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Note

Gas–liquid–solid chromatographic separation of lower aliphatic carbonyl compounds

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The gas–liquid–solid chromatography (GLSC), using graphitized carbon black as a support, for the analysis of lower boiling compounds has been widely reported by DiCorcia *et al.*[1–13]. These methods had a high resolving power for the separation, and no adsorption or tailing with polar compounds such as lower aliphatic amines, alcohols, phenols and fatty acids. Of the column packings used in these methods, 0.4% Triton X-100 on Carbopack A has been used[14] for the separation of acetaldehyde and other lower-boiling polar compounds such as methanol, ethanol, etc. With this method, but using Carbopack B as support, acetaldehyde separated completely from other lower-boiling compounds such as lower hydrocarbons, amines, ammonia, chlorides, alcohols and esters, compounds which are present in general environmental air[15]. However, the column packing was not sufficient for the separation of propionaldehyde, acrolein and acetone, compounds which have equal numbers of carbon atoms (C_3).

In this note, in order to achieve a rapid and simple separation of the nine lower aliphatic carbonyl compounds, tris-(2-cyanoethoxy)propane (TCEP) was used as a stationary phase for the column packing with Carbopack B as support. This stationary phase is strongly polar. It was found that 5% TCEP on Carbopack B (60–80 mesh) in a glass column (1.5 m × 3 mm I.D.) at 70° gave the best results. The peaks of propionaldehyde, acrolein and acetone were separated completely within 5 min.

EXPERIMENTAL

Reagents

Acetaldehyde was obtained from Merck (Darmstadt, G.F.R.). Propionaldehyde, acrolein, *n*-butyraldehyde, isobutyraldehyde, isovaleraldehyde and diethyl ketone were obtained from Tokyo Kasei Kogyo (Tokyo, Japan). Acetone and the column packing were obtained from Wako Pure Chemical Industries (Osaka, Japan). Ethyl methyl ketone was obtained from Katayama Chemical Industries Ltd. (Osaka, Japan). All reagents were guaranteed or reagent-grade chemicals.

Operating conditions of GLSC

The gas chromatograph used was a Shimadzu Model GC5AP$_5$F equipped with a flame-ionization detector (FID) and coequipped with a digital integrator (Shimadzu Model ITG-2A) for the determination of retention times. The analytical column was made of glass (1.5 m × 3 mm I.D.) packed with 5% TCEP on Carbopack B, 60–80 mesh. The column was preconditioned with the column oven temperature at 145° for 5 h, and a constant flow-rate of nitrogen (65 ml/min).

RESULTS AND DISCUSSION

The relative retention times of nine lower aliphatic carbonyl compounds, with a 5% TCEP column packing at 70°, are listed in Table I. The retention time of propionaldehyde was defined as unity.

TABLE I

RELATIVE RETENTION TIMES OF NINE LOWER ALIPHATIC CARBONYL COMPOUNDS

GLSC conditions: 5% TCEP on Carbopack B, glass column 1.5 m, 70°, nitrogen flow-rate 55 ml/min.

Compound	*Relative retention time*
Acetaldehyde	0.48
Propionaldehyde	1.00 (3.46 min)
Acrolein	1.15
n-Butyraldehyde	2.32
Isobutyraldehyde	1.75
Isovaleraldehyde	4.60
Acetone	1.39
Ethyl methyl ketone	2.91
Diethyl ketone	5.59

As shown in Fig. 1, propionaldehyde, acrolein and acetone, compounds with an equal number of carbon atoms (C$_3$), were separated completely within about 5 min.

Grob[16] reported the separation of the volatile compounds of cigarette smoke using a 25–50-m glass capillary column coated with tetraethylene glycol dimethyl ether (TED) and dinonylphthalate (DNP). However, the separation of the acetone and isobutyraldehyde peaks was not sufficient. For this particular analysis it is necessary to use a lower column temperature such as 0° or 40–50° for good separation. However, this generally cannot be carried out by the common gas chromatograph, and the method gives a lower sensitivity because some splitter is used for maintaining the high resolving power.

Using gas–liquid chromatography, the complete separation of the free lower aliphatic carbonyl compounds such as propionaldehyde, acrolein, isobutyraldehyde and acetone, generally requires long analysis times (*e.g.* more than 10 min) or there is no complete separation[17–24].

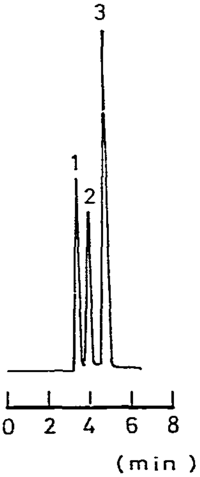

Fig. 1. Typical chromatogram of a mixture of propionaldehyde (1), acrolein (2) and acetone (3) comprising 10 μl of each compound in gaseous form. Conditions: 5% TCEP on Carbopack B 60–80 mesh, glass column 1.5 m, 70°, nitrogen flow-rate 55 ml/min.

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