Whisky – alcohols and esters

Split injection of malt whisky

Application Note

Food Testing & Agriculture

Authors

K. MacNamara

Irish Distillers Group Limited

Introduction

Gas chromatography using split injection and an Agilent CP-Wax 57 CB column separates 26 alcohols and esters in a sample of whisky in 43 minutes.

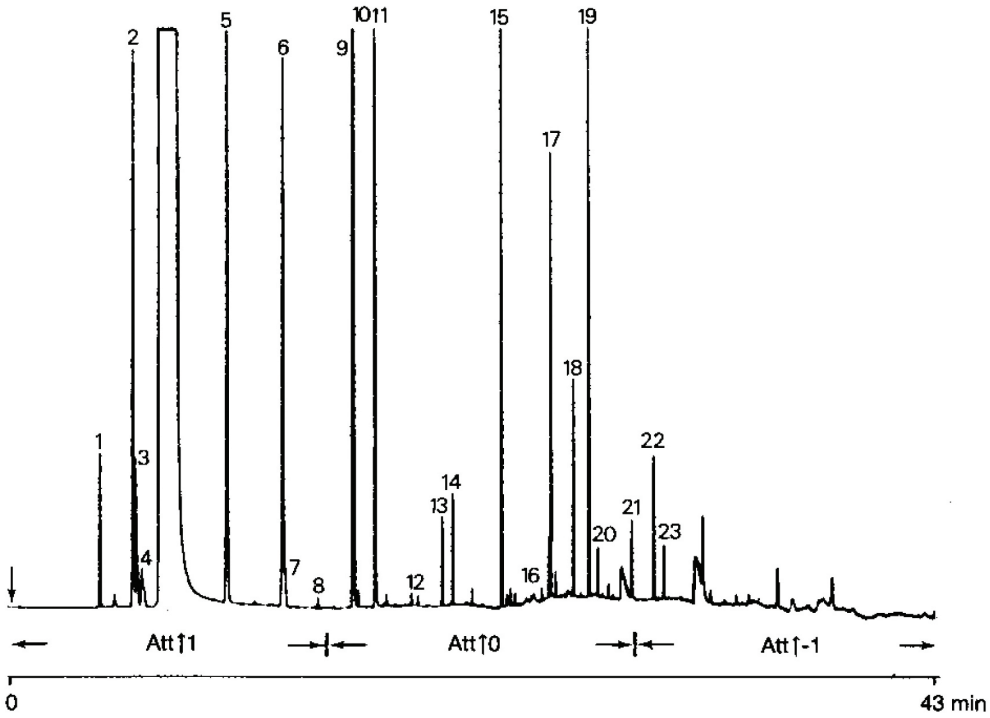
Agilent Technologies

Conditions

Technique	: GC-capillary
Column	: Agilent CP-Wax 57 CB, 0.32 mm x 50 m fused silica WCOT CP-Wax 57 CB (0.2 µm) (Part no. CP97753)
Temperature	: 40 °C, 10 min → 200 °C, 10 °C/min
Carrier Gas	: He, 110 kPa (1.1 bar, 16 psi), 24 cm/s
Injector	: Splitter, 75 mL/min, 240 °C
Detector	: FID, 240 °C
Sample Size	: 1 µL

Peak identification

1. acetaldehyde
2. ethylacetate
3. acetal
4. methanol
5. propanol
6. iso-butanol
7. iso-amylacetate
8. n-butanol
9. 2-methyl-1 -butanol
10. 3-methyl-1-butanol
11. n-pentanol
12. ethylactate
13. ethylcaprylate
14. furfural
15. ethylcaprate
16. 2-phenylethylacetate
17. ethyllaurate
18. 2-phenylethylalcohol
19. methylmyristate
20. ethylmyristate
21. myristylalcohol
22. ethylpalmitate
23. ethylpalmitoleate
24. ethylstearate
25. ethyloleate
26. ethyllinoleate



Peaks 11 and 19 are standards

Analysis of alcohols and esters in distilled spirits

Distilled alcoholic beverages can now be quickly and conveniently analyzed by a combination of capillary split and splitless injections of the actual sample on the same fused silica capillary column.

