D. Wetzel and G. Charalambous (Editors)
Instrumental Methods in Food and Beverage Analysis

Gas Chromatographic Technology in Analysis of Distilled Spirits

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Introduction

Aged distilled spirits constitute a complex mixture of some hundreds of flavour compounds in an ethanol-water matrix. These flavour compounds, or congeners, originate from the original raw materials and the subsequent processes of mashing, fermentation, distillation and ageing, which together produce the final product. Complex interdistillate reactions between congeners are also an important part of the flavour scenario, and this is particularly important during the ageing phase in oak barrels.

Tables 1 and **2** outline the principle congener classes found in whiskey, cognac and rum together with an indication of compound numbers by class [1]. The naturally occurring relative concentrations of these compounds can vary from high mg/l to low ng/l. Each congener in turn has an odour intensity and flavour contribution which is determined not only by its concentration, but also its unique sensory threshold value. For this reason the most abundant congeners may be the most amenable to analysis, but the resultant quantitative information may have little relationship to the perceived flavour of the spirit. On the other hand this type of information does describe the gross structure of the spirit and is an important data base for ensuring process continuity and product authenticity.

Chemical Class	Whiskey	Cognac	Rum
Hydrocarbons	7	15	38
Hydroxyl compounds	53	104	88
Carbonyl compounds	24	93	63
Carboxylic acids	35	43	30
Esters	79	195	115
Lactones	4	10	7
Acetals / Esters	21	43	76
O-Heterocyclics	7	23	41
N-Heterocyclics	28	10	23
Miscellaneous	11	10	16
TOTAL	269	546	497

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Table 1. *Number of volatile compounds, identified in whiskey, cognac and rum.*

Chemical Class	Whiskey	Cognac	Rum
Aliphatic compounds	187	382	309
Aromatic compounds	42	79	88
Terpenoid compounds	5	52	36
Heterocyclic compounds	35	33	64
TOTAL	269	546	497

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Table 2. *Number of volatile compounds, identified in whiskey, cognac and rum.*

In an interesting study Salo [2] prepared a synthetic whiskey using purified individual congeners in accurately known amounts, and with levels based on gas chromatographic data obtained from a real whiskey. Odour threshold values were used to determine the relative odour intensity of individual aroma compounds, and aroma fractions of alcohols, esters, acids, carbonyl compounds and mixtures of these compounds. The results clearly showed that the contribution of the most abundant congeners to the total odour intensity is quite low. The alcohol fraction accounted for 70% and the acid fraction 11% of the total congener concentration, yet both together only contributed 7.5% of the total odour intensity.

In the light of these facts a commercial producer of distilled spirits needs a particular analytical strategy to service and satisfy various needs, which might include:

- Rapid, high-throughput direct analysis of the abundant congeners for production process continuity and authenticity information.

- Various sample preparation techniques for enriching trace congeners from the ethanol-water matrix. These can usually be divided into simple enrichment procedures or more elaborate investigative schemes giving enriched compound classes that also facilitate sensory information.

- Use of the trace congener information provided by investigative research to devise further high-throughput analytical techniques that make use of advances in modern GC technology and detection systems.

The previous discussion constitutes a basis for the thematic content of this chapter which is to review historical and present chromatographic approaches to distilled spirits analysis, and to explore the potential and application of modern GC technology in this area. The term "GC technology" has been chosen to emphasise an instrumental dimension in the sense that very successful analytical schemes can be constructed if the gas chromatograph is regarded as something more than an oven and a column. Cold capillary programmable injection technology, and static and dynamic headspace, and large volume liquid injections that exploit the cold injector can produce systems for efficient routine analysis of spirits as is, or after minimum sample preparation. Newer detection modes and technologies can be exploited for similar benefits resulting from sensitivity and specificity enhancements. Capillary columns of such different coatings, dimensions

and phase ratios are now available that sample preparation schemes can be devised to make maximum use of these variables. The aim should be to tailer this technology to the nature and relative concentrations of the congeners and on this basis the following areas will be reviewed and explored.

Direct Injection: Review of various approaches using custom packed columns and modern capillary columns to profile the most abundant congeners without sample preparation. Use of specialised capillary injection techniques, especially in conjunction with mass spectrometric target selected ion monitoring, to extend the range of congeners that can be directly determined in the natural matrix. Introduction to a cooled injection system with programmable vaporisation as a universal capillary injection system.

Matrix Removal: Review of many of the approaches developed for this purpose ranging from simple solvent extraction, to multi-step combined extractive and instrumental schemes, which can give enriched subtractions with selective congener types. This gives an opportunity in turn to suit column selection (coating type and phase ratio) and detection strategy to individual congener groups.

Large Volume Injection: This is an important concept and technology for the future and has the potential to provide a natural link between data obtained from research investigations, and the need to produce rapid routine methods. If the compound contents of 500 µls of a simple extract can be transferred to the column, it offers the possibility of low-cost routine analysis of trace congeners. The fact that usually only 1-2 µl of complex extracts are used for analysis also represents an expensive waste of resources. Therefore compounds indicated as potential flavour contributors from classical multi-step sample preparation routes could be monitored by automated large volume injection of relatively simple sample extracts. The success of this technique relies on programmable injection technology with simultaneous solvent venting and retention of analytes of interest in the injector liner. The same cooling and venting properties of the programmable injector can be similarly exploited for large volume injection from either headspace or thermal desorption devices. In fact the design of these units can be greatly simplified when their operation involves a programmable injector.

Two Dimensional Chromatography: The separating power of single highly efficient capillary columns is in many cases not sufficient for complex subfractions and extracts obtained from distilled spirits. Very interesting selective sulphur and nitrogen traces are available but mass spectrometric identification of the compounds is often very difficult. The vastly increased separating power of serially coupled columns offers an efficient solution to this problem. Commercial apparatus is now available which allows two oven systems to be easily configured for computer controlled 2-dimensional separations, and quickly revert back to two independent gas chromatographs when not being used for this purpose.

