Improved Resolution of Alcoholic Beverage Components by Packed Column GC

Analysts can attain superior resolution of alcoholic beverages by using 80/120 Carbopack™ B AW/5% or 6.6% Carbowax® 20M. Carbopack 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 Carbopack 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 Carbopack B AW/5% or 6.6% Carbowax 20M

An 80/120 Carbopack 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

Packing: 80/120 Carbopack B AW/5% Carbowax 20M
Cat. No. 11812
Column: 2m x 2mm ID x 1/4” OD glass
Oven: 70° to 170°C at 5°C/min.
Carrier: nitrogen, 20mL/min.
Inj.: 0.5µL Scotch whiskey

1. Acetaldehyde
2. Methanol
3. Ethanol
4. Ethyl acetate
5. n-Propanol
6. Isobutanol
7. Acetic acid
8. Active amyl alcohol
9. Isoamyl alcohol

Figure B. Bourbon

Packing: 80/120 Carbopack B AW/5% Carbowax 20M
Cat. No. 11812
Column: 2m x 2mm ID x 1/4” OD glass
Oven: 70° to 170°C at 5°C/min.
Carrier: helium, 20mL/min.
Inj.: 0.5µL bourbon whiskey

1. Acetaldehyde
2. Methanol
3. Ethanol
4. Ethyl acetate
5. n-Propanol
6. Isobutanol
7. Acetic acid
8. Active amyl alcohol
9. Isoamyl alcohol

Figure C. Cherry Brandy

Packing: 80/120 Carbopack B AW/5% Carbowax 20M
Cat. No. 11812
Column: 2m x 2mm ID x 1/4” OD glass
Oven: 70° to 170°C at 5°C/min.
Carrier: helium, 20mL/min.
Inj.: 0.5µL cherry brandy

1. Acetaldehyde
2. Methanol
3. Ethanol
4. Ethyl acetate
5. n-Propanol
6. Isobutanol
7. Acetic acid
8. Active amyl alcohol
9. Isoamyl alcohol
10. Unknown
The capabilities of Carbopack B AW/5% Carbowax 20M were confirmed by Martin, Burggraff, 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 Carbopack B AW/5% 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 Carbopack 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 Carbopack B AW/5% 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 Carbopack 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

Of the nine compounds separated on Carbopack B AW/5% 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 Carbopack B AW/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 Carbopack B AW modified with the generic equivalent of 6.6% Carbowax 20M (100/120 Carbopack B 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 Carbopack B AW/3.35% Carbowax 20M.) Carbopack B/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 Carbopack B 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 Carbopack B AW/5% or 6.6% Carbowax 20M in packed glass columns. Analysts who
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 tem-
perature 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 spec-
trometry (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, 1ppm spike of cold-pressed cori-
der 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 polyeth-
ylene 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 1ppm 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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- ™ 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

References not available from Supelco.

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
Carbopack, Monopak, TightSpec — Supelco, Inc.
Carbowax — Union Carbide Corp.
Chromosorb — Varian Corp.
Fused silica columns manufactured under HP US Pat. No. 4,293,415.

Ordering Information:

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<td>TightSpec™ Packed Glass Columns, 2m x 2mm ID x 1/4&quot; OD, packed with 80/120 Carbopack B AW/5% Carbowax 20M&lt;br&gt;For Perkin-Elmer 900 and 3920 (not on-column injection)</td>
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<td>For Hewlett-Packard 5830 (6&quot; span, on-column injection)</td>
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For more information, or current prices, contact your nearest Supelco subsidiary listed below. To obtain further contact information, visit our website (www.sigma-aldrich.com), see the Supelco catalog, or contact Supelco, Bellefonte, PA 16823-0048 USA.