

Improved Resolution of Alcoholic Beverage Components by Packed Column GC

Analysts can attain superior resolution of alcoholic beverages by using 80/120 Carbowax™ B AW/5% or 6.6% Carbowax® 20M. Carbowax B AW/5% Carbowax 20M, developed specifically for analyses of distilled spirits, can be used to determine trace amounts of acetic acid, as well as fusil oils. More complex samples, such as wine and beer, should be analyzed on Carbowax B AW/6.6% Carbowax 20M. Using SPME to sample wines, and separating the analytes with a PAG column, clearly characterizes the aroma patterns of two muscat-type wines from different vineyards, and determines low concentrations of an additive.

Analysis of Alcohols Using Carbowax B AW/5% or 6.6% Carbowax 20M

An 80/120 Carbowax B AW 5% Carbowax 20M column separates nine components of distilled spirits: acetaldehyde, acetic acid, active amyl alcohol, ethanol, ethyl acetate, isoamyl alcohol, isobutyl alcohol, methanol, and n-propyl alcohol. Whiskey, brandy, rum, or vodka are analyzed easily on this packing. Analyses of Scotch whiskey (Figure A), bourbon (Figure B), and cherry brandy (Figure C) illustrate the high resolution that can be achieved with this packing.

Figure A. Scotch Whiskey

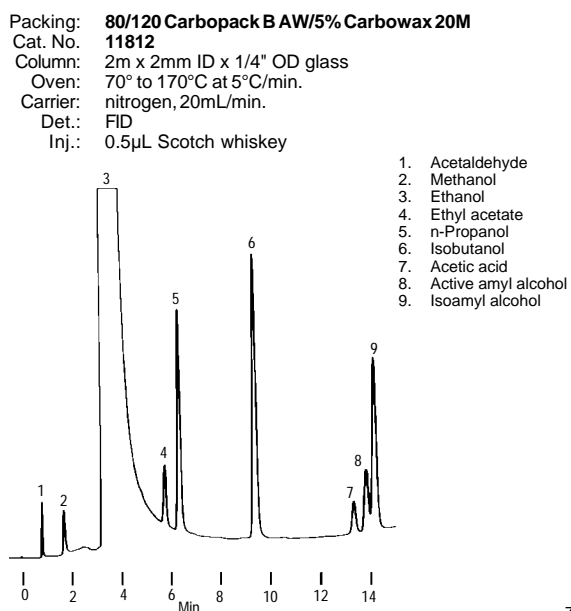


Figure B. Bourbon

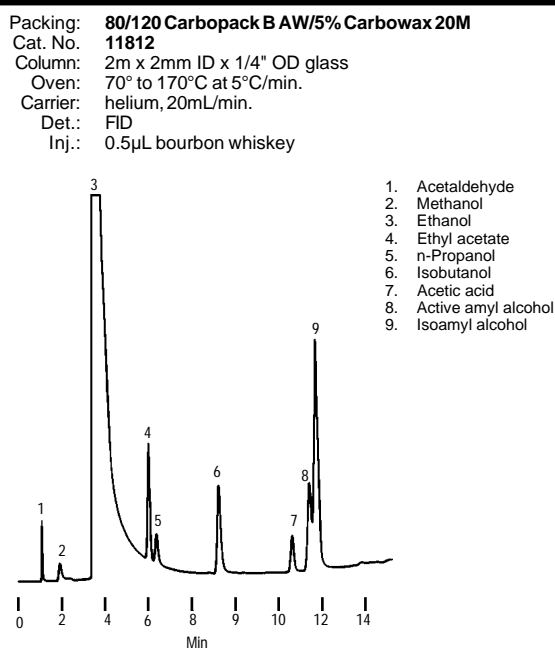
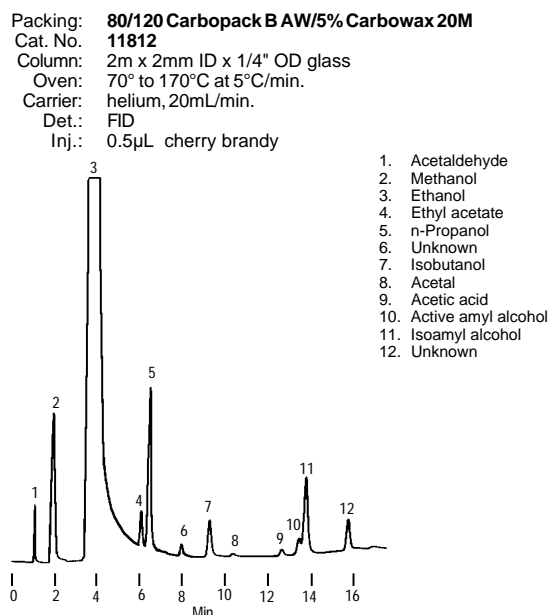