There are many different approaches for the determination of abundant and trace congeners in distilled spirits. In many cases the apparatus and techniques are unique to the particular group or laboratory, and it can be difficult for other workers to reproduce the exact scheme adopted. This chapter also contains some procedures favoured by one of the present authors (K MacN), but a

difference is that they are rooted as much as possible in a dialogue with a specialist instrument manufacturer, and are therefore based on commercially available systems. Finally much of the discussion and many of the examples centre around whiskey, but the methods and technology should be applicable to all distilled spirits.

Direct Injection

The most abundant compounds present in distilled spirits are the fusel alcohols and fatty acid esters, together with acetaldehyde and its acetal. Fusel alcohols are produced in fermentation from amino acids via decarboxylation and deamination, while the esters are formed in yeast cells. Acetaldehyde is the most abundant carbonyl compound and its reaction with the dominant ethanol produces diethyl acetal, or 1,1-diethoxyethane, at the mg/l level. **Table 3** gives typical amounts of these compounds found in malt and light blended whiskey. Full malt whiskeys are produced in traditional pot stills and tend to have upper range levels of these compounds. Lighter whiskeys are blends of pot still product and whiskey produced in column stills. Therefore depending on the degree of blending commercial whiskeys can have these major congeners in a concentration range of single figure mg/l to greater than 10^3 mg/l. Rapid separation and quantification of these compounds is important for reasons ranging from production consistency to market place authenticity and many different approaches have evolved, usually with the universal flame ionization detector.

Compound	Malt Whiskey	Blended Whiskey
Acetaldehyde	200 mg/l	76 mg/l
Ethyl Acetate	280 "	29 "
Diethyl Acetal	49 "	5 "
Propanol	350 "	570 "
iso-Butanol	990 "	450 "
Amyl Alcohols	1600 "	420 "
Ethyl Caprylate	22 "	3 "
Ethyl Caprate	32 "	10 "
Ethyl Laurate	12 "	8 "

Table 3. *Typical amounts of major congeners found in different types of whiskeys.*

Packed Columns. Before the introduction of modern fused silica capillary columns chromatographers relied on packed columns with their limitations of both low plate number, and low mass sensitivity at the detector due to solute diffusion in the packing. On the other hand they have the advantage of low cost, are easy to operate, and can be produced with many specific phases for different separation problems. Open tubular capillary columns offer much higher separating power but the availability of columns with unique phases is more limited than with packed columns. Since the phase selectivity has a major effect on separation certain packed phases have retained their applicability in distilled spirits analysis.

Duncan and Philp [3] used two gas chromatographic methods to directly determine a range of major congeners in whiskey. Using 5% polyethylene glycol 1500 on a 60-80 mesh support in a 10 ft. copper column they separated the major fusel alcohols and esters. Their second method involved using the same phase in a 27 ft. column but also incorporating in the column a small length in which dionyl sebacate was the stationary phase. This allowed the additional separation of ethyl acetate, diethyl acetal and isoamyl acetate. Brunelle [4] evaluated various stationary phases and produced a collaborative study which resulted in the adoption of an official final action of the AOAC. Kahn and Blessinger [5] reported some difficulties in this method and from their own investigations proposed two alternate methods. One of these allowed determination of ethyl acetate and fusel alcohols and was adopted as a first action alternate method. The second method allowed quantification of acetaldehyde and acetal as well as ethyl acetate and the fusel alcohols, but did not get approval until gas chromatographic instrumentation, in particular oven temperature control and programming, improved. The current AOAC official methods (16th Edition, 1995) recommend the following phases and conditions for packed column analysis of higher alcohols and ethyl acetate in distilled spirits.

1. 23% Carbowax 1500 on Chromosorb W, 60-80 mesh, acid washed. Oven 70°C isothermal.

2. 2% Glycerol and 2% 1,2,6-Hexanetriol on Gaschrom R, 100-120 mesh, non-acid washed. Oven 80°C isothermal.

Figure 1 shows a separation of whiskey congeners on this second phase, but using oven temperature programming for optimum separation.

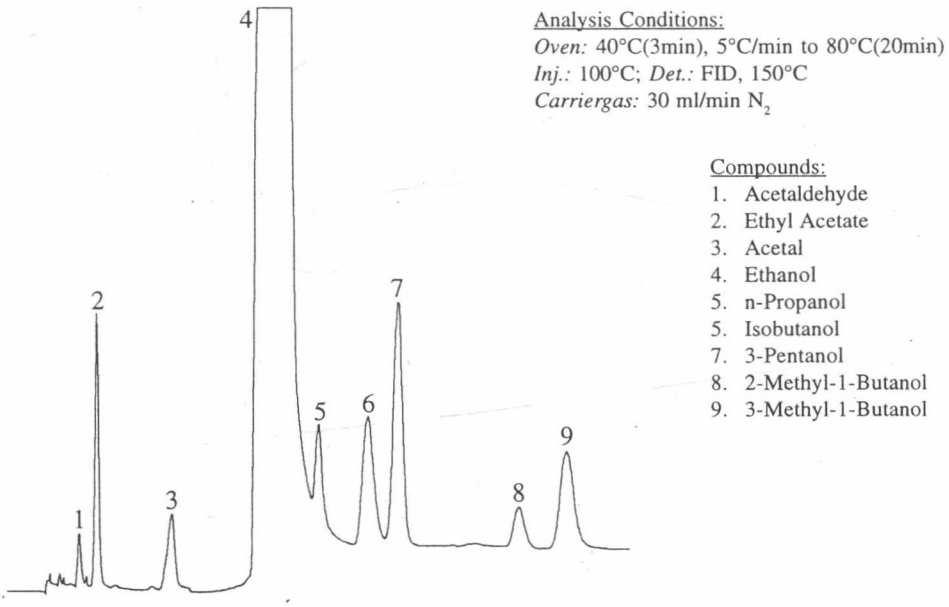
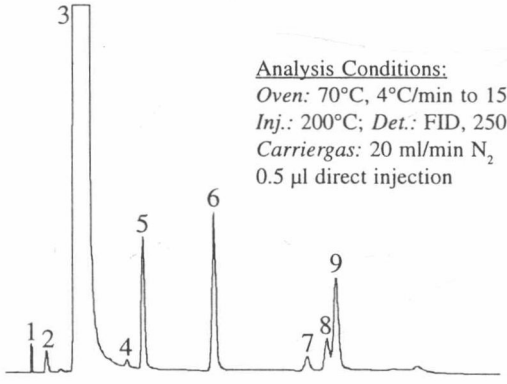


