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GAS CHROMATOGRAPHIC COLUMN FOR THE RAPID DETERMINATION OF CONGENERS IN POTABLE SPIRITS

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SUMMARY

The determination of minor components, including fatty acids, in potable spirits has been accomplished by using acid-washed (AW) Carbopack B, an example of graphitized carbon black, modified with PEG 20M. Quantitative data for selected compounds show that good precision can be obtained even at the level of a few parts per million. The determination of minor components in a commercial sample of Scotch whisky was carried out by using AW Carbopack B modified with 6.6% of PEG 20M.

Components present in concentrations of about 0.5 ppm can be determined with a precision of about 30%. An additional column packing (AW Carbopack B + 3.35% of PEG 20M) was used for determining those few components of minor interest which cannot be separated by the former column packing.

INTRODUCTION

The determination of individual congeners or secondary constituents present in alcoholic beverages is of importance not only to those engaged in the production of spirits, but also to Food and Drug Administration and Customs and Excise workers and toxicologists. This type of analysis is complicated by the large number of congeners present in small proportions.

The direct gas chromatographic method is undoubtedly the best method for determining individual minor components in potable spirits as it offers maximal simplicity, rapidity, sensitivity and accuracy[1–4]. There is a need for a chromatographic column able to separate microamounts of alcohols, acids, aldehydes and esters present in a water–ethanol mixture in a few minutes. Although there has been considerable work in this direction, no chromatographic system described in the literature is completely satisfactory. Whenever direct chromatography of aqueous alcohol solutions has been attempted, various difficulties have been encountered. Firstly, stationary phases are generally intolerant to water injections. Consequently, the chromatographic column deteriorates after some period of continuous use. Secondly, so far as we know the columns used for the analysis of higher alcohols and esters in alcoholic beverages are not able to elute acids. The official method for the determina-

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tion of acids in potable spirits is a titration which determines total acid and the results are calculated as acetic acid. Thirdly, the chromatographic determination of some minor components in distillates is hindered by the presence of excess amounts of ethanol. Last, in almost all instances the separation of 2-methylbutan-1-ol from 3-methylbutan-1-ol cannot be achieved by using conventional chromatographic columns. The quantitative determination of these two components is of importance in establishing the quality of an alcoholic beverage.

Recently, using graphitized carbon black (Carbopack B), suitably modified with 3% of polyethylene glycol (PEG) 20M and 2.4% of 1,3,5-tricarboxybenzene (trimesic acid), we were able to determine individual congeners present in an Italian potable spirit[5]. However, this column packing has two limitations: firstly, its relatively low thermal stability does not permit the column to be operated at temperatures higher than 160°C; secondly, the percentage of trimesic acid is a very critical parameter. At slightly higher percentages of trimesic acid, alcoholic compounds are eluted as tailed peaks owing to their tendency to form esters with the acidic modifier. If, on the other hand, the percentage of the acidic deactivating agent is decreased, acids are not eluted linearly.

Very recently, it has been shown that washing the surface of graphitized carbon black is effective in removing the surface sites that are responsible for chemisorption of acids[6]. The result is that the acidic deactivating agent is no longer necessary in order for symmetrical peaks for trace amounts of acidic eluates to be obtained.

The object of this paper is to show that the individual contents of minor components present in potable spirits, even at sub-parts per million levels, can be determined in less than 30 min by using acid-washed Carbopack B modified with PEG 20M. This column packing has been shown to be very stable for long periods of continuous use. Quantitation data reported for some congeners of interest show that good precision can be achieved at the level of a few parts per million. The chromatographic profile and the quantitative determination of minor components present in an actual sample of whisky are also presented.

EXPERIMENTAL

Carbopack B, which is an example of graphitized carbon black, was kindly supplied by Supelco (Bellefonte, PA, U.S.A.).