Figure C. Cherry Brandy



The capabilities of Carbowax 20M were confirmed by Martin, Burgraff, Dyer, and Buscemi (1) of the US Department of the Treasury, Bureau of Alcohol, Tobacco and Firearms. These analysts compared the performance of 80/120 Carbowax 20M to that of the column called for in the standard Association of Official Analytical Chemists (AOAC) procedure, 60/80 Chromosorb® W AW/23% Carbowax 1500. The Carbowax column offers these five advantages over the Chromosorb/Carbowax column:

1. Resolves methanol from ethanol (even methanol concentrations below 50ppm)
2. Resolves n-propanol from ethanol
3. Enables analysts to quantify acetic acid in one step
4. Resolves the amyl alcohols (2-methyl-1-butanol and 3-methyl-1-butanol)
5. Enables analysts to quantify acetic acid, methanol, ethyl acetate, and the higher molecular weight alcohols in alcoholic products by using a single analysis.

Acetic acid normally is determined in alcoholic beverages by titrating total acids with 0.1N NaOH and considering the total as acetic acid (AOAC 9.046). Wine samples are distilled (cash still), then titrated with 0.1N NaOH for total acids (AOAC 11.036-11.038), which are considered as acetic acid. The procedure used with a Carbowax 20M column gives a true acetic acid value. More study is needed to establish whether direct acetic acid determination is more useful than total acid determination, or if both methods are of equal value.

Figure D. Compounds Found in Alcoholic Beverages and Fermentation Products

Packing: **100/120 Carbowax B AW/6.6% PEG 20M**
 Cat. No. **11814**
 Column: 2m x 2mm ID glass
 Oven: 80°C to 200°C at 4°C/min.
 Carrier: nitrogen
 Det.: FID
 Inj.: 1µl of synthetic mixture in water: ethanol (50:50), 40:60ppm each component

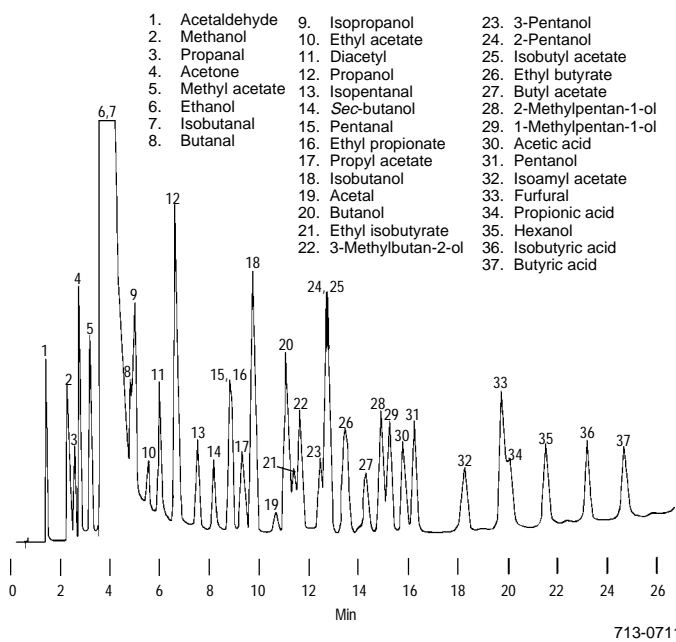
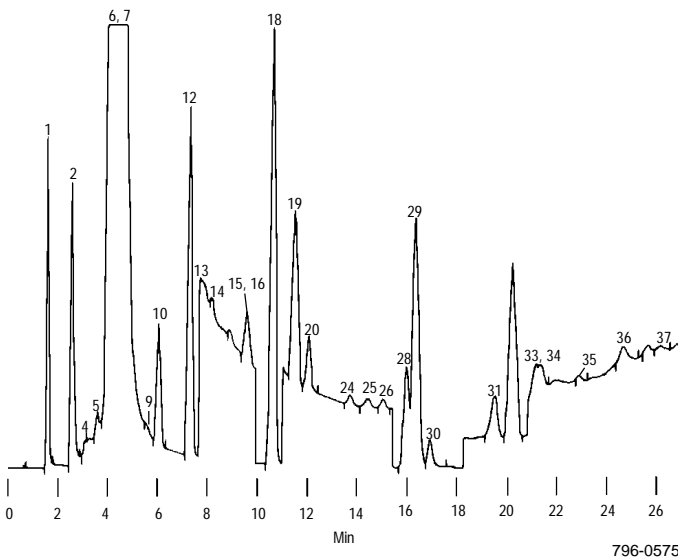