Distilled beverages such as whiskey, cognac, rum etc. are complex mixtures of aroma compounds in an aqueous ethanol medium. The individual compounds can be subdivided into various groups with the most important of these being the higher alcohols, fatty acid ethyl esters and fatty acids. To analyze all these compounds, time consuming extractions are required and different stationary phases are used, usually with packed columns. Attempts have been made to simplify and shorten the required extractions and these have been most successful when combined with the speed and greater resolving power of glass capillary columns. Now it is possible to omit the extraction procedure entirely using the new generation of the chemically bonded stationary phases on fused silica.

Experimental

Analyses were performed using a Hewlett Packard 5880 A Gas Chromatograph equipped with two split-splitless injection systems. A 0.32 mm x 50 m internal diameter fused silica capillary column was used, coated with 0.2 µm CP-Wax 57 CB. The properties of these columns have been previously described in detail.

Results and discussion

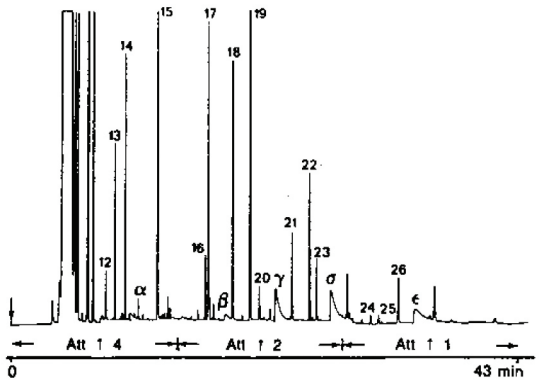
The separations shown in Chromatogram 1 and 2 are a split and a splitless injection of a malt whiskey, respectively. Peak identification is given in Chromatogram 1 . The combination of the split and splitless injection on the sample allows a total look at the principal congeners in the spirit. The split injection is ideal for pre-ethanol volatiles and higher alcohols - and compounds up to C16 ethyl esters with diminishing precision because of the low amounts of these compounds found in spirits. On the other hand, under the conditions outlined here, a good solvent effect is achieved with splitless injection and ca. 10 times more component is introduced on the column with corresponding increased precision and detection of a wide range of compounds for peaks eluting after ethyl myristate.

Retention time reproducibility is excellent in both cases and the thin stationary phase film thickness with temperature programming allows elution of all compounds of interest in a reasonable time. Acids can also be quantified using splitless injection but with a little more difficulty due to tailing. Acids marked α, β. γ, σ and ϵ in Chromatogram 2 are acetic, caproic, caprylic, capric and lauric acid, respectively. Initial experimentation on rinsing the capillary column with dilute solutions of phosphoric acid in methanol has resulted in decreased tailing and a better peak shape for these free acids.

The respective injection port split and splitless liners serve as traps for any non-volatile material present in samples, and our practice is to substitute a clean liner after every 70 to 100 injections. We have not experienced any noticeable efficiency drop or liquid phase rearrangement due to solvent stress with these columns.

Conditions

Technique	:	GC-capillary
Column	:	Agilent CP-Wax 57 CB, 0.32 mm x 50 m fused silica WCOT CP-Wax 57 CB (0.2 µm) (Custom-made)
Temperature	:	40 °C, 36 s ⟶ 100 °C, 30 °C/min ⟶ 200 °C, 5 °C/min solvent purge on at 48 s
Carrier Gas	:	He, 110 kPa (1.1 bar, 16 psi), 25 cm/s
Injector	:	Splitter, 240 °C
Detector	:	FID, 240 °C
Sample Size	:	1 µL



Peak identification

1. acetaldehyde
2. ethylacetate
3. acetal
4. methanol
5. propanol
6. iso-butanol
7. iso-amylacetate
8. n-butanol
9. 2-methyl-1-butanol
10. 3-methyl-1-butanol
11. n-pentanol
12. ethyllactate
13. ethylcaprylate
14. furfural
15. ethylcaprate
16. 2-phenylethylacetate
17. ethyllaurate
18. 2-phenylethylalcohol
19. methylmyristate
20. ethylmyristate
21. myristylalcohol
22. ethylpalmitate
23. ethylpalmitoleate
24. ethylstearate
25. ethyloleate
26. ethyllinoleate

Peaks 11 and 19 are standards

www.agilent.com/chem

Printed in the USA
31 October, 2011
First published prior to 11 May, 2010
A00052

Agilent Technologies