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Note

Modified graphitized carbon black for the gas chromatographic analysis of alcoholic beverages

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The direct gas chromatography of volatile compounds in aqueous alcoholic solutions is widely used as maximal simplicity, rapidity and accuracy can be obtained. However, serious problems are encountered in practice in this type of analysis, for various reasons. Firstly, many stationary phases do not permit injections of water. Secondly, the separation of some compounds is hindered by the presence of excess of ethanol. Thirdly, natural aqueous alcoholic solutions are complex mixtures. Therefore, the determination of the detailed composition of these mixtures, requires high-resolution gas chromatographic columns. Finally, the direct analysis of bacterial fermentation products and distillates, is complicated by the presence of variable amounts of free fatty acids.

Graphitized carbon black (Carbopack) modified with different amounts of different liquids has been shown to be effective in the analysis of low-boiling, polar compounds[1]. The separation of trace amounts of C_1–C_5 alcohols in water can be achieved by suitably modifying the Carbopack surface with PEG 1500[2,3]. Recently, this separation has been achieved in about 1 min by both using fine particles of TCEP-modified Carbopack and hydrogen as carrier gas[4]. However, these two types of chromatographic column are unsatisfactory in the direct analysis of aqueous alcoholic solutions as small amounts of fatty acids are eluted as tailing peaks owing to insufficient deactivation of the Carbopack surface.

The linear elution of free fatty acids at concentrations down to 0.5 ppm in water has been performed on Carbopack coated with 0.5% orthophosphoric acid and 3% PEG 20M[5]. However, the simultaneous determination of alcohols and acids on this column packing is hindered by the fact that alcohols are eluted as very tailed peaks. This effect can be explained by considering that orthophosphoric acid deposited on Carbopack tends to form esters with eluates the contain a hydroxyl group.

The object of this paper is to show that the analysis of free fatty acids in the presence of alcohols can be accomplished by modifying the Carbopack surface with suitable amounts of both PEG 20M and 1,3,5-tricarboxybenzene (trimesic acid). In particular, it was found that Carbopack B modified with 3% PEG 20M and 2.4% trimesic acid is able to fractionate a 50% aqueous ethanol solution containing 37 compounds that may be encountered in natural alcoholic beverages. The chromatographic profile from the direct injection of a sample of "grappa", an Italian spirit, is also reported.

EXPERIMENTAL

Carbopack B (60–80 mesh), which is an example of graphitized carbon black, was obtained from Supelco (Bellefonte, Pa., U.S.A.). It was ground and sieved to 100–120 mesh.

Coating of the Carbopack surface was carried out in the usual way[6], first depositing trimesic acid from methanol and, after the evaporating methanol, depositing PEG 20M from methylene chloride. The packing operation, which is very critical, has been described in detail elsewhere[6].

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

Hydrogen containing less than 2 ppm of both oxygen and water was used. When hydrogen is used as the carrier gas it is necessary to dilute it with nitrogen at the column outlet. This was done by introducing nitrogen in the line of the chromatographic apparatus designed for hydrogen with a flow-rate twice that of hydrogen.

RESULTS AND DISCUSSION

Fig. 1a shows the chromatogram obtained after the injection of ethanol-water (1:1) containing 40–60 ppm of each individual component that may be present in natural alcoholic drinks. Elution was accomplished by modifying the Carbopack B with 3% PEG 20M + 2.4% trimesic acid.

Symmetrical peaks were obtained for alcohols and aldehydes, whereas the peaks for fatty acids were slightly tailed. This demonstrates that the addition of trimesic acid is effective in deactivating the Carbopack surface and that no undesirable interactions take place between trimesic acid and alcoholic eluates.

The surface concentration of trimesic acid was found to be critical, and concentrations lower than 2.4% resulted in serious tailing of peaks relating to acids. On the other hand, at higher percentages alcohols were eluted as slightly tailed peaks, probably owing to anomalous interactions with trimesic acid.

Within a reasonably wide range of trimesic acid concentrations no changes in the elution times of the eluates were noted. This demonstrates that only synergistic effects of adsorption on the Carbopack surface and lateral interactions between the eluates and PEG 20M molecules are effective in determining the order of elution of the components of a given mixture. Therefore, the amount of PEG 20M is a critical parameter, which must be accurately adjusted in order to obtain the best fractionation of a complex mixture.