Figure E. Trace Components in Scotch Whiskey

Conditions and peak numbering as in Figure D.



Of the nine compounds separated on Carbowax 20M, only methanol may occasionally be difficult to detect because the methanol peak appears simultaneously with a slight baseline disturbance caused by water in the sample. When methanol is present in low ppm concentrations, as it is in rum, the baseline disturbance may mask the methanol peak. This disturbance is not large enough to interfere with detection of higher concentrations of methanol.

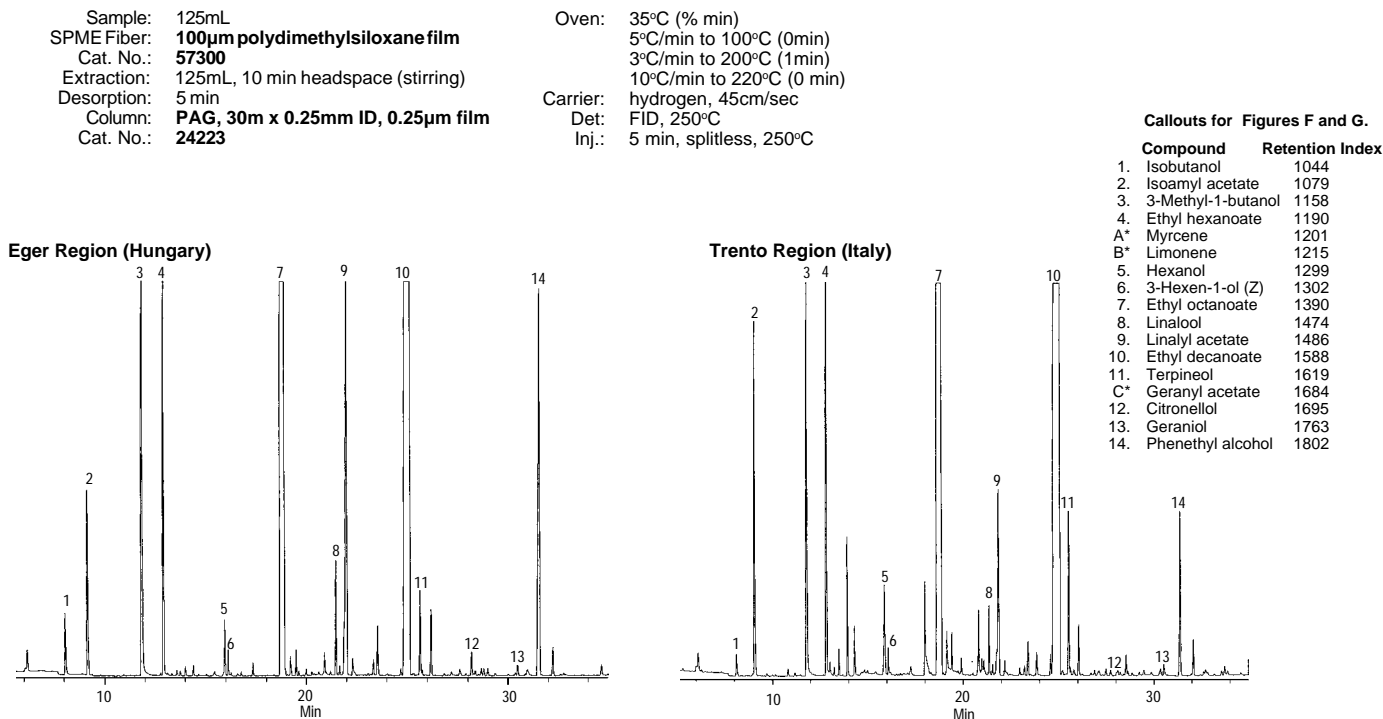
Analysts who monitor more than the nine conventional components of distilled spirits, or who analyze beer, wine, or other fermentation products, should be aware of another packing, 80/120 Carbowax 20M modified with the generic equivalent of 6.6% Carbowax 20M. This packing was developed for analyzing very complex mixtures of compounds in alcoholic beverages (1), and it separates such mixtures better than other packings can. It can also be used to detect acetic, propionic, and other low molecular weight carboxylic acids, compounds that are usually adsorbed on other columns.