The procedure for washing Carbopack with an acidic solution has been recently reported[6]. An aqueous solution of phosphoric acid (0.1 *M*) was used to wash the carbon surface as a first attempt. Very good results were obtained in terms of peak symmetry for both acids and alcohols if acid-washed (AW) Carbopack B was coated with more than 4% of PEG 20M. On the other hand, slightly tailed peaks for alcohols were noted at surface coverages of PEG 20M lower than 4%. This fact can be explained by assuming that, after the chemical treatment, traces of phosphoric acid still remain on the carbon surface, even after washing it with large amounts of distilled water. Then, at low surface coverages of PEG 20M, the terminal hydroxyl groups of the stationary phase are not sufficient to deactivate chemisorbed phosphoric acid, which gives strong interactions with alcoholic eluates.

This problem was eliminated by washing Carbopack B with an aqueous solution of a low-boiling acid, such as acetic acid, at a concentration of 0.3 *M*. By

changing the nature of the acid, no differences were noted in the gas chromatographic characteristics of the PEG 20M + AW Carbopack system, provided that the percentage of PEG 20M was higher than 4%. On the other hand, untailed peaks for alcohols were observed even on coating the acetic acid-washed Carbopack surface with relatively small amounts of modifying liquid.

The procedure for coating Carbopack B was similar to that reported previously[7].

Glass columns (2 m × 2 mm I.D.) were filled with the packing material by following a procedure described elsewhere[8]. The packed columns were conditioned under a flow of nitrogen at 240°C for about 15 h. Nitrogen was used as the carrier gas.

Standards were supplied by Fluka (Buchs, Switzerland). Ethanol used as the solvent was supplied by Carlo Erba (Milan, Italy). This compound contained 24.3 ppm (w/w) of methanol, 1.3 ppm of acetaldehyde and 1.1 ppm of acetic acid, as determined in our laboratory.

A Carlo Erba Model GI gas chromatograph equipped with a flame-ionization detector was used.

For measurements of peak areas a Hewlett-Packard 3385-A integrator was used.

RESULTS AND DISCUSSION

Fig. 1 shows the chromatogram obtained after injection of an artificial ethanol–water (1:1) mixture containing 40–60 ppm of each individual compound that may be present in natural alcoholic beverages. The elution was obtained by using AW Carbopack B modified with 6.6% of PEG 20M.

It can be seen that small amounts of acids, alcohols and aldehydes are eluted as symmetrical peaks. Also, under the conditions used only the peak for isobutanal, which is a congener of minor interest, is obscured by excess amounts of ethanol.

Using the column described above, accurate determinations of congeners of practical interest in potable spirits can be performed. It also appears that overlapping of some peaks of compounds of minor interest could be a partial limitation to the use of the system.

It has been reported that useful modifications to the fractionating power of liquid-modified graphitized carbon black can be achieved not only by changing the modifying liquid but also by varying its relative amount[9]. In order to fractionate all of the components of the complex mixture considered, many attempts were made by changing both the modifying liquid and its percentage, but no system was found to be completely suitable for the required purpose.

Therefore, we resorted to using an additional column packing capable of fractionating isobutanol, pentanal and pentan-2-ol from the other components of the artificial mixture. AW Carbopack B modified with 3.35% of PEG 20M was used with the purpose of determining the three compounds mentioned above; this column packing is more effective than the former in separating the two isoamyl alcohols of interest. This allows the accurate determination of these two compounds without the use of an electronic integrator.

Chemisorption of acids does not occur after acid washing of the surface of the carbon black. To substantiate this result and to determine the minimal amounts of