Figure1. *Separation of whiskey congeners, packed column.*

Cabezudo and co-workers perfected the mixed phase approach to congener separation [6]. A fortran program was devised to find the best combined phases from two to four single phases for a general purpose congener separation, or best combined phases for separation of specific groups of congeners. Analyses were carried out isothermally at 50°C and allowed elution and separation of up to 20 compounds. Di Corcia and co-workers pioneered the investigation and introduction of modified graphitized carbon black for GC analysis of distilled spirits [7]. They first used Carbopack B modified with Carbowax 20 M, and trimesic acid as acidic deactivating agent, but later found that this latter treatment was not necessary if the carbon surface was initially acid washed. Different Carbowax loadings were used for different congener groups and these columns also allowed elution of free fatty acids.

Martin [8] described a single procedure, using 80-120 mesh Carbopack B as solid support and 5% by weight Carbowax 20M as liquid phase, which allowed separation of acetic acid and the isomers of amyl alcohol. These columns are presently available in Silocosteel, which is stainless steel coated with a deactivated fused silica inner layer, and the manufacturers claim improved inertness, durability and flexibility compared to traditional glass packed columns [9]. **Figure 2** show separation of whiskey and rum congeners on these columns.



Analysis Conditions:
Oven: 70°C, 4°C/min to 150°C
Inj.: 200°C; *Det.:* FID, 250°C
Carriergas: 20 ml/min N_2
0.5 µl direct injection

Compounds:
1. Acetaldehyde
2. Methanol
3. Ethanol
4. Ethyl Acetate
5. n-Propanol
6. Isobutanol
7. Acetic Acid
8. active Amyl Alcohol
9. Isoamyl Alcohol

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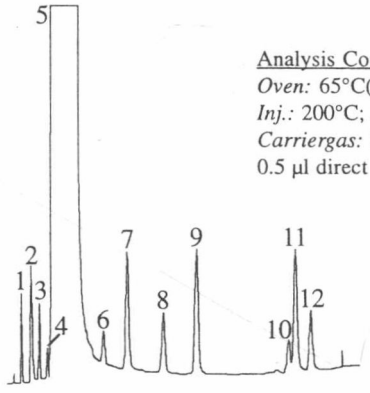


Analysis Conditions:
Oven: 65°C(5min), 4°C/min to 150°C
Inj.: 200°C; *Det.:* FID, 250°C
Carriergas: 20 ml/min N_2
0.5 µl direct injection

Compounds:
1. Acetaldehyde
2. Methanol
3. Acetone
4. Ethyl Formate
5. Ethanol
6. Ethyl Acetate
7. n-Propanol
8. sec-Butanol
9. Isobutanol
10. active Amyl Alcohol
11. Isoamyl Alcohol
12. n-Amyl Alcohol

Reproduced with permission from [9]

Figure 2. *Separation of whiskey (top) and rum congeners on 2m x 2mm 5% Carbowax 20M 80/120 CarboBlack B column.*

Finally a phase with a specific selectivity has recently been described [10] for monitoring compounds such as 2-propanol and acetoin in spirits and distilled wines. **Figures 3** and **4** compare separation of a standard solution of congeners on this column compared to the standard Carbowax 1500 phase. 2-Propanol and acetoin which can be markers for adulteration or oxidation changes coelute with the dominant ethanol on the standard phase.

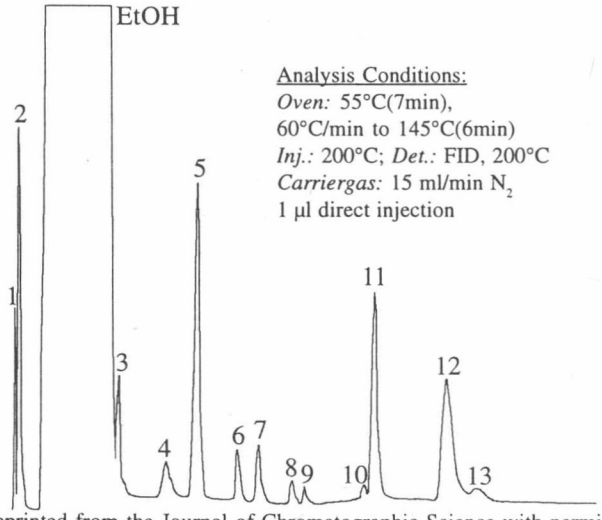


Figure 3. *Chromatogram of a standard solution using a 2m x 2mm MFE-Vinicol column.*

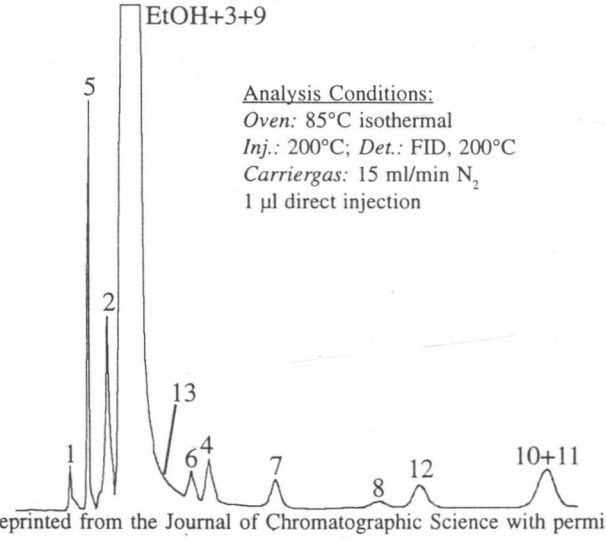


Figure 4. *Chromatogram of a standard solution using a 4m x 2mm Carbowax 1500 column.*

Capillary Columns. The open tubular design of capillary columns, where a phase without support packing is deposited as a thin film on the inner wall of a low internal diameter column offers significant performance advantages, but also places greater demands on the entire chromatographic operation. The practical differences between packed and open tubular column separation results from reduced intra brand broadening for individual solute molecules in the capillary and the much longer column lengths allowed by the open tubular design. These factors have been summarised by Jennings [11] as follows :

- A packed column will offer a range of flow paths to solute molecules giving a spread of residence times in the mobile phase. The open tubular design offers a single flow path with more uniform movement in and out of the mobile phase.

