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AppNote 3/2010

Automated Static and Dynamic Headspace Analysis with GC-MS for Determination of Abundant and Trace Flavour Compounds in Alcoholic Beverages Containing Dry Extract

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ABSTRACT

Direct injection for gas chromatographic profiling of alcoholic beverages is usually preferable, but where spirits and liquors contain appreciable amounts of non-volatile material, some mode of pre-treatment may be required to avoid both inlet and column contamination. This consideration applies in particular to products aged for extended periods in wooden barrels and especially products containing added sugar, as volatile artefacts from sugar decomposition in the hot injection port can also complicate the chromatogram.

In this paper a combination of static and dynamic headspace analysis is described for profiling both abundant and trace compounds in these products. Static headspace is used with a tenax packed injection port liner for the abundant compounds. Dynamic headspace uses an additional purging step to a second tenax liner which can then be desorbed to the same injection port liner used for the simple static headspace. In this case the previous abundant compounds are overloaded in the chromatogram but many additional trace compounds are now apparent. For both techniques the

only sample preparation required is dilution of the sample in a headspace vial and relevant automated sequences in either static or dynamic mode are also run from the same autosampler rail. A PTV injector in solvent vent mode is used in both cases for lowest detection limits. Application of this combined approach constitutes an effective routine analysis protocol for this particular class of products while avoiding dry extract contamination.

INTRODUCTION

Commercial distilled spirits are complex mixtures of flavour compounds in a dominant ethanol-water matrix [1,2] These compounds originate from the combined production processes of raw material extraction, fermentation, distillation, and in many cases, ageing in oak barrels. Except for some low volatility compounds originating from wood lignin breakdown during ageing, the majority of flavour compounds in distilled spirits are amenable to gas chromatographic analysis.

The matrix composition of distilled spirits is relatively clean and so direct injection without time-consuming sample preparation is possible. Abundant compounds at high mg/L levels can be quantified by simple split injection with flame ionisation detection [3,4] Additional compounds at low mg/L levels (higher esters and acids) can also be assayed by direct injection of 5-10 μL using a PTV injector for both removal of solvent and enrichment of compounds in the liner. This can be extended to 50-100 μL injections for even lower detection limits, but in this case sample introduction must avoid overloading of the injection port liner and subsequent sample loss through the split vent. Speed programmed injection is necessary and recoveries depend on complex interactions between many related sample and instrumental parameters [5].

However, there are many commercial alcoholic beverages which can contain relatively substantial amounts of non-volatile material, and for which direct injection techniques may not be suitable. Fruit spirits and liquors can contain high amounts of added sugar, and very old brandies and whiskies etc may contain higher than usual amounts of polyphenolic material from wood ageing. Without frequent liner exchange non-volatile material will accumulate and contaminate both inlet system and column. Added sugar in such products also degrades in the hot inlet to produce artefacts which complicates chromatograms.

In these cases there are additional techniques available which can avoid the unwanted effects of non-volatile material. These can be summarised as solid phase microextraction (SPME), stir bar sorptive extraction (SBSE) and headspace sorptive extraction (HSSE), static (HSS) and dynamic headspace sampling (DHS). All these techniques have many well documented applications in the literature [6-11]. With SPME a choice of sorbent materials is available but only limited sorbent volumes can be accommodated on the fibre. SBSE and HSSE can use much greater volumes of sorbent material, but this is almost always exclusively apolar polydimethylsiloxane. Headspace application could have the advantage that results may reflect more the actual sensory properties of the product analysed. Static headspace with intermediate adsorbent trapping was applied to spirit drinks containing dry extract for analysis of the principal abundant secondary alcohols and esters [7]. Automated dynamic headspace using replaceable adsorbent traps was used to profile volatile compounds in beer [12]. In this paper we describe the sequential application of static and dynamic headspace to profiling both abundant and trace compounds in an aged whiskey. Maximum sensitivity for each mode is achieved by using a PTV injector in solvent mode where the liner can also act as a cold trap. Use of a short 0.15 mm I.D. apolar capillary column with a phase ratio of 19 allows fast analysis with excellent separation of both abundant and trace compounds. All operations for both modes of analysis are amenable to total automation for unattended sequence operation.