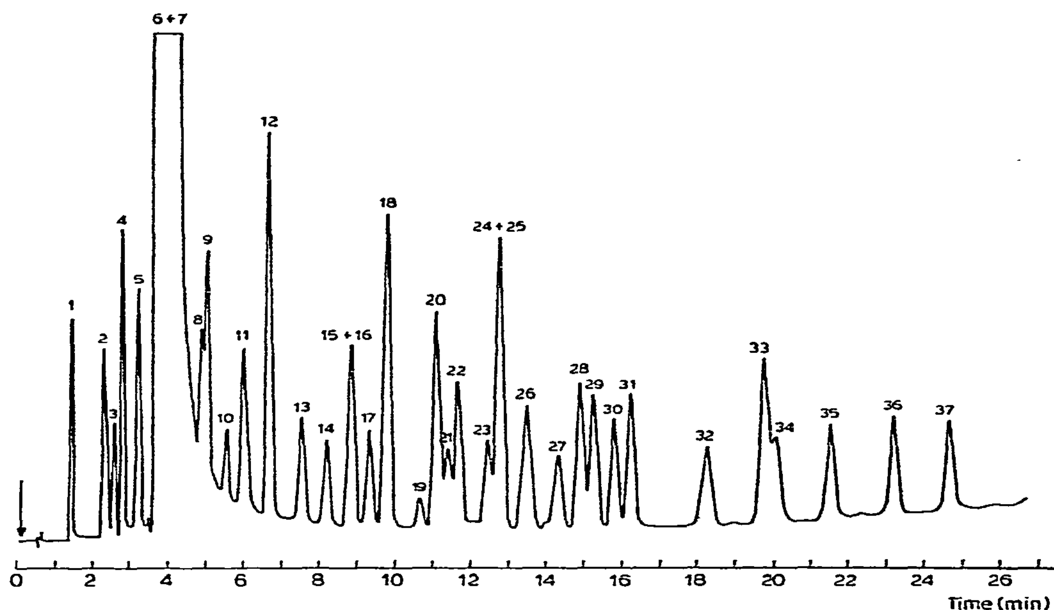

Fig. 1. Chromatograms of an artificial water–ethanol mixture eluted on AW Carbopack B modified with PEG 20M. Column, 2.0 m × 2 mm I.D; packing, AW Carbopack B (100–120 mesh) + 6.6% of PEG 20M; carrier gas, nitrogen; dead time, 32 sec; temperature, programmed from 80°C to 200°C at 4°C/min; sample size, 1 μl. Peaks: 1 = acetaldehyde; 2 = methanol; 3 = propanal; 4 = acetone; 5 = methyl acetate; 6 = ethanol; 7 = isobutanal; 8 = butanal; 9 = isopropanol; 10 = ethyl acetate; 11 = diacetyl; 12 = propanol; 13 = isopentanal; 14 = *sec.*-butanol; 15 = pentanal; 16 = ethyl propionate; 17 = propyl acetate; 18 = isobutanol; 19 = acetal; 20 = butanol; 21 = ethyl isobutyrate; 22 = 3-methylbutan-2-ol; 23 = 3-pentanol; 24 = 2-pentanol; 25 = isobutyl acetate; 26 = ethyl butyrate; 27 = butyl acetate; 28 = 2-methylpentan-1-ol; 29 = 3-methylpentan-1-ol; 30 = acetic acid; 31 = pentanol; 32 = isoamyl acetate; 33 = furfural; 34 = propionic acid; 35 = hexanol; 36 = isobutyric acid; 37 = butyric acid.

congeners in distillates that can still be measured with good precision, quantitative measurements of some compounds were made by using the above two column packings. Measurements were carried out by using the same experimental conditions as reported in the caption to Fig. 1. Methyl amyl ketone was chosen as the internal standard. Standard solutions at concentrations lower than 100 ppm were prepared by diluting the starting solution containing the reference compound with the ethanol–water solvent mixture. The results are reported in Table I. It appears that quantitative determinations at a level of 2 ppm can be made with an error of about 5% for compounds that are eluted well after ethanol. At the same level of concentration, the uncertainty in the measurement is higher than 5% for butanal and isopropanol, because these two compounds are eluted just after the broadened peak for excess amounts of ethanol. The anomalous behavior of the response factor of methanol can be explained by considering that the high-purity ethanol used for calibrated test solutions contains 24.3 ppm of methanol, plus 1.1 ppm of acetic acid and 1.3 ppm of acetaldehyde.

