-house procedures. All solutions were diluted to volume with 40% (v/v) ethanol in water. The linear velocity of He carrier gas of GC for each column was optimized to achieve the best separation. The injection and FID detection conditions were set according to the column supplier's recommendation or in-house procedures. Four columns from different suppliers were employed and compared in this work. The columns were chosen based on availability and suitability of each column for alcohol congeners separation as published in literature [4,5].

Instrument, Columns and Analytical Conditions

GC : GC-2010 with FID
Auto injector : AOC-5000
Columns : Capillary columns are used as below:

(1) CP-Wax 57 CB, 50 m L. x 0.25 mm I.D. x 0.20 µm δf (see Table 3)
(2) Supelcowax 10, 60 m L. x 0.53 mm I.D. x 1.0 µm δf (see Table 4)
(3) SPB-20, 40 m L. x 0.25 mm I.D. x 1.0 µm δf (Table 5)
(4) Supel-Q PLOT, 30 m L. x 0.32 mm I.D. (Table 6)

Table 1: Alcohols, aldehydes and other compounds monitored in local alcoholic beverages

Peak ID	Component
1	Acetaldehyde
2	Acetone
3	Ethyl acetate
4	Acetal
5	Methanol
6	Isopropanol
7	N-propyl acetate
8	N-propanol
9	N-butyl acetate
10	Isobutanol
11	Isoamyl acetate
12	N-butanol
13 13a	Isoamyl alcohol Active amyl alcohol
14	1-pentanol
15	Furfural

❑ Results and Discussion

The most popular packed column employed for alcohol congeners analysis is the Carbopack B packed with 5% or 6.6% Carbowax 20M [6]. This column provides excellent peak shape for methanol, resolves methanol from ethanol completely and separates two predominant fusel oils namely active amyl alcohol and isoamyl alcohol (see Figure 1 and Table 2).

Table 2: GC analytical conditions using Carbowax 20M Packed column (6.6% Carbowax 20M 80/120 Carbopack B, 2.60 mm I.D. x 2 m L)

Injection Temp.	175°C
Column Temp.	80°C (0.5 min), 4°C/min ~150°C, 10°C/min ~190°C (3 min)
Injection Mode	Direct
Carrier Gas	N_2
Column Flow	14 mL/min
Injection Volume	1.0 µL
Detector	200°C, FID

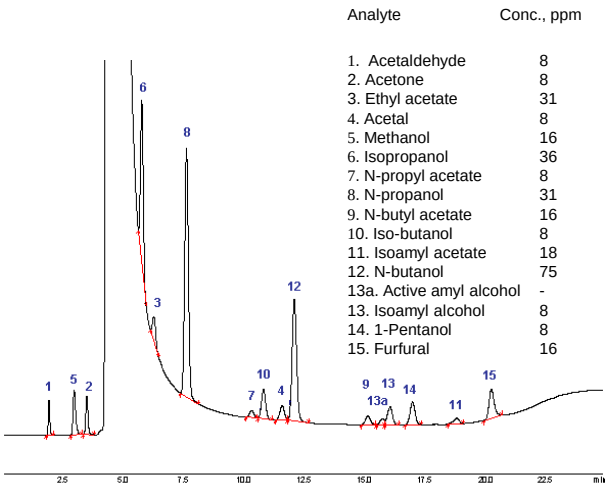


Figure 1: GC-FID result of 15 alcohol congeners on 6.6% Carbowax 20M 80/120 Carbopack B, 2.60 mm I.D. x 2 m L.

Comparison of four capillary columns

Supelcowax 10 and CP-Wax 57 CB columns are both made of 100% chemically bonded polyethylene glycol making these columns highly polar. The compounds tested showed similar elution patterns for both columns (Figures 2 and 3) under the optimized conditions (Tables 3 and 4). In particular, the peak of methanol exhibited a characteristic broad shape. The smaller internal diameter of CP-Wax 57 CB resulted in full baseline separation of acetal from ethyl acetate and active amyl alcohol from isoamyl alcohol (Figure 2). While, the higher loading capacity of the wide bore Supelcowax 10 column enabled better separation of propyl acetate from ethanol (Figure 3).