- Solute molecules also experience a similar wider residence time spread in the stationary phase due to its much higher concentration in a packed column and its non-uniform film thickness.

- Packing materials are inefficient at heat transfer and so a range of temperatures will exist across any transverse section of the packed column. Solute volatiles are affected and this again leads to dispersion of individual molecules of the same solute.

These factors therefore express themselves as compounds that elute with wide peak widths after short residence times in packed columns and mass sensitivity at the detector will be low for later eluting compounds. Co-elution and overlapping cannot be easily avoided. For this reason specific phase selection is very important for packed columns as the separation factor has to be optimised to compensate for these inherent disadvantages.

The open tubular design brings its own difficulties, principally in terms of the need for increased GC hardware sophistication, and especially the problem of transferring the sample compounds in a narrow band to the small diameter capillary column. The earliest columns were glass and required special deactivation procedures with delicate handling and manipulation. The trend at that stage was also to modify packed column instruments and the technique was largely confined to specialist laboratories. The introduction of robust, flexible, fused silica columns and chromatographs with dedicated capillary pneumatics, injectors and detectors, and especially more precise oven temperature control (Hewlett-Packard 5880A) finally made the technology much more accessible.

Grob et. al. were among the first to investigate direct analysis of distilled spirit congeners on glass capillary columns [12]. They used a column coated with Carbowax 400 and injected with splitting and an oven starting temperature of 25°C. This phase was not bonded to the column wall in the sense that it was not non-extractable and so the first 60 cm of the column was left without phase to avoid its removal and subsequent redeposition problems, which condensation at the low initial temperature could cause. De Nijs and de Zeeuw reported a chemically bonded Carbowax on fused silica which they termed CP Wax 57 CB [13]. This column was resistant to washing with polar solvents such as methanol and even water, and had an upper temperature limit of 220°C. MacNamara used this column with split injection to profile the major congeners in distilled spirits [14] and **Figures 5** and **6** shows typical separations for a standard mix of congeners and a whiskey.

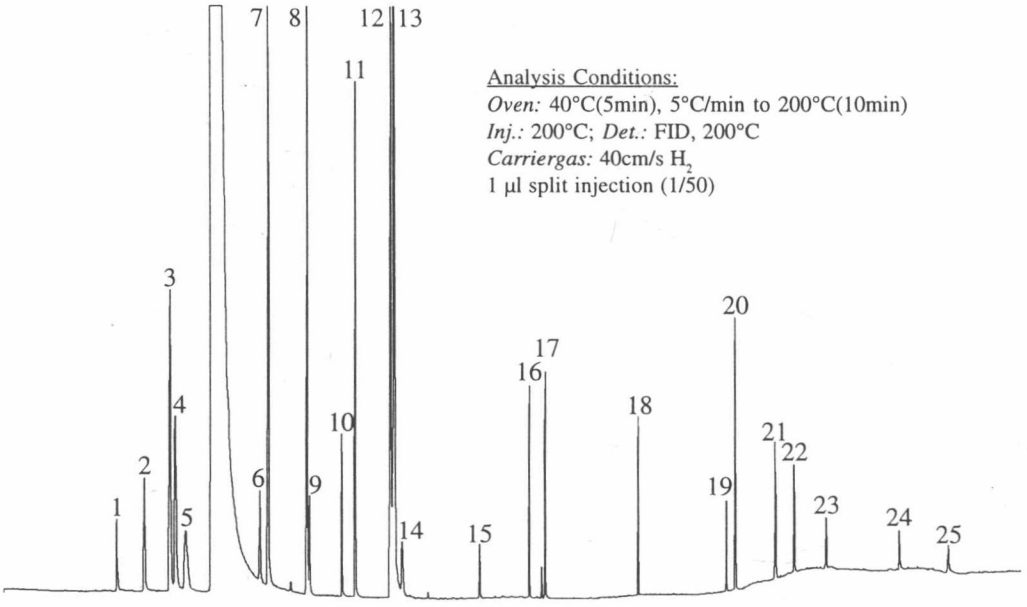


Figure 5. *Split capillary separation of a standard congener mixture in 40% v/v ethanol on a 50m x 0.25mm x 0.25µm CP-Wax 57 CB column.*

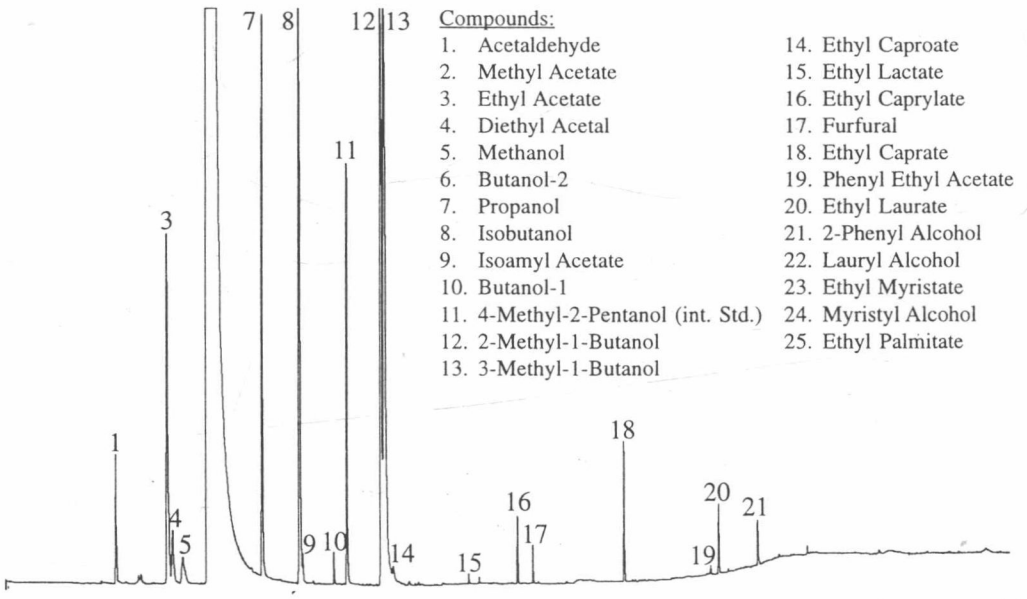


Figure 6. *Split capillary separation of a commercial whiskey on a 50m x 0.25mm x 0.25µm CP-Wax 57 CB column.*