EXPERIMENTAL

Instrumentation. Analyses were performed using a 7890 GC equipped with a 5975 Mass Selective Detector (Agilent Technologies), Thermal Desorption Unit (TDU, Gerstel), PTV inlet (CIS 4, Gerstel) and MPS 2 with headspace and DHS option (Gerstel), figure 1.

Figure 1. GERSTEL MPS 2 with DHS on an Agilent Technologies 7890 GC.

Analysis conditions static headspace.
Trap: Tenax TA
MPS: 60°C incubation temperature (10 min)
          2.5 mL injection volume

Analysis conditions dynamic headspace DHS.
Trap: Tenax TA
DHS: 30°C trap temperature
          60°C incubation temperature (10 min)
          50 mL purge volume
          10 mL/min purge flow
          10 mL dry volume
          5 mL/min dry flow
TDU: solvent venting
          20°C (1 min); 720°C/min;
          110°C (1 min); 720°C/min;
          300°C (3 min)

Analysis conditions.
PTV: Tenax TA liner,
          solvent vent (60 mL/min) at 0 kPa
          splitless (2 min)
          20°C (0.2 min); 10°C/s; 300°C (5 min)
Column: 25 m CP-SIL 5CB (Varian)
          $d_i = 0.15$ mm $d_f = 2.0$ μm
Pneumatics: He, constant flow = 0.5 mL/min
Oven: 40°C (10 min); 10°C/min;
          300°C (6 min)
MSD: Scan, 28 - 350 amu

Aqueous and high water content samples can often be problematic for headspace analysis. The presence of water vapor in the headspace above the sample can lead to poor precision. Operating the PTV inlet in solvent vent mode using a Tenax-filled liner significantly reduces the amount of water transferred to the analytical column.

The GERSTEL Dynamic Headspace System (DHS) is an accessory for the MultiPurpose Sampler (MPS) which enables dynamic purging of the headspace above a sample. Analytes in the purged headspace are trapped onto 2 cm sorbent beds in compact glass tubes, an optional dry purge allows reduction of water content. The thermal desorption tube is then placed into the Thermal Desorption Unit (TDU) and thermally desorbed into the pre-cooled CIS 4 inlet, where the analytes are cryofocused to improve peak shape before introduction into the column. Applying the solvent vent mode at the TDU before transfer of analytes to the CIS provides an additional venting step of e.g fusel alcohols. Figure 2 shows a schematic of the trapping and desorption process.
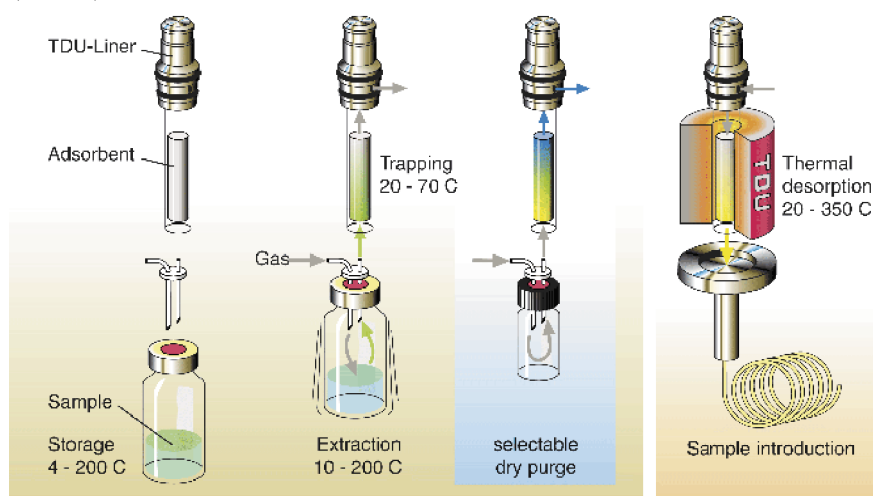

Figure 2. Schematic View of DHS Process.