We found that concentrations of PEG 20M slightly lower than 3.0% gave optimal separations of methyl acetate from ethanol and ethyl propionate from 3-methyl-2-butanol. However, in this situation propionic acid–pentanol, acetone–ethanol and propanol–butanal separations become limiting factors. On the other hand, concentrations of PEG 20M slightly higher than 3.0% give an optimal separation of isobutyric acid from butyl acetate, although propionic acid–pentanol and acetic acid–3-methyl-2-butanol separations are then unsatisfactory.

As mentioned above, when alcoholic liquids are chromatographed directly, serious difficulties arise in separating some compounds from excess amounts of ethanol. In a first attempt, we used suitably modified Carbopack C with a surface

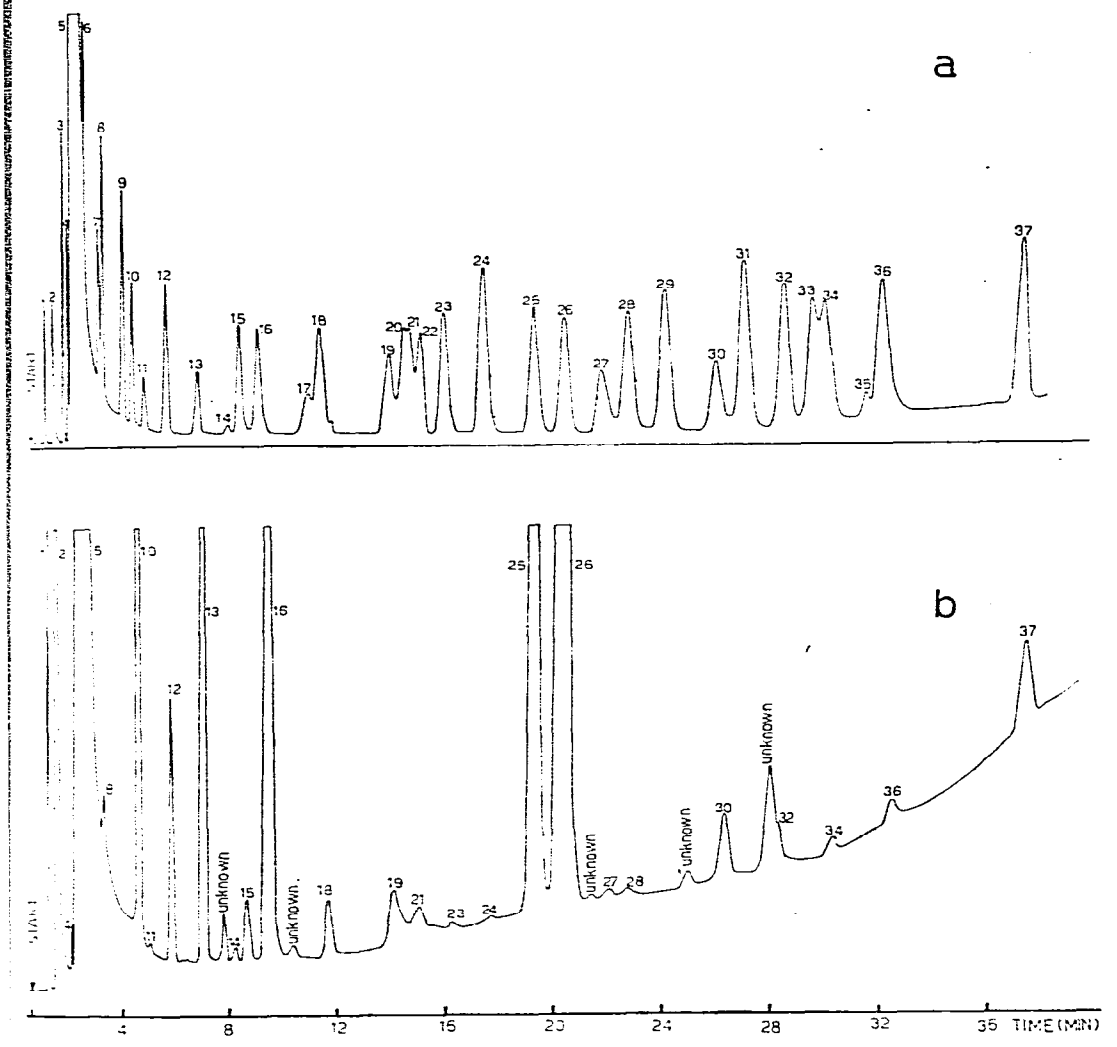

Fig. 1. Chromatograms of aqueous alcoholic solutions containining free fatty acids. Column, 2.3 m × 2 mm I.D.; packing, Carbopack B (100–120 mesh) + 2.4% trimesic acid + 3% PEG 20M; carrier gas, hydrogen; dead time, 16 sec; temperature, programmed from 80° to 150° at 1.7°/min. (a) Sample size, 0.35 μl; sample concentration, 40–60 ppm of each compound; detector sensitivity, 16 × 10^{-12} A.f.s. Peaks: 1 = acetaldehyde; 2 = methanol; 3 = propanal; 4 = acetone; 5 = ethanol; 6 = methyl acetate; 7 = isopropanol; 8 = isobutanal; 9 = butanal; 10 = propanol; 11 = diacetyl; 12 = ethyl acetate; 13 = 2-butanol; 14 = 2-methylbutanal; 15 = 3-methylbutanal; 16 = isobutanol; 17 = pentanal; 18 = 1-butanol; 19 = acetic acid; 20 = 3-methylbutan-2-ol; 21 = ethyl propionate; 22 = propyl acetate; 23 = 3-pentanol; 24 = 2-pentanol; 25 = 2-methylbutan-1-ol; 26 = 3-methylbutan-1-ol; 27 = propionic acid; 28 = 1-pentanol; 29 = ethyl isobutyrate; 30 = furfural; 31 = isobutyl acetate; 32 = ethyl butyrate; 33 = butyl acetate; 34 = isobutyric acid; 35 = 2-methylpentan-1-ol; 36 = butyric acid; 37 = 1-hexanol. (b) Sample size, 0.4 μl; detector sensitivity, 8 × 10^{-12} A.f.s. Peak numbering as in (a). Sample concentration: 1 = 50; 2 = 320; 4 = 3; 8 = 7; 10 = 1[illegible]; 11 = 1; 12 = 40; 13 = 180; 14 = 3; 15 = 16; 16 = 310; 18 = 17; 19 = 24; 21 = 7; 23 = 1[illegible]; 24 = 0.9; 25 = 480; 26 = 1050; 27 = 1.8; 28 = 1.5; 30 = 25; 32 = 18; 34 = 3; 36 = 4; 37 = 1[illegible] ppm.