Figure D shows the separation of 37 compounds on Carbowax 20M AW modified with the generic equivalent of 6.6% Carbowax 20M (100/120 Carbowax 20M AW/6.6% PEG 20M not commercially available.) All of the components have been separated except ethanol/isobutanol, pentanol/ethyl propionate, and 2-pentanol/isobutyl acetate. (If necessary, these pairs can be separated on 80/120 Carbowax 20M AW/3.35% Carbowax 20M.) Carbowax 20M AW/6.6% Carbowax 20M can also be used to analyze trace components in Scotch whiskey (Figure E). Compare this analysis to that of the same brand of Scotch in Figure A. With Carbowax 20M AW/6.6% Carbowax 20M, beer or wine samples usually are analyzed by head space analysis to prevent contamination of the column inlet with nonvolatiles from the sample.

Column Considerations

It is difficult to pack columns that have the high efficiency needed for the separations shown in this bulletin. For this reason, we recommend that analysts purchase 80/120 Carbowax 20M AW/5% or 6.6% Carbowax 20M in packed glass columns. Analysts who

Figure F. Comparison of Muscat Wines by SPME/GC



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wish to pack their own columns with these packings should use glass tubing to obtain the most inert and efficient columns. Columns made with metal tubing adsorb acetic acid, and do not separate active amyl and isoamyl alcohols as well as glass columns. Similarly, the column ends must be plugged with phosphoric acid-treated glass wool, because untreated or silanized wool adsorbs acetic acid. These packings have an upper temperature limit of 225°C and a recommended lower limit of 60°C.

Analysis of Alcohols Using SPME/GC

The low concentration of most volatile components in wine makes extraction and concentration necessary before analysis by gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS). The extraction method, solid phase microextraction* (SPME), can be used to characterize wine aromas and detect extraneous flavor additives. Two wines from the same grape variety were analyzed — wines originating from the Eger wine region of Hungary and from the Trento wine region of Italy. Additionally, 1 ppm spike of cold-pressed coriander seed oil in wine was accurately detected using this method.

SPME requires no solvents or complicated apparatus. It can be used to concentrate volatile and nonvolatile compounds in both liquid and gaseous samples. An SPME unit consists of a length of fused silica fiber coated with a phase film. The fiber is attached to a stainless steel plunger in a protective holder. A 100µm PDMS (polydimethylsiloxane) SPME fiber was exposed to the headspace of the wine for 10 minutes at ambient temperature. After sampling, the fiber was retracted into the SPME needle, then inserted into a GC injection port and exposed for 5 minutes to desorb the analytes of interest.

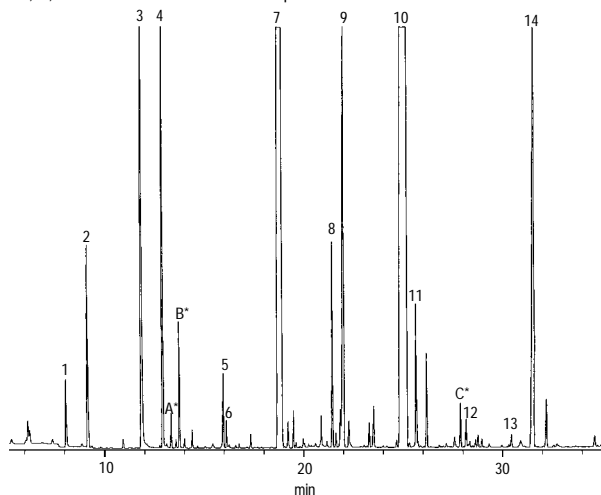
A polyalkylene glycol (PAG) capillary GC column separated the analytes. The PAG phase has similar characteristics to the polyethylene glycol (PEG) phase, but retention indices are somewhat different. This can be advantageous for separating components that are not well resolved on a PEG column. Our results show that the PAG column is suitable for headspace SPME wine aroma characterization. Chromatograms of the two muscat wine samples show large characteristic differences between the respective wine regions (Figure F). This distinction is of major importance in wine analysis, providing an analytical look at the origin of a wine sample.