Sample Preparation. No sample preparation other than transferring the samples into empty 10 mL screw cap headspace vials is necessary.

Results and Discussion

Figure 3 shows a typical trace obtained using the headspace approach. The fusel or higher alcohols together with ethyl acetate and the and the principal straight chain fatty acid esters up to dodecanoic acid ethyl ester dominate the chromatogram. Interesting also in the initial elution space are clear peaks for important trace aldehydes, ethyl esters and acetals. Of particular importance are the ethyl esters of short chain fatty acids, called fruit esters due to their pleasant aromas. Pungent aldehydes and their sweet acetals with various alcohols can also affect perceived aroma.
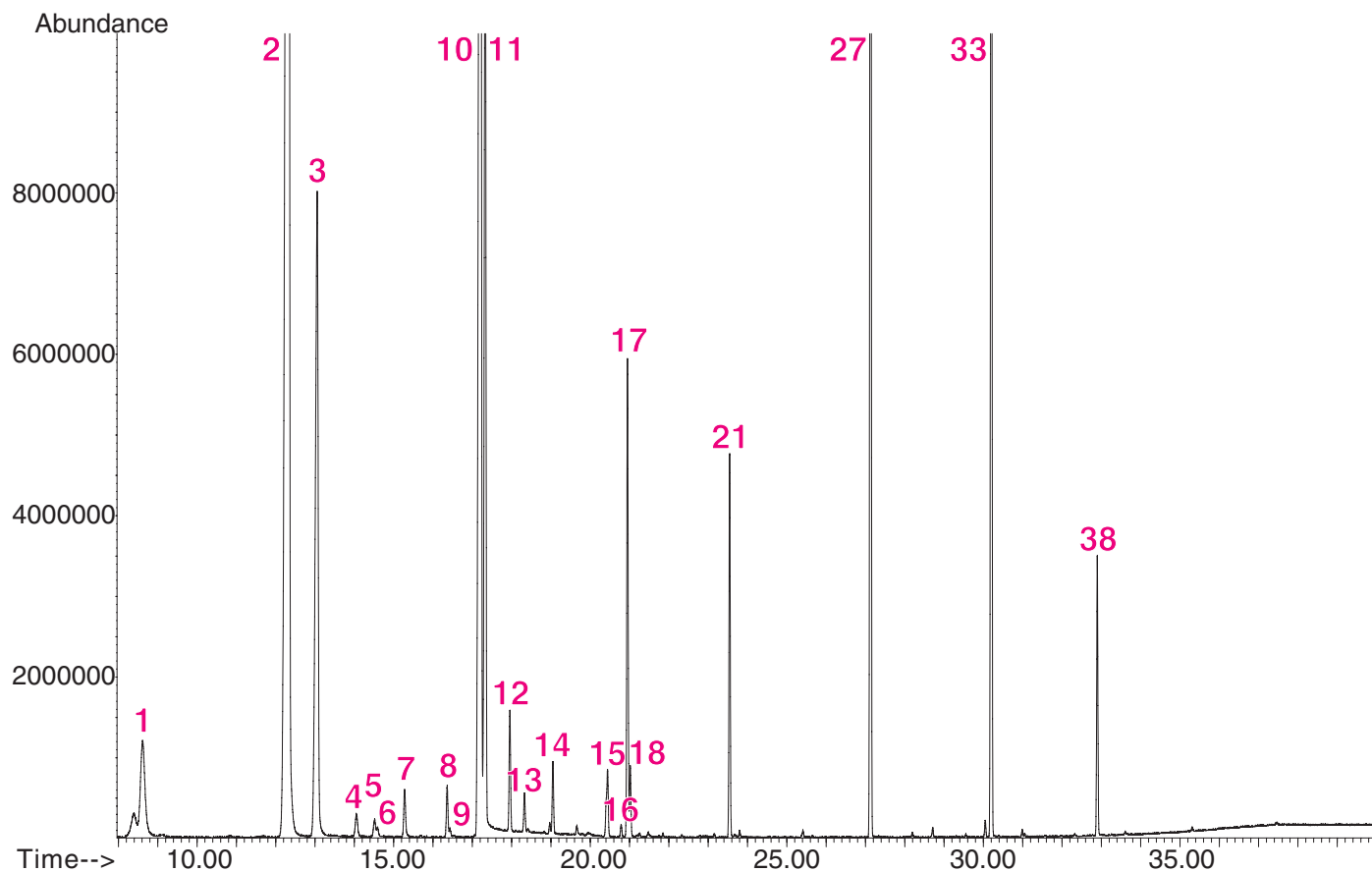
Figure 3. Static headspace chromatogram of an aged whiskey, compound identification see table 1.