TABLE I

QUANTITATIVE DATA FOR SELECTED COMPOUNDS ELUTED ON AW CARBOPACK B + 6.6% OF PEG 20M

Results are concentrations (ppm, w/w) ± standard deviations for 6 determinations.

Compound	*Concentration (ppm, w/w)*			
	100	*50*	*10*	*2*
Acetaldehyde	0.920 ± 0.013	0.930 ± 0.012	1.05 ± 0.06	1.35 ± 0.09
Methanol	1.22 ± 0.013	1.85 ± 0.05	4.27 ± 0.27	16.0 ± 1.5
Isobutanal*	0.937 ± 0.014	0.910 ± 0.013	0.900 ± 0.051	0.87 ± 0.09
Butanal	0.941 ± 0.016	0.931 ± 0.033	0.842 ± 0.092	0.702 ± 0.18
Isopropanol	1.101 ± 0.013	1.110 ± 0.022	1.171 ± 0.052	1.504 ± 0.123
Ethyl acetate	0.943 ± 0.011	0.942 ± 0.018	0.937 ± 0.037	0.929 ± 0.056
Propanol	1.031 ± 0.013	1.033 ± 0.015	1.028 ± 0.043	1.029 ± 0.071
2-Methyl-pentan-1-ol	1.007 ± 0.014	1.007 ± 0.016	1.010 ± 0.032	1.013 ± 0.052
Acetic acid	0.551 ± 0.008	0.580 ± 0.015	0.572 ± 0.026	0.684 ± 0.039
Propionic acid	0.864 ± 0.011	0.871 ± 0.020	0.878 ± 0.039	0.912 ± 0.054
Hexanol	1.091 ± 0.015	1.093 ± 0.026	1.073 ± 0.046	1.068 ± 0.054
Butyric acid	1.011 ± 0.013	1.016 ± 0.024	1.100 ± 0.054	1.016 ± 0.056

* Data obtained by using AW Carbopack B + 3.35% of PEG 20M.

The column packing used for quantitation has a relatively high thermal stability. Thus, the increase in the baseline during temperature programming is minimal. This is made evident by the fact that 2 ppm of well retained compounds, such as hexanol and butyric acid, can be determined with good precision.