CP Wax 57 is a unique phase with a unique selectivity, and major advantages are separation of the following pairs:

ethyl acetate - diethyl acetal

isobutanol - isoamyl acetate

isomers of amyl alcohol

Diethyl acetal and isoamyl acetate have quite low sensory thresholds, but in addition exhibit azeotropic behavior with ethanol and water which effect their behavior during distillation. **Table 4** gives composition and boiling point data for the ternary azeotropes of these two compounds with ethanol and water, and shows that the net boiling points of the compounds have been reduced to below the boiling point of the common ethanol-water azeotrope.

A-Component, B.P. (°C)	B-Component, B.P. (°C)	C-Component, B.P. (°C)	Azeotropic Data			
			B.P. (°C)	Wt. (%A)	Wt. (%B)	Wt. (%C)
Water, 100	Ethanol, 78.3	Diethyl Acetal, 103.6	77.8	11.4	27.6	61.0
Water, 100	Ethanol, 78.3	Isoamyl Acetate, 142.0	69.0	not stated		

Table 4. *Ternary azeotropes of ethanol/water with diethyl acetal and isoamyl acetate.*

Distillation fluctuations or non-equilibrium conditions can therefore affect the levels of these compounds in a spirit, and even though their absolute concentrations will be quite low, perceived aroma can be influenced through their high odour intensities. The information in **Figure 5** and **6** traces is also a balance which is determined by the injection split ratio. The split ratio is used to meter the proportion of the injection volume delivered to the column and is a trade-off between resolution before and just after the ethanol peak, and useful sensitivity for later eluting compounds. If the split ratio is too low resolution and peak shape for pre-ethanols suffers due to a reverse solvent effect [12] if it is too high detection of the late eluters becomes more difficult. The late eluting compounds in these traces, where the split injection amounts are much less than could have been delivered to a packed column, highlight previous comments on increased detector mass sensitivity.

This column is also very stable and our experience is to obtain 2 years daily use without any deterioration in performance. A baseline separation for the amyl isomers is not achieved but this is not necessary for accurate ratioing due to the 70/30 proportions usually found in distilled spirits. A more polar phase such as Carbowax 400 with much lower viscosity will baseline separate 2- and 3-methyl-1-butanol (**Figure 7**) but is a non-bonded phase and has an upper temperature limit of only 100°C. A disadvantage is that CP Wax 57 does not elute symmetrically free fatty

acids and an alternative approach is necessary for these compounds. Masuda et. al. [15] injected whiskey directly with splitting to a relatively apolar 5% phenylmethyl silicone capillary and achieved separation of a combination of alcohols and esters together with acetic, octanoic, decanoic and dodecanoic acids.

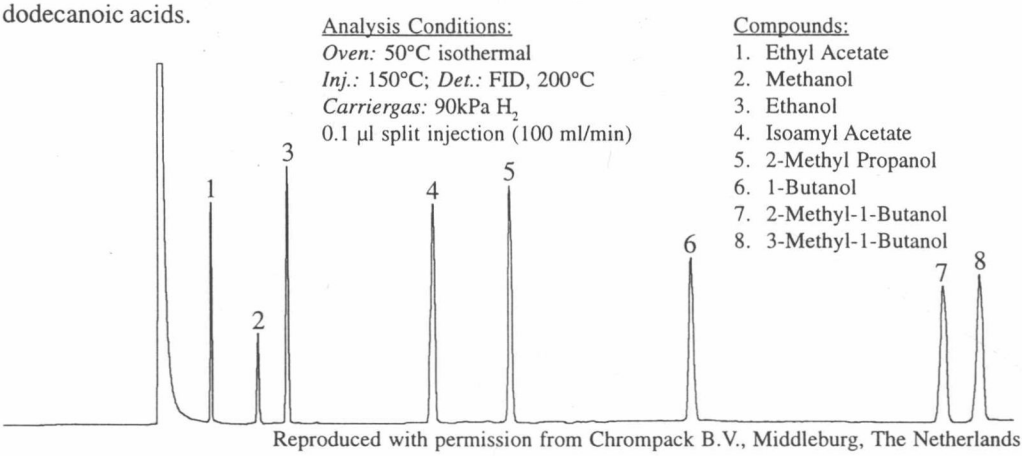


Figure 7. *Separation of a testmix on a 50m x 0.32mm x 0.2µm Carbowax 400 column.*

Direct splitless injection of distilled spirits is also possible and can give additional and complimentary data to that produced by split injection of the same sample [16]. **Figure 8** shows a direct splitless injection of a whiskey on an FFAP phase, which is a standard Carbowax polymer modified with nitroteraphthalic acid. The splitless injection transfers much more matrix and congeners to the column and gives increased peak areas for late eluting and minor congeners, together with symmetrical peaks for free fatty acids. The resolution of peaks around the solvent has been