Figure 4 in turn shows the chromatogram obtained when the same sample is injected after dynamic headspace stripping. Analytes up to the C5 alcohols have been partially vented in the TDU since their elution in the chromatogram would give only limited information due to chromatographic crowding, but now much more compound detail is apparent in the remaining elution space. Many interesting esters of both straight and branched chain higher esters are visible and it is even possible to profile some acids. Nonanal and Decanal have been reported previously in beer, wine and cognac, and both are used in the flavour and fragrance business. Both injection modes are very reproducible and do not normally require use of internal standards.
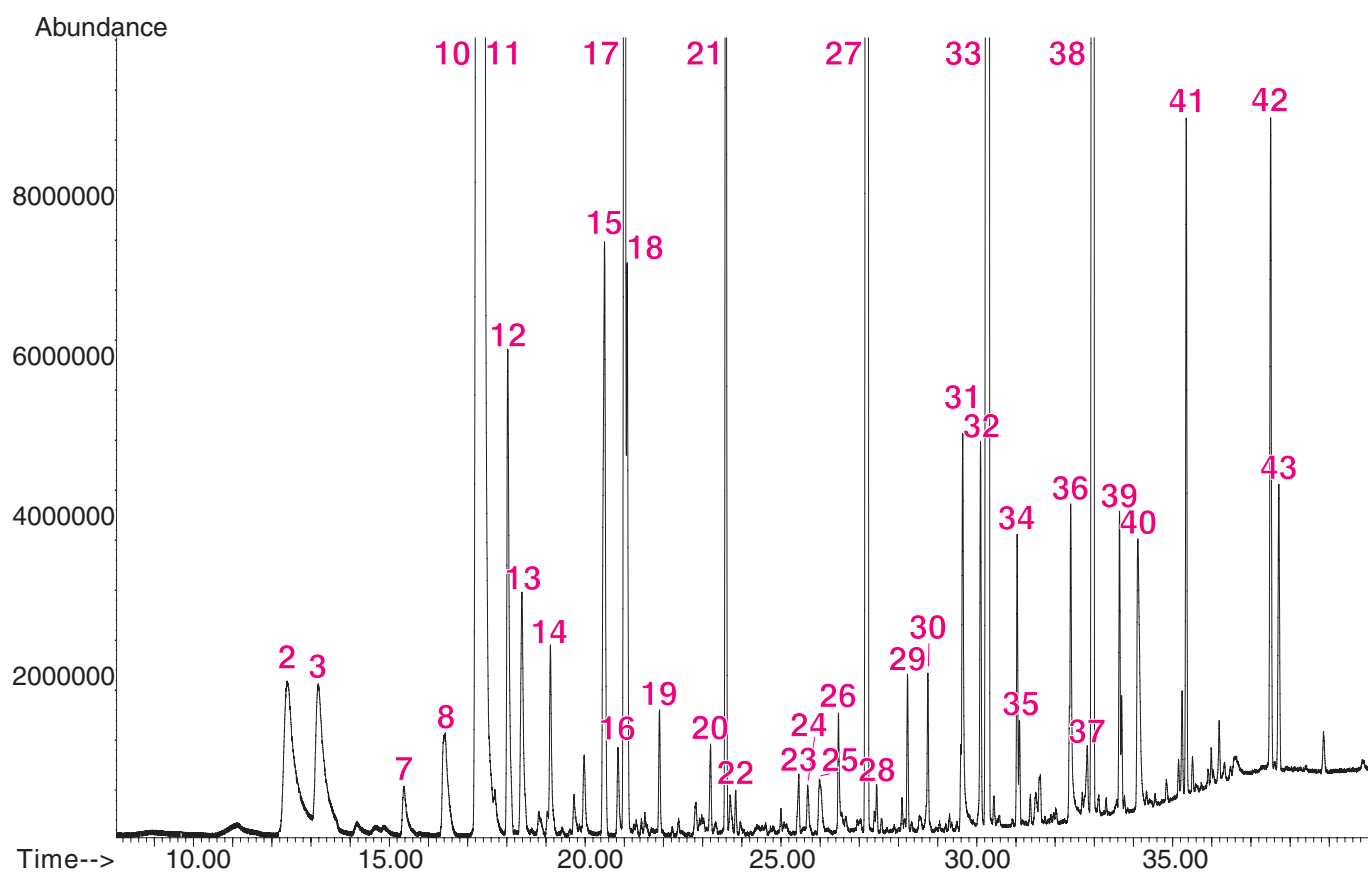
Figure 3. Dynamic headspace chromatogram of an aged whiskey, compound identification see table 1.