area of about 10 m^2/g. In this instance, however, the peaks for propanol, acetone, methyl acetate, isopropanol and isobutanol were overlapped by the overloaded peak for ethanol. This drawback was eliminated by using Carbopack B, which has a loadability much higher than that of Carbopack C because its surface area is about ten times higher. As can be seen, by injecting 0.35 μl of an artificial alcoholic solution excellent separations, except for methyl acetate, were obtained for compounds eluting just after or before ethanol.

The column packing under consideration was not affected by injections of water. In fact, the uninterrupted use of this column for more than ten days did not result in noticeable changes in elution times or tailing of peaks. The only effect of the introduction of water into the column was some broadening of the peak for methanol. When methanol is present in trace amounts, its accurate determination can be hindered by this effect. This drawback can be eliminated simply by increasing the starting temperature by about 15°, a symmetrical peak for methanol being obtained which is still separated from those of acetaldehyde and ethanol.

It is noteworthy that a short elution time was sufficient for fractionating such a complex mixture. This is due partly to the use of hydrogen as the carrier gas[4] and partly to the use of relatively fine Carbopack particles. As shown elsewhere[4], decreasing the particle diameter of Carbopack decreases the plate height. This effect offers the advantage of permitting rapid analyses of complex mixtures to be carried out by shortening chromatographic columns.

Fig. 1b is a chromatogram obtained by direct injection of 0.4 μl of a sample of "grappa", an Italian distillate of pressed grapes. As can be seen, trace amounts of free acids can be determined and, except for ethyl butyrate, all other compounds can be separated from each other and from excess amounts of ethanol.

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