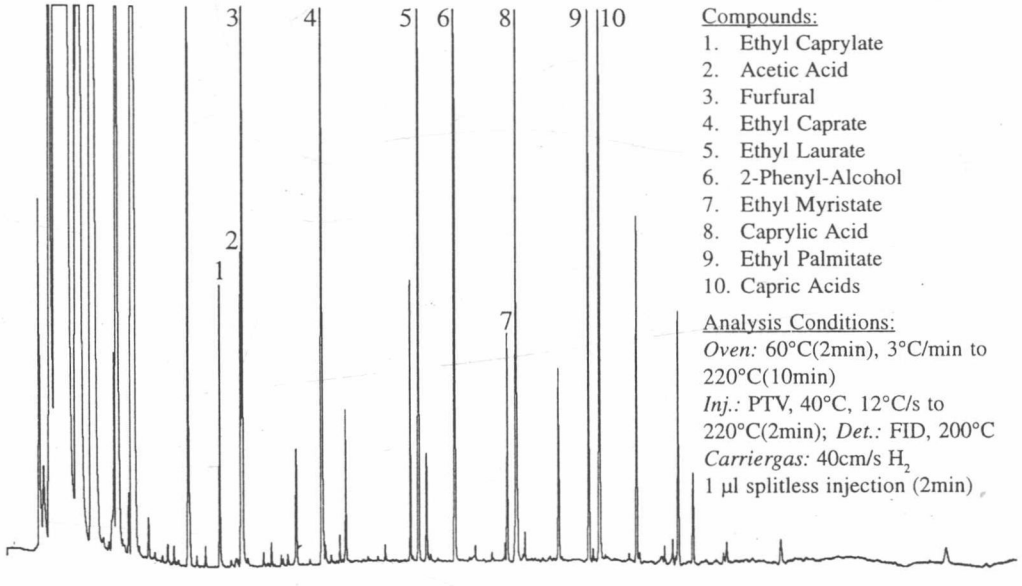


Figure 8. *Splitless injection of a whiskey on a 60m x 0.25mm x 0.25µm FFAP column.*

destroyed but this information is available from a corresponding split injection of the same sample. Therefore each injection mode gives unique and complimentary information which builds a comprehensive profile of the most abundant congeners. This approach was applied to quantify thirty three compounds in 14 samples of each of two different malt whiskeys [17]. Using linear discriminant analysis techniques a very good differentiation of the two types could be obtained (**Figure 9**) and it is also clear that the intra variation in one of the whiskeys is more pronounced. Further statistical testing showed that five compounds alone could account for 98.5% of the variation. Four of these compounds were quantified from the splitless part of the analyses.

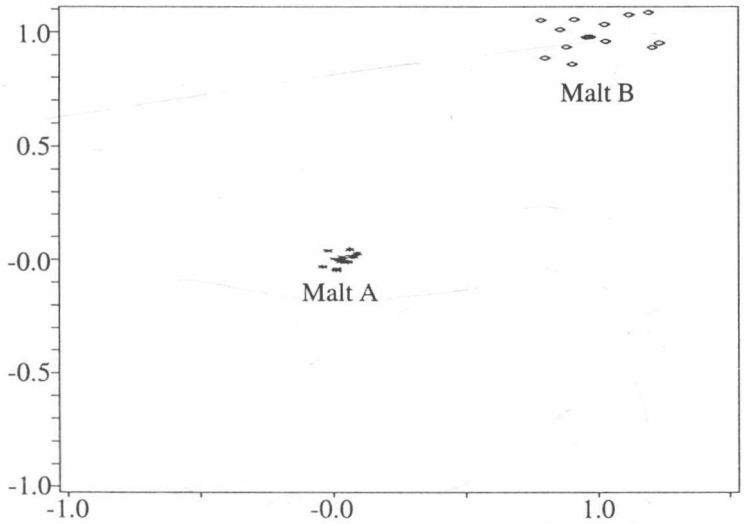


Figure 9. *Differentiation of whiskeys using direct injection congener data.*

Figure 10 shows Chernoff faces for the two whiskey sets constructed on these five compounds.

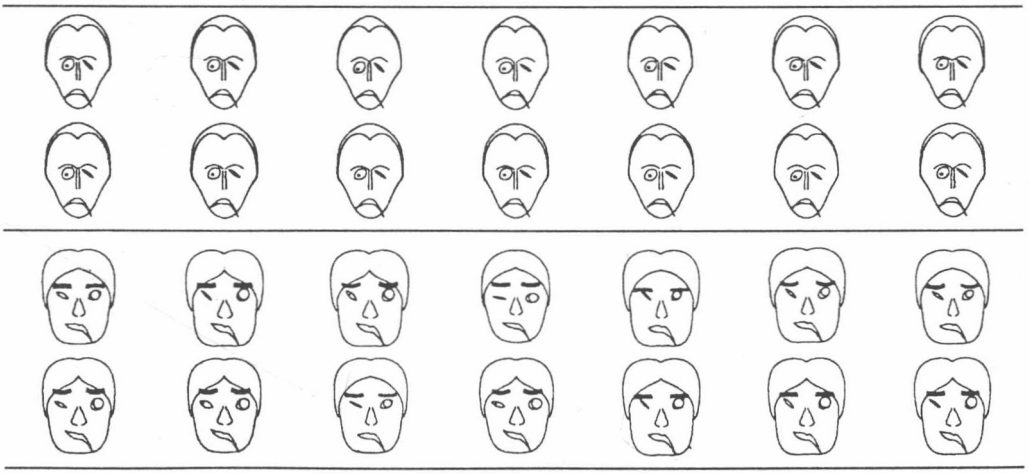
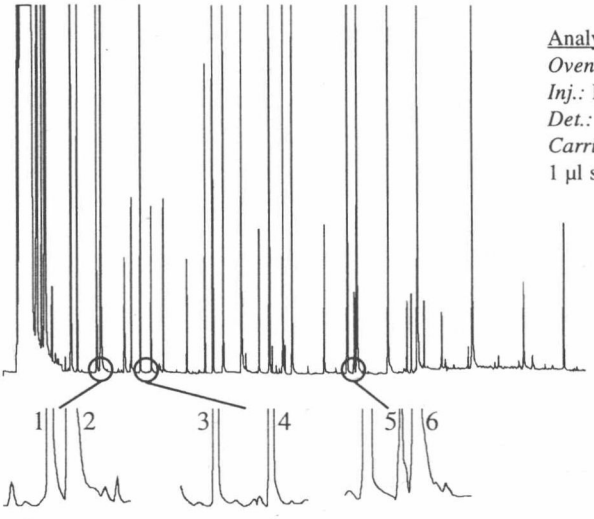