Table 3: GC Analytical Conditions using CP-Wax 57CB capillary column

Injection Temp.	200°C
Column Temp.	50°C (10 min), 5°C/min ~140°C, 10°C/min ~190°C (3 min)
Injection Mode	Split, 1:10
Carrier Gas	He
Linear Velocity	25 cm/sec
Injection Volume	1 µL
Detector	210°C, FID

Analyte	Conc., ppm	Analyte	Conc., ppm
1. Acetaldehyde	21	9. N-butyl acetate	12
2. Acetone	13	10. Iso-butanol	11
3. Ethyl acetate	15	11. Isoamyl acetate	17
4. Acetal	11	12. N-butanol	11
5. Methanol	12	13a. Active amyl alcohol	-
6.. Isopropanol		13. Isoamyl alcohol	11
7. N-propyl acetate	11	14. 1-Pentanol	16
8. N-propanol	10	15. Furfural	14

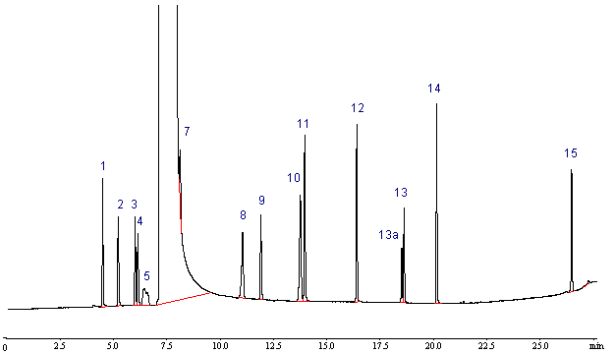


Figure 2: Alcohol congeners on CP-Wax 57 CB column

Table 4: GC analytical conditions using Supelcowax 10 capillary column

Injection Temp.	200°C
Column Temp.	45°C (5 min), 5°C/min ~65°C, 10°C/min ~200°C (0.5 min)
Injection Mode	Split, 1:5
Carrier Gas	He
Linear Velocity	31 cm/sec
Injection Volume	1 µL
Detector	260°C, FID

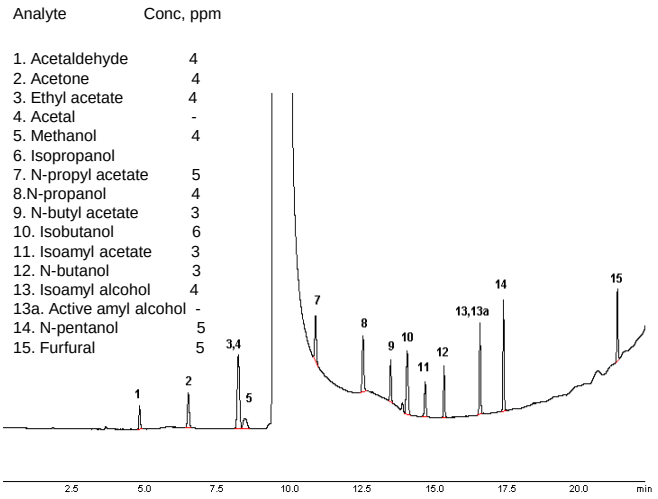
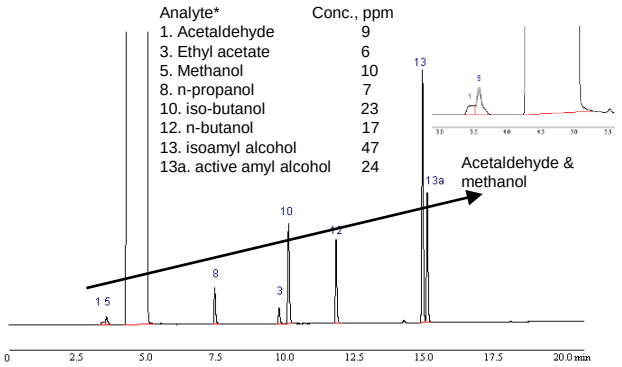


Figure 3: Alcohol congeners on Supelcowax 10 column

The SPB-20 capillary column, on the other hand, can be classified as an intermediate polarity column. Figure 4 shows the separation profile of this column. Its stationary phase is made of bonded poly(20% diphenyl / 80% dimethylsiloxane). The high phenyl content of the column produced a different elution order when compared to polyethylene glycol-based columns, which makes it suitable for confirmation analysis. One drawback of this column is the partially overlapping of two important congeners, acetaldehyde and methanol.