Cold-pressed coriander seed oil is occasionally added to increase the muscat flavor of wine. The oil is typically used in the 10 to 20ppm concentration range — enologists vastly recognize it by taste in this range. At lower concentrations it may still add a slight muscat flavor, but is difficult to identify by taste. Sampling by headspace/SPME with GC analysis using a PAG column can easily identify such adulteration. Figure G shows wine from the Eger region spiked with 1 ppm cold-pressed coriander seed oil. The peaks marked with an asterisk (*) are characteristic of this oil.

The headspace SPME sampling technique, in combination with GC analysis, easily distinguishes muscat wines of different origins and detects small concentrations of cold-pressed coriander seed oil additive. Use of this efficient and accurate sample preparation method will benefit analysts trying to ascertain or prove the origin of wines and the use of additives in wine.

Figure G. Muscat Wine Spiked with 1ppm Cold-Pressed Coriander Seed Oil

Conditions and callouts: see Figure F.
Peaks A, B, and C are characteristic of cold-pressed coriander seed oil.



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♦ US Patent pending. European patent #0523092. Technology licensed exclusively to Supelco.

◊ We recommend using these packings in glass columns.

■ "Carbowax 20M" and "PEG 20M" are similar materials. Carbowax is Union Carbide's trademark for polyethylene glycol polymers.

■ Initially you must order both holder and fiber assembly. Holder is reusable indefinitely. Use with AutoSampler requires Varian SPME upgrade kit (available from Varian).

References

- Martin, G.E., J.M. Burggraff, R.H. Dyer, and P.E. Buscemi, *J. Assoc. of Anal. Chem.*, (Vol. 64, No. 1, 186, 1981).
 - DiCorcia, A., R. Samperi, C. Severini, *J. Chromatogr.*, 198, 347-353 (1980).
 - DiCorcia, A., R. Samperi, C. Severini, *J. Chromatogr.*, 170, 245-248 (1979).
- References not available from Supelco.

Ordering Information:

Description	Cat. No.
TightSpec™ Packed Glass Columns, 2m x 2mm ID x 1/4" OD, packed with 80/120 Carbopack B AW/ 5% Carbowax 20M	
For Perkin-Elmer 900 and 3920 (not on-column injection)	23846
For Hewlett-Packard 5830 (6" span, on-column injection)	custom
Packings[◊]	
80/120 Carbopack B AW/5% Carbowax 20M, 15g	11812-U
80/120 Carbopack B AW/6.6% Carbowax 20M, 15g	11814
Monopak™4g, just enough packing for one column	11914
SPME Fiber, 100µm polydimethylsiloxane, pk. of 3	
For manual sampling	57300-U
For Varian 8100/8200 AutoSampler or HPLC	57301
SPME Holder[■]	
For manual sampling	57330-U
For Varian 8100/8200 AutoSampler or HPLC	57331
PAG Fused Silica Capillary Column	
30m x 0.25mm ID, 0.25µm film	24223

Acknowledgment

These packings are part of a series developed in cooperation with Dr. Antonio DiCorcia of the University of Rome (2,3). We are indebted to Dr. DiCorcia and his coworkers for chromatograms D and E. The Elsevier Scientific Publishing Company, Amsterdam, kindly gave us permission to publish their figures (from reference No. 1).

The section on analysis of alcohols using SPME/GC was written in conjunction with G. Vas, Research Institute for Viticulture & Enology of Agricultural Ministry, Eger, Hungary.

Trademarks

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Carbowax — Union Carbide Corp.

Chromosorb — Manville Corp.

Fused silica columns manufactured under HP US Pat. No. 4,293,415.

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BULLETIN 790C