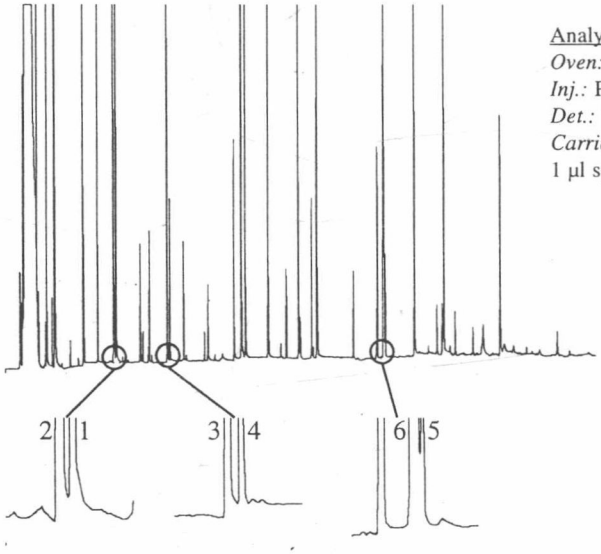
Figure 10. *Chernoff faces for malt A (top) and malt B, constructed on different levels of five compounds.*

One problem which detracts from the usefulness of direct splitless injection is the variability of FFAP columns from different commercial sources. This is related to different procedures for modifying the Carbowax phase with nitroteraphthalic acid to induce acidity. The treatment probably produces an ester linkage which can be more easily hydrolysed by certain solvents and conditions. A result of this is that the acidity can be removed with repeated injections and the phase will slowly evolve into standard Carbowax, with increasingly deteriorating acid peak shape. **Figure 11** show this phenomenon in its early stages. After about 50 injections the column is loosing acidity and is eluting acids faster than a new column. The pairs furfural and acetic acid, and $C_{16:1}$-ester and C_{10}-acid, have actually inverted, and the C_{10}-ester and C_4-acid pair are about to.



Analysis Conditions:
Oven: 60°C(2min), 3°C/min to 220°C(10min)
Inj.: PTV, 40°C, 12°C/s to 220°C(2min)
Det.: FID, 200°C
Carriergas: 40cm/s H_2
1 µl splitless injection (2min)

Compounds:
1. Furfural
2. Acetic Acid
3. C_{10}-Ester
4. C_4-Acid
5. $C_{16:1}$-Ester
6. C_{10}-Acid



Analysis Conditions:
Oven: 60°C(2min), 3°C/min to 220°C(10min)
Inj.: PTV, 40°C, 12°C/s to 220°C(2min)
Det.: FID, 200°C
Carriergas: 40cm/s H_2
1 µl splitless injection (2min)

Compounds:
1. Furfural
2. Acetic Acid
3. C_{10}-Ester
4. C_4-Acid
5. $C_{16:1}$-Ester
6. C_{10}-Acid

Figure 11. *Splitless injection of a whiskey on a new (top) and a deteriorating 60m x 0.25mm x 0.25µm FFAP column.*

After further use acid peak shape begins to deteriorate and the column must be changed. This behavior and its extent differs with similar columns from different manufacturers. With columns that allow a reasonable number of injections, direct splitless analysis gives rapid useful information that must be balanced against costs of higher column usage.

Splitless injection is a complicated process involving slow transfer of compounds of interest to the capillary column for refocusing and separation. In conventional hot splitless injections a pressure wave is created by the explosive vaporisation of the sample, giving a non-homogenous vapour cloud which is a recipe for discrimination. The same effect distributes the sample and any involatiles it may contain to every corner of the injection liner. Compounds of interest can be lost through the septum purge and involatiles have a greater chance of reaching the column entrance. Cold programmable injection (PTV), where the sample is deposited cold in a glass liner which is then linearly programmed to the desired final temperature, is aesthetically and technically superior to conventional flash vaporisation. Both discrimination and decomposition of labile substances have been shown by various authors to be dramatically reduced [18-20].

When a sample is deposited cold in a programmable injector its compound content can be uniformly removed by programmed heating and any involatiles tend to remain relatively undispersed in a section of the liner. One such injector (Gerstel CIS-3) also has a septumless head which both simultaneously avoids septum particle problems, and the need for a septum purge flow which gives discrimination and general loss of compounds. **Table 5** gives reproducibility of absolute peak areas for 6 replicate autosampler runs of ppm solutions of C_{13}-C_{20} hydrocarbons in hexane using cold split and splitless injection. The numbers given are expressed as % relative standard deviation from the 6 runs.

Mode	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}
split	1.12	0.98	0.90	0.58	0.83	0.82	0.72	0.65
splitless	0.86	1.06	1.04	1.52	0.68	0.64	1.02	0.73

Table 5. *Reproducibility of absolute peak areas for cold split and splitless PTV injection.*

There is no essential difference in the reproducibility of the split mode compared to the splitless mode and both offer a reliable and reproducible method for capillary sample introduction.

One important variable in splitless injection is the splitless or transfer time and cold injectors have a distinct advantage here. They have liners with smaller internal diameters than conventional injectors to provide a low thermal mass and allow rapid heating. This in turn allows a higher carrier gas velocity in the smaller i.d. liner and means transfer of the compounds to the column is faster and occurs at lower temperature. This can be even further enhanced by using pressure programming (a higher inlet pressure) during the splitless transfer. **Figure 12** shows the effect of liner diameter on the splitless transfer of the C_{30} hydrocarbon in hexane. 75% is transferred to the column at a temperature of 210°C for the 1.2 mm i.d. liner, and 290°C is required for the 3.4 mm i.d. liner [21].