Table 5: GC Analytical Conditions for SPB-20 capillary column

Injection Temp.	150°C
Column Temp.	35°C (5 min), 5°C/min ~100°C (1.0 min)
Injection Mode	Split, 1:10
Carrier Gas	He
Linear Velocity	30 cm/sec
Injection Volume	1 µL
Detector	250°C, FID



** Tested only for eight standards*

Figure 4: GC analysis of 15 alcohol congeners on SPB-20 capillary column

The Supel-Q plot capillary column contains a porous sorbent made from copolymer of ethylbenzene and divinylbenzene. The ethanol matrix interfered with the peak of isopropanol for all capillary columns, except this one. This was the only column tested that was able to resolve isopropanol from the ethanol matrix (see Figure 5). However, while this column separates the most number of peaks, significantly smaller and broader peaks with slight tailing was observed. This can be attributed to the column inherently high adsorption characteristic.

Table 6: GC Analytical Conditions for Supel-Q Plot Capillary column

Injection Temp.	200°C
Column Temp.	50°C, 10°C/min ~150°C, 5°C/min ~210°C, 40°C/min ~250°C (5 min)
Injection Mode	Split, 1:10
Carrier Gas	He
Linear Velocity	30 cm/sec
Injection Volume	1 µL
Detector	270°C, FID

Analyte	Conc., ppm	Analyte	Conc., ppm
1. Acetaldehyde	43	9. n-Butyl acetate	35
2. Acetone	43	10. Isobutanol	32
3. Ethyl acetate	27	11. Isoamyl acetate	29
4. Acetal	26	12. N-butanol	39
5. Methanol	32	13. Isoamyl alcohol	28
6. Isopropanol	29	13a. Active amyl alcohol	-
7. N-propyl acetate	40	14. 1-Pentanol	-
8. N-propanol	29	15. Furfural	42

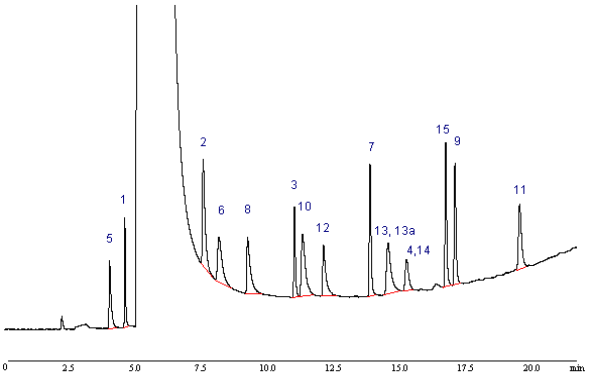


Figure 5: GC analysis of 15 alcohol congeners on Supel-Q plot capillary column

❑ Conclusions

This study shows that the separation of the 15 alcohol congeners which are the major components found in alcoholic beverages can be achieved using capillary columns. A capillary column is thus a possible alternative to replace the conventional packed column for alcoholic beverage analysis. However, the study also reveals that none of a single packed (Carbowax 20M) or a capillary column can fully separate all the 15 alcohol congeners. As an option, the use of two different capillary columns may provide a better solution, which can be accomplished on the Shimadzu GC-2010, a GC system designed for dual-column analyses of a same sample with two FID detectors simultaneously.

❑ References

[1] AOAC Official Methods 972.10. Alcohols (Higher) and Ethyl Acetate in Distilled Liquors, 2000, 17th ed.
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[3] Official Journal of the European Communities L333/36. Determination of Volatile Substances and Methanol of Spirit Drinks.
[4] Restek Technical Guide. Analyzing Alcoholic Beverages by Gas Chromatography. www.restekcorp.com
[5] Supelco Application Note 164. The Analysis of Alcoholic Beverages on a 30m x 0.25mm ID x 1.0um SPB-20 Capillary Column. www.sigmaaldrich.com
[6] Supelco Bulletin 790C. Improved Resolution of Alcoholic Beverage Components by Packed Column GC. www.sigmaaldrich.com

Disclaimer: The Shimadzu GC-2010 system and the data in this Application News are intended for Research Use Only (RUO). Not for use in diagnostic procedures.

SHIMADZU
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SHIMADZU Philippines Corporation
11F Sunlife Centre, 5th Avenue corner Rizal Drive
Bonifacio Global City, Taguig City, Philippines 1634
www.shimadzu.com.ph
Tel: +63-2869 9563 Fax: +63-2519 9285

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