Table 1. Compound identification.

No.	Compound
1	Propanol
2	Ethyl acetate
3	Isobutanol
4	3-Methyl butanal
5	2-Methyl butanal
6	1-Butanol
7	1,1-Diethoxy methane
8	Propionic acid ethyl ester
9	n-Propyl acetate
10	3-Methyl-1-butanol
11	2-Methyl-1-butanol
12	Isobutyric acid ethyl ester
13	Isobutyl acetate
14	Butyric acid ethyl ester
15	Butyric acid 2&3-methyl-ethyl ester
16	Isobutyraldehyde diethyl acetate
17	Isoamyl acetate
18	2-Methyl-1-butyl acetate
19	Butyraldehyde diethyl acetal
20	Acetaldehyde ethyl amyl acetal
21	Hexanoic acid ethyl ester
22	Hexyl acetate

No.	Compound
23	Heptanoic acid ethyl ester
24	Nonanal
25	ß-Phenyl ethyl alcohol
26	Octanoic acid
27	Octanoic acid ethyl ester
28	Decanal
29	ß-Phenyl ethyl acetate
30	Nonanoic acid ethyl ester
31	Decanoic acid
32	Ethyl trans-4 decenoate
33	Decanoic acid ethyl ester
34	Octanoic acid 3-methyl- butyl ester
35	1-Ethyl propyl octanoate
36	Capric acid isobutyl ester
37	Dodecanoic acid
38	Decanoic acid ethyl ester
39	Pentadecanoic acid 3-methyl-butyl ester
40	Pentadecanoic acid 2-methyl-butyl ester
41	Tetradecanoic acid ethyl ester
42	Ethyl-9-hexadecenoate
43	Hexadecanoic acid ethyl ester

CONCLUSIONS

A combination of static and dynamic headspace techniques offers a useful complimentary approach for profiling major and minor components in alcoholic beverages, especially those with not insubstantial levels of dissolved solids. All constituent parts of each analysis are instrumentally automated and no off-line sample preparation is required.

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