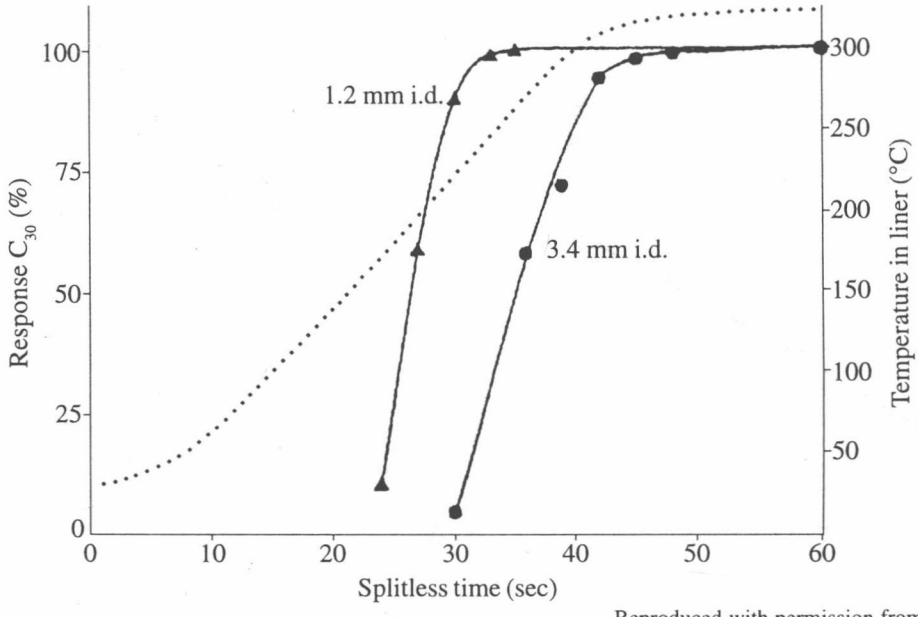


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Figure 12. *Effect of liner diameter on PTV splitless transfer. Dashed line: actual temperature in the liner.*

Cold programmable injection is the method of choice as a universal capillary injection technique and avoids the different disadvantages of hot split/splitless and cold on-column approaches. It can also be used for large volume injection applications and adapted to headspace and thermal desorption devices, and these areas will be investigated later.

An additional major advantage of capillary columns is that their small volumetric flow requirements allow the use of low-cost benchtop mass spectrometers as GC detector. The column can be directly interfaced to the ion source and the latest PC-based control and data reduction technology make this technique very accessible. When such a GC-MS is used in selected ion monitoring mode (SIM), the range of compounds that can be detected and quantified by direct splitless injection of spirits is profitably increased. In the SIM mode only characteristic ions from selected compounds are monitored continuously, rather than scanning all ions over a mass range. In the former case the time spent detecting the ion current at a particular mass is a much higher percentage of the total cycle time than in scanning mode. This is manifested as an apparent increased instrument sensitivity but is in fact due to a much higher signal-to-noise ratio.

The application of this approach means that higher esters can be directly quantified in light whiskeys where their level is at low or sub-ppm level due to a high blend ratio. The same approach can be used for similar level trace phenolics that contribute to peatiness in full malt whiskeys. In practice operating procedures are established which involve programming the instrument acquisition parameters to monitor specific ions from the known compounds in specific retention time windows. Ions to be monitored must be carefully chosen as there is always the danger of interference from the same ions from other compounds. To make the best use of this approach a dedicated software package [22] is recommended for target compound analysis.

In general the three principles inherent to target compound analysis are:

- Presence and integration of all the target ion masses.
- All ions must co-elute within a retention time window.
- Target ion ratios must fall within a calibrated range.

A compound is determined to be present if the characteristic ions (a reference ion and up to 2 qualifier ions) are detected co-elulting in a specified retention time window and they meet the ion ratio tests (**Figure 13**). The specified retention time windows for locating the characteristic ions can be defined in terms of absolute or relative retention time, or retention time relative to an internal standard. The ion co-elution test is then performed and this usually employs a small absolute time window to test for co-elution.

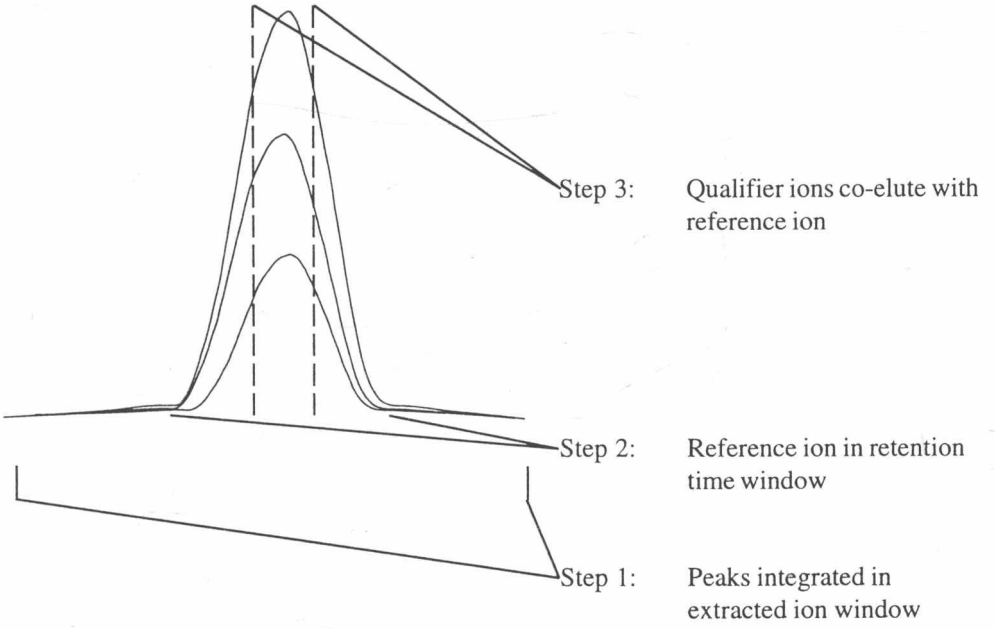

Figure 13. *Target concepts.*

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This window can be as small as one scan (or 0.025 mins) and is quite a strenuous test. When this test fails, even after optimum adjustment of instrument parameters, the entire analytical methodology needs to be re-evaluated. The final test is the ion ratio test, and the area ratio of the qualifier ions to the reference ion must fall within a target ion ratio limit, which is defined as acceptable variance of the ion ratio from the calibrated ratio. The calibrated/expected ion ratio for each qualifier can be automatically determined using the ion ratio from a calibration run.

When compound parameters and calibration data are correctly programmed, samples can be automatically run and processed with comprehensive report generation. **Figure 14** shows a selected ion monitoring TIC for 7 compounds in a very light blend after 1 µl direct splitless injection, with