Fig. 2 shows the chromatogram obtained after direct injection of 1.5 μl of

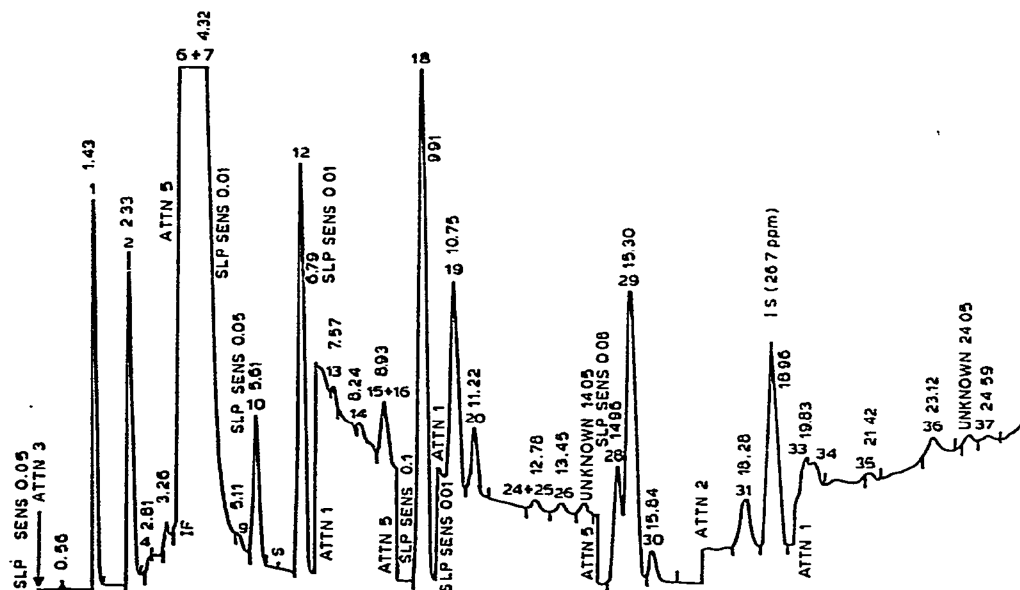

Fig. 2. Chromatogram of a commercial sample of Scotch whisky (Johnny Walker Red Label). Experimental conditions and peak numbering as in Fig. 1A.

an actual sample of Scotch whisky (Johnny Walker Red Label), using AW Carbopack B + 6.6% of PEG 20M.

An additional column packing of AW Carbopack B + 3.35% of PEG 20M was used for the determination of those few components which are not separated by the former column packing. Methyl ethyl ketone was used as the internal standard in this instance as the peak for methyl amyl ketone overlaps that for isoamyl acetate.

The results obtained are given in Table II. The mean standard deviations obtained over a set of ten determinations for components present at concentration under 1 ppm were about 25%. As can be seen, the agreement between the data for isoamyl alcohols obtained with the two column packings is good. The increase in the baseline just before the appearance of the ethanol peak is due to water. This disturbance by water does not affect significantly the determination of traces of acetone and methyl

TABLE II

DETERMINATIONS OF CONGENERS IN A COMMERCIAL SAMPLE OF SCOTCH WHISKY

Results are concentrations (ppm, w/w) ± standard deviations for 6 determinations.

Congener	*AW Carbopack B + 6.6% of PEG 20 M*	*AW Carbopack B + 3.35% of PEG 20M*
Acetaldehyde	24 ± 2	
Methanol	34 ± 2	
Acetone	0.41 ± 0.05	
Methyl acetate	2.4 ± 0.5	
Isobutanal	— —	1.6 ± 0.3
Isopropanol	1.8 ± 0.6	1.7 ± 0.2
Ethyl acetate	82 ± 1	
Propanol	260 ± 2	
Isopentanal	0.54 ± 0.07	
sec.-Butanol	0.42 ± 0.06	
Pentanal }	2.85 ± 0.09	0.2 ± 0.1
Ethyl propionate }		2.8 ± 0.3
Isobutanol	415 ± 3	
Acetal	11.5 ± 0.5	
Butanol	1.4 ± 0.2	
Pentan-2-ol }	0.56 ± 0.09	Traces
Isobutyl acetate }		0.4 ± 0.1
Ethyl butyrate	0.61 ± 0.03	
Unknown (t_R: 14.05 min)	0.68 ± 0.07	
2-Methylbutan-1-ol	101.2 ± 0.9	106.5 ± 0.6
3-Methylbutan-1-ol	282 ± 2	297 ± 1
Acetic acid	54 ± 1	
Isoamyl acetate	7.4 ± 0.4	
Furfural	3.1 ± 0.4	
Propionic acid*		1.2 ± 0.1
Hexanol	0.3 ± 0.1	
Isobutyric acid	0.6 ± 0.2	
Unknown (t_R: 24.05 min)	0.6 ± 0.2	
Butyric acid	0.5 ± 0.2	

* Data for propionic acid were obtained from the second column as the electronic integrator added the areas for furfural and propionic acid.

acetate. By using AW Carbopack B modified with 3.35% of PEG 20M the isopropanol peak appears on the terminal part of the tail of the peak for ethanol, thus making the determination of traces of isopropanol more accurate than by using AW Carbopack B modified with 6.6% of PEG 20M.

As far as column stability is concerned, no significant variation of column performance was noted during continuous use for 2 months. During this period, about 200 samples of aqueous alcoholic solutions were injected directly into the column packings. The only precaution used was to keep the columns at 220°C overnight after a few days of use, in order to eliminate from the column high-boiling compounds contained in the caramel that is used as an additive for whisky.

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